Optical and optoelectronic properties of one-dimensional CdS nanostructures

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**OPTICAL AND OPTOELECTRONIC PROPERTIES OF
ONE-DIMENSIONAL CdS NANOSTRUCTURES**

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OPTICAL AND OPTOELECTRONIC PROPERTIES OF ONE-DIMENSIONAL CdS NANOSTRUCTURES

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Abstract

The optical and optoelectronic properties of one-dimensional CdS nanowires and nanobelts have attracted a great deal of attention during the past decade owing to their visible range bandgap, excellent optical properties and large surface-to-volume ratio. In this report, the photoconductivity spectroscopy and photoluminescence spectroscopy are utilized to investigate the optical and optoelectronic properties in one-dimensional CdS nanostructures, mainly focusing on the laser cooling of semiconductors and related topics.

A photoconductivity measurement system has been built up. The system includes the integration of a low temperature microscopy cryostat with an electrical and optoelectronic measurement system and a programming data acquisition system. The photoconductive characteristics of the individual CdS nanobelts have been carried out on this home-built system. The gain and response speed in CdS nanobelts are comparable with the reported results. The sensitivity of the photoconductivity can be tuned to be enhanced at certain wavelengths by the cavities formed inside the silicon oxide on the substrate or within the nanobelts themselves. The photoconductivity measurement provides an indirect method to evaluate absorption in nanostructures, which is indispensable to quantify the cooling power for the laser cooling of semiconductors.

The electric field dependence of photoconductivity near the band edge region has been investigated in detail. The Franz-Keldysh effect, Stark effect and field induced exciton ionization have been observed. The Franz-Keldysh effect has been pin-downed by the exponential decay tail and quasi-oscillations right above the band edge while the large Stark shift has been demonstrated by the redshift of the exciton peaks with an applied electric field. The field-induced exciton ionization has been confirmed by the presence of the exciton peaks in photoconductivity spectra. All those effects contribute to the absorption tail, which is essential for the anti-Stokes luminescence, the basis of laser cooling of semiconductors.

The temperature and thickness dependent photoluminescence spectra have been investigated. The rich distinct features and resolvable free exciton peaks of CdS nanobelts indicate the high crystalline quality of our samples. The redshift of emission peaks due to the presence of the reabsorption effect in the thick nanobelts has been observed. The blue shift of the free exciton emission peak is present beyond the quantum confinement regime as the size is decreased. The blue shift exhibits temperature dependence. Surface depletion induced quantum confinement is introduced to explain this blue shift. The red shift of the photoluminescence spectra covered by a layer of polymer further supports the surface depletion induced quantum confinement explanation. The size dependent emission can shed light on how to select nanobelts with proper thicknesses to achieve the maximum cooling temperature.

The electron phonon coupling is significantly enhanced in CdS nanobelts, which is evaluated by the Huang-Rhys factor. The enhanced electron phonon coupling under a resonant conduction is believed to be the origin of the strong anti-Stokes luminescence. The thickness and temperature dependent anti-Stokes luminescence spectroscopy has been performed in order to find out the proper temperature range and thickness range for laser cooling of semiconductors.

The net laser cooling of semiconductors has been demonstrated for the first time in CdS nanobelts owing to the enhanced electron phonon coupling, high external quantum efficiency and negligible background absorption. We have achieved the net laser cooling for the starting temperatures at both 290 K and 100 K. It is expected that net laser cooling at much lower starting temperature would be achieved if the proper temperature measuring method could be developed. The pumping power and thickness dependent laser cooling have been investigated systematically. Further, all solid-state cryocoolers have been developed by using the CdS nanobelts. We have successfully cooled the silicon on insulator substrate by the CdS nanobelts dispersed on the substrate.

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Citations to Published Work

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Chapter 1 Introduction

1.1 Nanostructures

Nanostructures generally refer to the structures with at least one dimension smaller than 100 nm. It is believed that the nanoscience and nanotechnology was initiated by Feynman in his talk “There is a plenty of room at the bottom” in 1959. In that talk, he described the possibility of direct manipulation of the individual atoms as a powerful platform of chemistry synthesis. However, the nanoscience and nanotechnology did not emerge as a field until 1980s when Drexler developed and popularized a conceptual framework for nanotechnology³. The field of nanoscience and nanotechnology was further advanced by the synthesis of a variety of nanomaterials such as quantum dots^{4,5}, nanotubes⁶, fullerenes⁷ and recently nanowires⁸. Owing to the invention of the various observation tools together with the development of the nanostructure synthesis methods, nanoscience and nanotechnology have become one of the most extensively investigated topics in the last two decades and will continuously attract more people to participate in this field.

The development of nanostructures not only provides a good platform for fundamental research but also shows potential applications in many areas. In particular, nanostructures with high crystalline quality are important for the fundamental research, such as the electric and magnetic transport properties, thermal transport properties, optical properties, chemical reaction mechanism and so on so forth. As we know, Newton’s law governs the macroscopic world while the atomic and sub-atomic objects obey quantum mechanics. However, there is a gap between them. It is believed that microstructures or nanostructures bridge the gap since some newly emerging phenomena are anticipated in nanoscale, which cannot be accurately described by either classical or quantum mechanics. Therefore, nanostructures with high crystalline quality provide an ideal platform to conduct the fundamental research in this specific regime.

Nanostructures exhibit several unique properties compared with their bulk counterparts. Due to their small sizes, nanostructures show promises as building blocks for the large scale integrated environmental-friendly devices, which consume less materials and energy. Besides, the integrated devices might have better performance and functionalities since we can intentionally design specific sizes, shapes, dimensionalities or composites of the small building blocks based on specific requirements. Quantum effect is another unique property of nanostructures. As one or more dimensions are shrunk down to nanoscale, the quantum confinement starts to play a role due to the limited number of atoms along the confinement direction. For example, in the GaAs quantum wells, the energy band is split into many subbands as the widths of the quantum wells are reduced to around the bulk exciton Bohr radius of the GaAs⁹. In addition, the orbits of excitons become squeezed if the size of the nanostructures is less than the Bohr radius. As a result, the separation between the electron and hole increases resulting in a large exciton binding energy as well as a large bandgap energy¹⁰. Further, the Raman selection rule $q=0$ for optical phonons in nanostructures is relaxed such as the phonons away from the zone center participate the Raman scattering resulting the redshift of the Raman peaks^{11,12}.

Beneficial from their large surface-to-volume ratio, nanostructures show promising potential applications including the lithium ion battery¹³⁻¹⁵, supercapacitors^{16,17}, energy harvesting^{18,19}, medicine²⁰ and a few to name. For instance, a plenty of semiconductor nanostructures have been proven as good candidates for gas sensors²¹, biosensors^{22,23} and mass storage devices. The performance of catalysts can be greatly improved by using nanostructures because of their large surfaces^{24,25}. Researches on the lithium battery, supercapacitor and water splitting also benefit a lot from the large surface area of the nanostructures.

In general, two mainstream approaches can be used to create nanostructures, namely top-down and bottom-up approaches^{26,27}. For the top-down approach, the nanostructures are created in bulk materials by a combination of lithography and etching techniques. However, it is difficult to rationally create nanostructures with desired chemical and physical properties²⁶. Besides, the cost of fabricating the nanostructure via top-down approach exponentially increases as the size shrinks. In contrast, top-down approach is a very powerful alternative route to the top-down approach and has been used widely to synthesize nanostructures. In this approach, the

nanostructures are assembled from the defining key nanometer-scale metrics, which make it possible to create structures equipped with an unique function or a combination of functions by precisely controlling and tuning the chemical composite, dimensionalities, shape and size²⁶.

Coming along with the promising potential applications of nanostructures are great challenges in practice. The small size of nanostructures requires very expensive equipments such as scanning electron microscope and nanomanipulator to observe and precisely handle in small quantities. So far, no available method is able to precisely handle nanostructures in large quantities, which limits their industrial applications. For example, a plenty of literatures have reported the excellent performance of individual nanowire photodetectors. However, the difficulty in large-scale integration is the main obstacle for nanowire photodetectors to be applied in practice. Furthermore, although many methods have been developed to synthesize the nanostructures, there is no universal methods to repeatedly create nanostructures in large yield as desired, thus still far beyond the industrial applications. In addition, the nanostructures are difficult to be theoretically dealt with due to the number of atoms they contain, which is too large for first-principle calculations and too small for statistical mechanics. As a result, no accurate theory can be applied and empirical theories are often used to explain experimental results, which prevents the thorough understanding of what has been observed.

In summary, the field of nanostructures has become one of the most active research fields in the past two decades due to their importance in fundamental researches and in the potential applications. Considerable progresses have been made meanwhile many challenges still exist in this field.

1.2 Dimensionality and size dependence of optical properties in semiconductor nanostructures

Compared with their bulk counterparts, optical properties in semiconductor nanostructures show significant differences, which originate from quantum confinement effect and surface effect. The optical properties of nanostructures are strongly dependent on their electronic band structure and density of states, both of

which will be strongly altered by quantum confinement. Nevertheless, the surface states due to the large surface area, compositional variation or modulation and local dielectric environment will further influence the electronic and optical properties of nanostructures.

Figure 1-1 The schematic images of structures with different dimensionalities: (a) 3D, bulk semiconductors; (b) 2D, nanobelts or nanoribbons, quantum wells; (c) 1D, nanowires, nanotubes; (d) 0D, quantum dots. (e-h) The electronic band structures and (i-l) Density of states for 3D, 2D, 1D and 0D structures²⁸.

Both the electronic band structures and density of states are dependent on dimensionality and size. By applying the simple particle-in-box model in quantum mechanics, the energy dispersion relation of a free electron in a three dimensional (3D) box can be expressed as^{1,28}:

$$E(k_x, k_y, k_z) = \frac{\hbar^2}{2m_e} (n_x^2 k_x^2 + n_y^2 k_y^2 + n_z^2 k_z^2) \quad (1-1),$$

where m_e is the effective mass of electrons; n_x, n_y, n_z are integers; k_x, k_y, k_z are wave vectors related to the box of dimensions L_x, L_y, L_z via $(k_x, k_y, k_z) = (\frac{2\pi}{L_x}, \frac{2\pi}{L_y}, \frac{2\pi}{L_z})$ (Figure 1-1a). In 3D materials, large L_x, L_y, L_z leads to very small wave vectors k_x, k_y, k_z resulting in continuous states in all three dimensions (Figure 1-1e) and $E^{1/2}$ dependent DOS (Figure 1-1i). If we reduce the size along one dimension such as x direction down to the bulk exciton Bohr radius (2D, Figure 1-1a), the wave vectors become discrete along the x direction while maintain continuous in the other two directions. As a consequence, the 2D-subbands appear with an energy spacing of $\frac{\hbar^2 k_x^2}{2m_e}$ while 2D-subbands keep continuous along the other two dimensions such as y and z directions (Figure 1-1f). The DOS changes to step-like structures in 2D (Figure 1-1j). If the size is further reduced along x direction, a larger wave vector k_x is obtained leading to a larger band gap energy. Reducing the size of one more direction, *e.g.*, y direction, a 1D structure is resulted (Figure 1-1c). In 1D nanostructures, the energy band splits into a series of 1D-subbands but remains continuous only along z direction (Figure 1-1g). The DOS in 1D exhibit spike-like features (Figure 1-1k). Finally, in 0D structures (Figure 1-1d), the energy dispersion becomes discrete points at all three dimensions (Figure 1-1h) and the DOS changes to horizontal lines (Figure 1-1l).

Optical properties of semiconductors can be determined by a few optical spectroscopic approaches, such as optical absorption and photoluminescence spectroscopy. The transition between subbands can be observed in both photoluminescence spectra and absorption spectra for those low dimensional structures with size at least one dimension comparable to the bulk exciton Bohr radius. The extra peaks in photoluminescence spectra reflecting the transition between subbands emerges while the steps, spike or distinct peaks in absorption spectra appears near the band edge region compared with that of bulk structures. The band edge in absorption spectra or the emission peaks in photoluminescence spectra would blue shift as the size further decreases. For example, the PbS quantum dot photodetectors have been proven to be able to function from mid-infrared to visible range by adjusting the diameter of PbS quantum dots²⁹⁻³¹. The emission peaks tuned

by the diameter of nanowires or quantum dots have been demonstrated as well³². All those examples reflect the size and dimensionality dependent electronic band structures.

Apart from the quantum confinement effect, the surfaces of semiconductor nanostructures play important roles in determining the optical properties. The large amount of surface states in nanostructures lead to strong surface depletion and surface electric field. The surface electric field will modify the confinement potential to be smaller than the actual geometrical size of nanostructures, which gives rise to confinement effect beyond the quantum confinement regime³³. Such effect can be reflected by the blueshift of the emission peaks with the size, which is considerably larger than the Bohr radius of the exciton of the material (see Chapter 4). The surface states may act as both radiative recombination and non-radiative recombination centres³⁴. Radiative surface recombination centres would lead to the surface emission modifying the emission profile and the biexponential decay time-resolved photoluminescence spectra while nonradiative recombination centres could give rise to the weak emission. Owing to the large surface area in nanostructures, the surface may trap one kind of photogenerated carriers while allows the other kind of carriers circulates many times resulting in a large photoconductivity gain³⁵. In addition, surface states may enhance the photodetection response speed due to the fast surface recombination rate³⁶.

Furthermore, the surface electric field would spatially separate the photogenerated electrons and holes, resulting in the change of the strength of the electron-phonon coupling in nanostructures³⁷. Although a plenty of investigations have been carried out on the size dependent electron-phonon coupling strength, it is still a relevant and controversial topic³⁸⁻⁴⁰. We found enhanced electron-longitudinal optical phonon coupling strength in CdS nanobelts resulting in strong anti-Stokes luminescence under a resonant conduction⁴¹. As a consequence, net laser cooling of semiconductors is achieved in CdS nanobelts for the first time.

In summary, the optical properties can be modified by both the quantum confinement and surface effects. Quantum confinement effects modify the electronic band structures in the quantum confinement regime while the surface effects are induced by introducing the surface states owing to the large surface area and the

surface dangling bonds. Motivated by the interesting phenomena and related possible applications, the investigations on the optical properties of semiconductor nanostructures have attracted a great deal of attention and will attract more researchers to devote to this field in the future.

1.3 Laser cooling of solids

In this thesis, the core theme is laser cooling of semiconductors in CdS nanobelts. We have discussed the optical properties of semiconductor structures above, which are indispensable for understanding the mechanism of the laser cooling in semiconductors. In this subsection, the background of laser cooling will be introduced.

Laser cooling of solids or optical refrigeration was first proposed by Peter Pringsheim in 1929⁴², more than 30 years before the invention of the laser. The concept has been applied to the Doppler cooling of gas⁴³ and the cooling of ultra-dense gas by collision redistribution⁴⁴. Four Nobel prizes have been given to the field of laser cooling.

Figure 1-2 Schematic image of upconversion luminescence in rare-earth doped systems where the energy levels are discrete⁴⁵ (a) and direct band gap semiconductors where the energy levels are continuous (b).

Laser cooling of solids exhibits compact, vibration and cryogen free and high reliability and has a wide range of potential applications including all solid-state cryocoolers, athermal lasers or self-cooling lasers⁴⁵⁻⁴⁸. The basic principle of laser cooling is anti-Stokes luminescence. In detail, the specifically designed high purity

materials absorb photons with energy $h\nu$ below the mean fluorescence energy $h\nu_f < h\nu$ and during the emission process the lattice thermal vibration energy is taken away by the emitted photons resulting in the laser cooling of solids⁴⁵. To realize the net laser cooling of solids, the material requires having high purity with proper spaced energy levels and a high external quantum efficiency. Due to those special requirements, the materials for the optical refrigeration are confined to rare-earth (RE) doped crystals or glasses and direct band gap semiconductors so far⁴⁵.

Figure 1-3 (a) The absorption and anti-Stokes luminescence spectra of 5% doped Yb^{3+} ion in a YLF crystal (up panel) and the cooling efficiency (bottom panel)⁴⁷. (b) The cooling temperature surface plot versus the pumping wavelength⁴⁹.

In the rare-earth doped systems, the anti-Stokes luminescence occurs in rare-earth elements while the phonons are supplied by the host materials⁴⁵. The energy levels of rare-earth elements are discrete and are distinguishable (Figure 1-1a), thus, the electron distribution follows the Boltzmann distribution. As the temperature decreases, the population of the electrons in higher states of ground state manifolds diminishes⁴⁷. As a consequence, the upconversion luminescence cannot occur and the net laser cooling is impossible at certain temperatures^{47,50}. The lowest achievable temperature in the rare-earth doped systems is around 110 K⁴⁷. In contrast to the rare-earth doped systems with discrete atomic energy levels, the excitonic resonance in direct band gap semiconductors dominates the upconversion luminescence in which the continuous energy band involves. An incident light beam with the right energy $h\nu$ excites electrons from the top of the valence band to the bottom of the conduction

band. After thermalization, the photons with energy $h\nu_f$ larger than the incident photon energy $h\nu$ are emitted, carrying away heat from the semiconductors (Figure 1-1b). Since the electrons in semiconductors follow Fermi-Dirac statistics, the lowest cooling temperature can reach around 10 K according to theoretical investigations^{50,51}.

Because of the difficulty of obtaining high purity materials, the net laser cooling has not been realized until 1995 when the first demonstration of net cooling of solid was achieved in ytterbium-doped glass⁵². Since then, great effort has been devoted to improve the cooling efficiency and to reach a larger cooling temperature in a variety of the RE doped crystals and glasses^{49,53-57}. To date, the minimum achievable temperature of ~ 110 K starting from room temperature has been realized in a 5 % doped Yb: YLF crystal, which surpasses the thermoelectric Peltier cooler (Figure 1-2b)⁴⁹.

Compared with the atomic resonance involved in the RE doped crystals and glasses, laser cooling of semiconductors exhibits a number of advantages. Semiconductors are anticipated to exhibit more efficient pump light absorption, much lower achievable cooling temperature and direct integrability into electronic and photonic devices^{41,45}. Although many theoretical^{50,51,58-61} and experimental⁶²⁻⁶⁴ studies have addressed various aspects of the laser cooling of semiconductors, no net cooling has been achieved in semiconductors until recently the first demonstration of net laser cooling was achieved in CdS nanobelts by our group in Nanyang Technological University⁴¹. We will elaborate our findings in detail in Chapter 5-6.

In summary, the laser cooling of solids exhibits a wide range of applications including all solid-states cryocoolers and athermal lasers with advantages of compactness, vibration- and cryogen-free and reliability and remarkable progress has been made in this field. So far laser cooling from ambient temperature to 110 K has been achieved in RE-doped systems while the net laser cooling of semiconductors was demonstrated in CdS nanobelt for the first time. The advantages and the potential applications of laser cooling of semiconductors motivate us to contribute in this field.

1.4 Motivation and objectives of this thesis

The knowledge on how size affects the emission beyond the quantum confinement region is essential for electronic and optoelectronic applications; however, this underlying mechanism is still not well understood and further investigations are required. In addition, the deep understandings of size and dimensionality dependent electroabsorption are indispensable for nano-electroabsorption modulators; however, the electroabsorption of semiconductor nanowires or nanobelts as a dependence of electric field strength, size, and dimensionality remains elusive. We started with the investigations on size dependent emission and electroabsorption in CdS nanobelts and nanowires. Later, we discovered the laser cooling of the semiconductors in CdS nanobelts. It turned out that the size dependent emission and electroabsorption we studied were helpful for understanding the mechanism of laser cooling and can be harmonically unified into the laser cooling of semiconductors. Therefore, this thesis focuses on achieving the net laser cooling and laser cooling associated topics in CdS nanobelts. Since the laser cooling of semiconductors relates to the emission, absorption and electron-phonon interaction, there are four objectives in this thesis, including (1) the thickness dependent emission, which is helpful for selecting proper nanobelts to demonstrate laser cooling; (2) the absorption tail under different applied source-drain electric field, which is crucial for the analysis of the laser cooling; (3) thickness dependent electron-phonon interaction; (4) demonstration of laser cooling of CdS nanobelts themselves and cooling of other thermal loads anchored to CdS nanobelts.

1.5 Organization of the thesis

Based on what has been discussed in section 1.4, the rest of this thesis is organized as follows.

In Chapter 2, the synthesis of the CdS nanobelts and the characterizations including morphology, thickness and crystalline structures are introduced in detail. Since measurement of the absorption for individual nanobelt is impossible, the photoconductivity gain is devised to quantify the absorption which requires fabricating electrodes on individual nanobelts. Therefore, the details of the device fabrication and electric measurement setup would be present next. Then, the home-

built photoconductivity measurement setup including the setup construction, data acquisition system and calibration is described. Finally, the introduction of the micro-Raman spectroscopy is present as well. The micro-Raman spectroscopy has been used to conduct photoluminescence measurements and laser cooling of semiconductors.

The deep understanding on the anomalous blueshift of the emission peaks beyond the quantum confinement regime is crucial for both the optoelectronic applications and laser cooling of the semiconductors. However, no universal explanation is available for this phenomenon. The thickness dependent photoluminescence spectra of individual CdS nanobelts beyond the quantum confinement regime at various temperatures are systematically discussed in Chapter 3. To interpret the results, the surface depletion induced confinement is proposed and further verified by the emission spectra of nanobelts after surface passivation.

In Chapter 4, the photoconductivity measurement on individual CdS nanobelt devices both at room temperature and low temperatures are performed. The spectral response, switch characteristic and response speed are evaluated. The interference effect due to the silicon dioxide layer on the substrate and the nanobelts themselves is discussed. The electroabsorption including Stark effect, Franz-Keldysh effect and field induced exciton ionization are systematically investigated, which are essential for the analysis of laser cooling and electroabsorption modulators.

In Chapter 5, the electron phonon interaction and anti-Stokes luminescence in CdS nanobelts are present. This is the basis of the laser cooling of semiconductors. The resonant Raman scattering and Huang-Rhys factor in CdS nanobelts are given. The anti-Stokes luminescence in CdS nanobelts are confirmed due to the multiple longitudinal-optical phonon-assisted transition rather than two photon absorption by the power dependent integrated anti-Stokes luminescence intensity. The strong electron phonon coupling in CdS nanobelts is further verified by the long tails and exciton ionization at low temperatures in photoconductivity spectra.

In Chapter 6, the demonstration of laser cooling and associated issues such as emission extraction efficiency, external quantum efficiency and free carrier absorption in CdS nanobelts are discussed. The upconversion emitted photon may be trapped inside the nanobelts due to the total reflection at the surfaces or interfaces, which is detrimental to the laser cooling. The emission extraction efficiency is used to describe the percentage of the escaped photons. It is also an important factor to achieve the net laser cooling, which is evaluated through the geometrical analysis. Another crucial

factor is external quantum efficiency, which is obtained by the temperature dependent time resolved photoluminescence spectra. The free carrier absorption, responsible for the main contribution of the background absorption, is discussed as well. The net laser cooling of semiconductor is demonstrated by using pump-probe luminescence thermometry. The thermal analysis is conducted in order to explain the experimental results. Finally, the thickness dependent cooling temperature is investigated both experimentally and theoretically.

An all solid-state cooler is demonstrated in Chapter 7, which is realized by using CdS nanobelts to cool the silicon on insulator (SOI) substrate. The temperature is measured by using the ratio of the Si Raman Stokes to anti-Stokes intensity. The starting temperature dependent cooling temperature is investigated as well. Finally, the laser cooling of the SOI substrate and laser cooling of CdS nanobelt itself are carried out on the same belt to compare between them.

Finally, the summary of the whole thesis and a brief outlook on the field of laser cooling of semiconductors and photoconductivity is given in Chapter 8.

Chapter 2 Sample Synthesis and Instrumentation

2.1 Cadmium sulphide (CdS) nanostructure synthesis and characterizations

CdS is an important II-IV group direct bandgap semiconductor with a band gap of 2.5 eV at room temperature. There are two crystalline structures in CdS, namely, zinc blende and wurtzite structures⁶⁵. Due to its excellent optical properties, CdS has been considered to be a very promising material for electrical and optoelectronic applications including field-effect transistors⁶⁶, waveguides^{67,68}, lasers⁶⁹, solar cells⁷⁰ and field emitters³⁶. Besides, it is also offer a good platform for fundamental research⁷¹. A variety of methods have been developed to synthesize the CdS nanostructures with different sizes, shapes and various morphologies such as quantum dots, nanowires^{67,72-74}, nanorods^{72,75}, nanotubes^{76,77} and nanobelts^{78,79}. In this section, we will focus on the one-dimensional CdS nanostructures synthesis and characterizations.

2.1.1 CdS nanostructure synthesis

The CdS nanobelts used in this thesis were synthesized in a home-built vapour transport chemical vapour deposition (CVD) system based on the physical vapour transport growth method, which is a very simple and accessible way to provide vapour phase for the nanostructure synthesis⁸⁰. Figure 2-1a shows a picture of the home-built chemical vapour deposition setup in our group. All components are labelled correspondingly at side. The simplified schematic of the setup is given in Figure 2-1b with the labelling of the gas flow, furnace, the location of the source materials and the location where nanostructures are collected. A variety of nanostructures including II-IV group compound nanostructures CdS^{78,81}, CdSe⁸¹, CdTe⁸¹, ZnTe⁸², ZnSe nanowires and nanobelts, Bi₂Se₃ nanowires⁸³ and ZnO nanowires⁸⁴ have been synthesized in this setup. For physical evaporation, the powder or condensed source materials will be vaporized at an elevated temperature resulting

in vapour phase which is then transported by the carrier gas and subsequently deposited onto the substrate inside the quartz tube.

Figure 2-1 (a) The picture of our home-built CVD system. All components are labelled at the left side except the pump. (b) The schematic image of the setup. The location of source materials and the position of the as-grown nanostructures collected are indicated.

The CdS nanobelts were synthesized via thermally evaporating CdS powder (Alfa Aesar, 99.999%) in a horizontal tube furnace. In detail, a quartz boat with CdS powder was placed at the center of the furnace. A Si substrate dispersed with 30 nm Au nanoparticles was put around 10 cm away at the downstream of the source material. After the quartz tube was pumped down to a base pressure of 10 mTorr, a carrier gas of 30 sccm H_2 was introduced. After waiting for 10 minutes when both the gas flow and pressure reach stable, the power of the furnace heating resistor was switched on. The CdS powder was heated up to around 670 °C within 5 minutes and was maintained at this temperature thereafter. The pressure was kept at 4 Torr during the whole process. After 30 minutes, the power of the furnace heating resistor was switched off and the quartz tube was naturally cooled down to room temperature with the H_2 gas flow maintained. A layer of bright yellow substance covering the whole Si substrate was observed as shown in Figure 2-2a. From the optical picture (Figure 2-2a), we could see that the growth yield was quite high. The CdS nanowires used in this thesis were grown in the same setup but with different parameters. A heating

temperature of 720 °C was used and maintained in a carrier gas of 50 sccm Ar for 30 minutes. During the whole growth process, the pressure was maintained at 50 Torr. After naturally cooled down to room temperature in Ar atmosphere, the Si substrate gave a dark yellow colour in appearance.

2.1.2 Nanostructure characterizations

Scanning electron microscopy

Since the resolution of optical microscopy is limited by optical diffraction, structures with size smaller than the half wavelength of the light used to image cannot be resolved. Scanning electron microscopy (SEM) is an indispensable tool to investigate the morphology of the nanostructures. As proposed by Louis De Broglie, electron has both wave-like and particle-like character. The wavelength of an electron λ relates to its momentum p via Planck constant h as $\lambda = h/p$. Since the energy of the electrons used in SEM is around 5-30 keV, the relativistic effect has to be taken into consideration. The wavelength of the electron beam after corrected by relativistic effect can be expressed as⁸⁵

$$\lambda = \frac{h}{\sqrt{2m_0eV(1 + \frac{eV}{2m_0c^2})}} \quad (2-1),$$

where m_0 is rest mass of the electron, V is the accelerating electric potential used to accelerate the electron beam, e is the element electron charge and c is the speed of light in vacuum. Therefore, eV is the kinetic energy of the electron beam. As seen from expression (2-1), the larger the accelerating electric potential, the shorter the wavelength of the electron beam is. The shorter wavelength would give a higher resolution. For a typical SEM with accelerating electric potential 5 kV, the wavelength of the electron beam is as short as ~10 pm, which means it can in principle image structures with size around 10 pm. However, we control the electron beam by using a series of magnetic lenses, which would greatly reduce the resolution capability. In practice, the resolution of SEM reaches around 10 nm.

To better understand how SEM works, it is essential to gain some knowledge about the interaction between electron and matter. When a high energy electron beam impacts on a specimen, a variety of signals will be produced, which includes secondary electrons, backscattered electrons, Auger electrons, inelastically scattered electrons, elastically scattered electrons, characteristic X-ray, bremsstrahlung X-ray and light. Depending on certain specific signal to be detected, there are various different characterization techniques. For example, Auger electron spectroscopy detects the Auger electrons while energy-dispersive X-ray spectroscopy only collects the characteristic X-ray.

The secondary electrons emitted from the shallow surface layer are collected to obtain the morphology image since the secondary electrons are very sensitive to the surface morphology. The secondary electron detector collects electrons with energy less than 50 eV to form an image. For the emitted electrons with energy more than 50 eV, a backscattering electron detector is used⁸⁶. The SEM images used in this thesis were constructed from the signals obtained by a secondary electron detector.

Figure 2-2 (a) An optical picture of the as-grown CdS nanobelts. (b) The SEM image of as-growth CdS nanobelts with high magnification. (c) The SEM image of as-growth CdS nanobelts in a relative large area.

To obtain a good SEM image, charging effect should be avoided. For an insulator sample, the incident electrons will accumulate at the surface resulting in a local electric field, which will repel the successive incoming electrons. As a result, the images will constantly drift, which causes a lower resolution and the inaccurate boundary position. Therefore, when we prepare the sample, we should either use a

conductive substrate or sputtering a layer of Au for insulating substrate to avoid charging effect. In this thesis, the CdS nanostructures were grown on the heavily doped Si substrates, which are essentially conductive. Therefore, we can directly take SEM images by using the as-grown samples. In addition, using a low acceleration voltage (below 5 kV) is helpful to minimize the charging effect.

The SEM images in this thesis were taken on a JEOL 7001F field emission SEM. Figure 2-2b displays an SEM image of as-grown nanobelts with a high magnification. As seen from the SEM image, the CdS nanobelts are 2-3 μm in width and several tens of microns in length. Figure 2-2c shows an SEM image of the as-grown CdS nanobelts indicating the very high density.

Atomic force microscopy

Atomic force microscopy (AFM) is a type of scanning probe microscopy with very high resolution (around atomic resolution) in its z-scanning direction. AFM is a versatile and very powerful technique for imaging, measuring and manipulating the matter at nanoscale. A very sharp tip (with a radius of curvature ~ 10 nm) is connected to the end of a cantilever and scans above a sample surface to be imaged. Since van der Waals force always exists between any two objects and can be either attractive force or repulsive force depending on the distance between them, the cantilever would deflect from its original position when it interacts with the sample surface: it bends toward (away from) the surface when the force between them is attractive (repulsive) force. Accordingly, based on the type of forces between the cantilever and sample surface, two imaging modes are available for AFM: contact mode (repulsive force) and non-contact mode (attractive force). The cantilevers can be specifically designed so that we can select certain mode by using different type of cantilevers. During the imaging process, a laser beam is used to magnify the small bending and the magnified bending signals are collected by a position-sensitive detector (PSD). Scanning is realized by mounting the sample onto piezoelectric scanners. Through recording the PSD output, an image of the surface morphology and phase can be reconstructed.

In this thesis, all AFM images were acquired on a Nanoscope III system (Veeco Instrument). The non-contacted mode was used. Figure 2-3a shows an

example of the topography image indicating a very uniform width. In order to obtain the thickness information, a red line was drawn across the nanobelt and the section profile along the red line was shown in Figure 2-3b. As seen from the section profile, the nanobelt measured here is around 30 nm in thickness and exhibits quite flat surface.

Figure 2-3 AFM image: (a) The topography image of an individual CdS nanobelt. (b) The section profile along the red line in (a). The thickness of the measured belt is around 30 nm and the width of the belt is 2.2 μm. The thicker strip at the right side is Ti/Au electrode which is used for the photoconductivity measurement. The square on the top left side is an alignment marker made of Ti/Au.

X-ray diffraction

X-ray diffraction (XRD) is a widely used and non-destructive technique to reveal the information about the crystalline structures and size of nanostructures. X-ray is an electromagnetic wave with a very short wavelength comparable to the atomic interplanar spacing in crystals. The X-ray illuminates on a crystal will undergo diffraction called Bragg's diffraction. The collected diffraction signals contain the information on the crystalline structures as well as the size of nanostructures. Bragg's law plays a very important role in determining the crystalline structures, which can be expressed as

$$n\lambda = 2d \sin \theta \quad (2-2),$$

where n is an integer, λ is the wavelength of the incident X-ray, d is the interplanar spacing and θ is the angle between the incident X-ray and the specific crystal plane. By extracting the FWHM of the peaks, one can get the size of the nanostructures based on the Scherrer equation⁸⁷.

Figure 2-4 XRD spectrum of the as-grown CdS nanobelts taken by the Bruker D8 Advance Diffractometer. The peaks are indexed correspondingly in the plot.

In this thesis, powder XRD spectrum measurement of the as-grown CdS nanobelts was carried out using a Bruker D8 Advance Diffractometer (Cu $K\alpha$ $\lambda=0.15419$ nm, Nickel filter, 25 kV, 40 mA). Figure 2-4 shows the XRD spectrum of the as-growth CdS nanobelts labelled with the indices of corresponding peaks. Since the density of the nanobelts is quite high forming a thick layer, the locked coupled mode is selected. The scan speed is around 0.5 degree per minutes. The diffraction patterns distinctly indicate the good crystalline quality of the obtained CdS nanobelts. The peak around $2\theta=33^\circ$ could be attributed to Si substrate. All the other diffraction peaks can be readily indexed to the hexagonal phase of CdS with calculated lattice constant $a=4.139$ Å and $c=6.720$ Å, which are well in agreement with the reported values (JCPDS card No. 41-1049). No peaks of impurities are detected, indicating the high purity of the products.

Transmission electron microscopy and selected area electron diffraction

Transmission electron microscopy (TEM) is another indispensable imaging tool to investigate the crystalline structure, composites and properties in the

submicroscopic details of nanostructures. Due to its high resolving capability, TEMs have been widely used in the field of material science, chemistry, electronics and life science. Compared with optical microscopy, TEMs are capable of imaging at very high resolution, comparable to the atomic interplanar spacing of crystals, due to the small De Broglie wavelength of the energized electron beam used. For example, the typical energy of the electron beam used in TEMs is 200 keV, corresponding to a wavelength of 2.5 pm. The principle of a transmission electron microscopy is based on interaction between the electrons and matter. While the secondary electrons are collected by SEMs, the TEMs collect the transmitted electrons. Therefore the specimens used for TEMs must be very thin (typically thinner than 100 nm for high resolution TEM) so that the electrons can pass through the specimens.

Figure 2-5 (a) Low magnification TEM image of CdS nanobelts. (b) Selected area electron diffraction pattern. The corresponding indices are indicated in the figure. (c) High resolution TEM image of CdS nanobelts. The lattice fringes can be clearly seen and the lattice spacing is 0.317 nm, corresponding to the (0001) zone axis⁷⁸.

When an energetic electron beam passes through a thin specimen, the electrons will suffer different scattering due to the different thickness and different composites, which gives rise to different contrast. The contrast difference is used to construct the images. Similar to Bragg's diffraction during the interaction between X-

ray and the crystal specimens, Bragg's diffraction will occur when the electron beam passes through a crystal specimen. Bragg's diffraction will alter the intensity of the direct beam and further produce the contrast called "diffraction contrast". It should be noted that the electron diffraction obeys the Bragg's law stated in equation (2-2) as well. The contrast information is then magnified and focused by a group of magnetic lenses onto an imaging device such as photodiode or charge coupled device (CCD) to record the information. Figure 2-5a gives the low magnification TEM image of CdS nanobelts dispersed on a copper grid.

High resolution TEM (HRTEM) can be used to observe the lattice fringes or crossed lattice fringes due to the phase coherence. The lattice fringes stems from the interferences between the incident beam and diffraction beams or among the diffraction beams. From the lattice fringes, the lattice spacing can be obtained and the growth direction can be determined. Figure 2-5c displays the HRTEM image of an individual CdS nanobelt. The lattice fringe can be clearly distinguished and the spacing between the lattice planes along the length of the nanobelt is measured to be 0.317 nm, which is consistent with (0001) planes of CdS. This indicates that the CdS nanobelts grow perpendicular to (0001) direction.

Furthermore, we can acquire the selected area electron diffraction (SAED) pattern of a crystal by changing the strength of the intermediate lens of TEM. When an electron beam pass through a crystal sample, scattering and diffraction will occur. The electron diffraction is also governed by the Bragg's law stated in equation (2-2) and thus the direction of the diffracted electrons will depends on the orientation of the crystals. If the diffracted electrons are collected by a detector such as CCD, we can construct the diffraction pattern based on the output signals from CCD. From SAED pattern, one can obtain the information about the reciprocal space, which is necessary to study the lattice structures of a crystal. Figure 2-5b shows the SAED pattern of an individual CdS nanobelt. The bright spots indicate the good crystalline quality of the materials. By detailed analysis, we can determine that the crystalline structure of the investigated CdS nanobelt is hexagonal structure.

2.2 Device fabrication

In this thesis, the two-probe field-effect transistor (FET) devices were used to investigate the optoelectronic properties of the CdS nanostructures. For the electrical and optoelectronic measurements, the devices should be fabricated on insulating substrates. The as-grown nanostructures are on bare Si substrates which are highly conductive and thus required to be transferred to insulating substrates. Besides, since we investigate the optoelectronic properties of individual nanowire and nanobelt, the alignment markers are required to fabricate first in order to put electrodes exactly on the nanostructures we want to investigate. In this section, the device fabrication procedure will be introduced in detail.

Figure 2-6 The schematic flow chart of fabricating alignment marker substrates by using the two-layer resist technique.

The electrodes for individual nanowire and nanobelt FET device used in this thesis are patterned by using an electron beam lithography system converted from a JEOL 7001F field emission SEM equipped with a nanometer pattern generation system (NPGS). We give the schematic flow chart of fabricating alignment marker substrates by using the two-layer resist technique in Figure 2-6. A Si substrate with 500 nm SiO₂ has been used for device fabrication. Before spin-coating resist, a 5 minute sonication in acetone is carried out to remove adsorbed particles and a plasma treatment was followed in order to clean the organic residues. Lift-off resist methyl

methacrylate 8.5 (MMA (8.5) MMA, Micro Chem) is dropped to the substrate and spun at 4000 RPM for 1 minute. The thickness of the coated MMA is around 200 nm. Then the substrate is heated to 180 °C on the hot plate for a 5 minutes soft baking. Subsequently, imaging resist Polymethyl methacrylate 4 (PMMA4, Micro Chem) is applied and spun at 4000 RPM for 1 minute, which gives the thickness around 300 nm. Soft bake at 180 °C for 8 minutes is followed. The marker pattern is designed according corresponding requirements and the run file is generated by using the NPGS software. After exposed by electron beam, the pattern is developed in a developer for 1 minute. The developer solution is a mixture of methyl isobutyl ketone (MIBK) (99.5%, Sigma) with isopropanol alcohol (IPA) (99.7%, Sigma) in a ratio of 1:3. After rinsed by IPA and blown dry by N₂ gas, the substrate was transferred into a thermal evaporator chamber. 5 nm Cr and 45 nm Au films are evaporated followed by lift-off process, which is carried out in a 60 °C bath of acetone. Finally, the substrate with markers is ready to be used for device fabrication.

For device fabrication, the as-grown nanostructures are required to be transferred to the substrate with markers. The as-grown CdS nanostructures are sonicated into IPA solvent and then dispersed onto the cleaned substrate with markers. The pictures of the area with alignment markers and dispersed nanostructures are taken and used to design the pattern which was used to generate the run file for electron beam exposure later. The lift-off resist and imaging resist are coated on the samples, the same as the procedure for making marker substrate. Compared with fabricating marker substrate, one more alignment step by using the alignment markers is required to tell the system where the electrodes should put. After developing for one minute, the sample is dipped into 5% HF etching for 3 seconds to remove the oxide or contaminate layer on the surface which can prevent the nanowires to form good contact with electrodes. After etching, the sample is immediately put into the thermal evaporator chamber to pump down for metal deposition. It is very critical to select proper metallic materials for electrodes. The selected metallic materials should be stable in air and the work function of used materials should match the Fermi level of the nanostructure in order to form a good Ohmic contact. In CdS nanostructure devices, Ti and Au are used. 50 nm Ti film is used as adhesion and functioning layer while 50 nm Au film is evaporated to protect the Ti film from being oxidized. After the lift-off process, the devices are ready for the electric and optoelectronic

measurements. Sometime a rapid thermal annealing is required to form alloy at the contact area which is helpful to form an Ohmic contact.

Figure 2-7 (a) The optical image of the CdS nanobelt devices. Limited by the view field of the optical microscopy, the outside big electrodes cannot be seen in this image. (b) The SEM image of two CdS nanobelt devices. Both the channel and width of the electrodes are 1 μm .

Figure 2-7a shows the optical image of the CdS nanobelt devices. The nanostructures are too small to be seen in the optical image and the electrodes are enlarged layer by layer in order to connect to chip carrier for the optoelectronic measurements. Figure 2-7b displays the SEM image of an individual CdS nanobelt device. Both the channel of the device and width of electrodes are 1 μm .

2.3 Electrical measurement setup

In electrical measurement, we can either measure a voltage by forcing a current or measure a current by applying a voltage. From the electrical measurement, information such as resistance, conductance, carrier mobility and density, electron-phonon interaction strength can be obtained. Besides, many interesting phenomena such as quantized conductance and hot exciton transport in nanostructures are able to be observed through electric measurement. In this thesis, the electric measurement is used to identify the contact before photoconductivity measurement.

In a nanostructure device, good contacts are desirable and key to the success of making measurement. Varying with using different contact materials, three classes

of contacts can form: blocking contacts, Ohmic contacts and injecting contacts. A picture illuminates these three types of contacts as shown in Figure 2-8. A blocking contact cannot replenish carriers when they are drawn out of the material by applied electric field. For an injecting contact, carriers drawn in from contact have time to cross the material before the material can achieve charge neutrality by dielectric relaxation by applying sufficiently high electric field. The current varies non-linearly with the applied voltage. In an Ohmic contact case, the current changes linearly with the applied electrical field. Sometimes, a rapid thermal annealing is necessary after metal deposition in order to get good Ohmic contact.

Figure2-8 I-V curves of three classes of contacts: (a) an Ohmic contact, (b) a blocking contact and (c) an injecting contact⁸⁸.

Figure 2-9 The optical picture of the Lakeshore probe station equipped with the Agilent B1500A semiconductor device analyser.

The electrical measurement in this thesis was carried out in a lakeshore probe station (TTP4 Probe Station, Lake Shore Cryotronics, Inc.) coupled with a semiconductor device analyser (Agilent B1500A). A picture of the setup is shown in Figure 2-9. All important components are labelled at the side of the picture.

The probe station is a cryogenic manipulated-probe station equipping with four independently manipulated probe arms, an optical system, a turbo pump system, a transfer line and a temperature controller. The probe station can be used for non-destructive electric measurement of devices with a diameter smaller than 2 inches. Each of the manipulated probe arms is able to hold a DC, microwave and other probe for specific applications. In this thesis, the probes used are brazen copper probes. An additional cable can be connected to the sample holder inside the chamber so that the back-gate voltage can be applied for the FET device measurement. The optical system consists of the light source, camera, monitor and microscope to view the devices to be tested. The turbo pump system equipped with a turbo pump and a cold cathode gauge is used to evacuate the probe station chamber in order to perform device test under vacuum or low temperature measurement, and the cold cathode gauge measures the high vacuum. The transfer line carries the liquid nitrogen or liquid helium from a Dewar to the probe station refrigerator while the temperature controller regulates the temperature of the chamber. With these systems, the probe station is capable of providing temperatures from 4.2 K to 475 K.

The Agilent B1500A semiconductor device analyser is a PC-based instrument with the capabilities of current-voltage (IV), capacitance-voltage (CV), pulse generation, fast IV, and time-domain measurement. It has been used for a wide range of semiconductor device characterizations due to its low-current and low-voltage measurement capabilities. The analyser is equipped with four independent source/monitor units (SMU) which can apply DC voltage, DC current, pulse voltage and pulse current. The SMU can provide DC voltage as high as 110 V and DC current as large as 100 mA. In this thesis, a two-probe configuration is adopted and a DC voltage is forced during the IV measurement.

2.4 Photoconductivity measurement setup

Photoconductivity of a semiconductor is a phenomenon where the conductance of a semiconductor changes under light illumination^{88,89}. It includes many simultaneous and/or subsequence physical processes such as photon absorption and carrier excitation, hot carrier relaxation, charged carrier transport and recombination and so on. Therefore, photoconductivity technique provides a method to study the plentiful physical properties of semiconductor. Besides, photoconductivity related effects are the physical fundamentals of many optoelectronic applications including photodetection, energy transfer of solar cells, solid state lasers, and electro-photo modulators. Finally, photoconductivity technique has a unique advantage in the research of nano-materials and nano-devices due to the maturity of device fabrication techniques and the high sensitivity of lock-in measurements. In comparison, it is impossible to measure absorption in an individual nanowire or nanobelt. The photoconductivity spectroscopy can circumvent this challenge because the photoconductivity spectrum can partially reflect the absorption.

Figure 2-10 Typical optical processes in an n-type semiconductor involving in the photoconductivity process. (1) Excitation of the host material by absorption of light with energy equal to or greater than the band gap. (2) Excitation of a bound electron at an imperfection level. (3) Thermal freeing of a trapped electron. (4) Optical freeing of a trapped electron. (5) Optical freeing of a captured hole. (6) Thermal freeing of a captured hole. (7) Capture of a photoexcited hole by an imperfection centre. (8) Capture of a photoexcited electron by a centre which has previously captured a

photoexcited hole, resulting in recombination of the carriers. (9) Capture of a photoexcited electron by an electron trapping centre⁹⁰.

The various processes involved in photoconductivity are illustrated in Figure 2-10. When the energy of incident photons is larger than the bandgap, intrinsic absorption would occur. An electron in the valence band by absorbing one photon is excited to the conduction band and leaves a hole in the valence band. The excited electron and hole may contribute to the conductivity if they do not recombine in the following transport process. When a bunch of photons incident on the sample, a great amount of excited electrons and holes will be generated. The photogenerated carriers are the main contribution to the increase of the electrical conductivity. Besides, photons can excite electrons from the valence band to impurity energy levels or from impurity energy levels to the conduction band. These electrons and holes can also increase the electrical conductivity. The trapping and releasing of the photogenerated carriers will occur as well, which may influence the response speed of a photoconductor⁹⁰.

2.4.1 Setup construction

The photoconductivity measurement was carried out in a home-built photoconductivity measurement setup. Figure 2-11a shows a picture of the setup. All the components of the setup have been labeled at the side. The schematic of the setup is given in Figure 2-11b.

A tungsten halogen lamp (250 W) was used as an excitation source. The tungsten lamp produces a very broad continuous spectrum ranging from ultraviolet to infrared, namely from 300 nm to 2500 nm. The output light of the tungsten lamp is dispersed by a monochromator (Horiba JY HR320) equipped with three gratings which can be selected according to the specific requirements. The monochromator with three available gratings is capable of continuous tuning from 200 nm to 2000 nm. The detailed information on the gratings is listed in the Table 2-1. A long pass filter is used at the entrance of the monochromator in order to prevent the high order harmonic light passing through the monochromator. Five long pass filters are equipped with the setup, as listed in Table 2-2. Due to the limited available long pass filter, the setup has a practical working range from 300 nm to 1600 nm.

Figure 2-11 Photoconductivity measurement setup. (a) The picture of the home-built photoconductivity measurement setup. All components are labeled at the side. (b) The schematic of the measurement setup.

The monochromatic light beam output is collimated by a group of lenses and then is split into two beams: one is used to illuminate the devices mounted on the cryostat cold finger while the other is directed onto a pyroelectric detector (Newport 70362) to monitor the intensity of the incident light, in order to normalize the photon flux at different wavelengths. The pyroelectric detector is chosen because it has no

dispersion. The photocurrent of a FET device is amplified by a preamplifier, which converts the current signal to a voltage signal. Both the amplified photocurrent and the light intensity signal are collected by two lock-in amplifiers (Stanford SR830). A mechanical chopper is used to modulate the incident light and provides the reference signals for lock-in amplifiers. For the spectral response measurement, an oscilloscope (Agilent DSO 5032A 300 MHz) is used with a time resolution of ~10 ns. The spectral resolution and detection resolution of the setup are around 1 nm and 1 pA, respectively. Equipped with a liquid helium continuous flow cryostat (Cryo Industry of America, USA), the photoconductivity measurement can be conducted from 4.2 to 340 K. A data acquisition (DAQ) card is used to provide the voltage in order to extract the photogenerated carriers. The output of the DAQ card ranges from -10 V to 10V.

Table 2-1 The parameters of the gratings equipped on the home-built photoconductivity measurement setup.

Grating	Grooves/mm	Blaze wavelength	Scanning range
No. 1	1800	400 nm	300-600 nm
No. 2	1200	750 nm	600-1000 nm
No. 3	600	1500 nm	1000-1600 nm

Table 2-2 The list of the cut-on wavelength for the long wavelength pass filters on the home-built photoconductivity measurement setup.

Filter No.	1	2	3	4	5	6
Cut-on wavelength	309 nm	400 nm	570 nm	695 nm	830 nm	blank

2.4.2 Data acquisition system

The data acquisition system includes the device control, synchronization between devices and data recording. The flow chart of the data acquisition system is shown in Figure 2-12. In detail, we need to allocate the resource for each device, initialize the monochromator, filter wheel and lock-in amplifiers which includes the

parameter setting, and finally release the occupied resource. During the measurement process, two loops are involved: the control loop is used to control devices and the measurement loop is responsible for the data acquisition. Therefore, the communication between those two loops is essential so that the correct data would be recorded. For example, during the wavelength scanning, once the monochromator moves to the setting wavelength, the control loop will send a message to the measurement loop and awake the measurement loop to collect the data.

Figure 2-12 The flow chart of the data acquisition system used for the home-built photoconductivity measurement system.

As seen from Figure 2-12, three types of scanning can be carried out on the system, which are wavelength scanning, voltage scanning and time scanning. The wavelength scanning is used to obtain the spectral response of the measured devices. During the initialization process for the wavelength scanning, the applied voltage, the parameters for lock-in amplifiers, the scanning wavelength interval and the data file location are set properly while the grating and filter are real-time adjusted according to the specific measuring requirements. After initialization, a message will be sent to lock-in amplifiers once the grating moves to the starting wavelength. After that, the system will read the data from lock-in amplifiers and record to the pre-assigned data file. Then the grating will move to the next wavelength and repeat the procedure until the stopping wavelength is reached. Finally, the resource held by monochromator, wheel filters and lock-in amplifiers will be released after scanning.

Figure 2-13 The front panel of the data acquisition system in the home-built photoconductivity measurement system: monochromator control.

The voltage scanning is used to investigate the photocurrent as a function of applied voltage during illumination of a certain wavelength or in the darkness. During the voltage scanning, the wavelength, grating and filter are fixed. Similar to the wavelength scanning except the voltage is scanned, each time after the voltage varies, the control loop will send a message to the system and the measurement loop will read

data from the lock-in amplifiers. The switch characteristic and response speed can be measured during the time scanning, in which both the voltage and wavelength are fixed during the initialization process. After a certain time interval set by the users, the system automatically read data from lock-in amplifiers for switch characteristic measurement and read data from oscilloscope for response speed measurement.

Figure 2-14 The front panel of the data acquisition system in the home-built photoconductivity measurement system: lock-in amplifier control.

Laboratory Virtual Instrumentation Engineering Workbench (LabVIEW) was used to program the data acquisition system for photoconductivity measurement. LabVIEW, originally released for Apple Macintosh in 1986, is widely used for instrumental control, data acquisition and industrial automation. LabVIEW is a system design platform and development environment for graphical language. Figure

2-13 displays the front panel of the monochromator control, which include monochromator initialization, the grating and filter selection, slit and mirror settings. Figure 2-14 shows the front panel of the lock-in amplifier control, from which the parameters can be set. Two lock-in amplifiers are used: one is used for the photocurrent measurement and another is used for the incident light intensity measurement. The front panel of the measurements includes the wavelength scanning, voltage scanning, time scanning and data display by graphics and table as shown in Figure 2-15. Noted that the graphical display, according to specific measurements, four types of data can be displayed, which are photocurrent, total current, light intensity and photoresponsivity.

Figure 2-15 The front panel of the data acquisition system in the home-built photoconductivity measurement system: measurement control.

2.4.3 System calibration

After the extensive instrumentation work to integrate all the different components, calibration must be performed before we make sure that the measurement system is able to give the correct result. A commercial Si photodiode S2387 (HAMAMATSU, Germany) is used to calibrate the system. The standard

database of the photodiode is given in Figure 2-16a and the spectrum acquired in our home-built system is shown in Figure 2-16b. The profile of the spectrum we acquired is similar to the standard database and the error of photosensitivity at the peak position is less than 8%, which is reasonable given that the standard curve may vary from batches to batches and devices to devices. The calibration data verifies that our home-built measurement system is reliable. The photoconductivity measurement of a typical CdS nanobelt device has been carried out in the setup as well, as shown in Figure 2-16c. The detailed information on the measurement configuration will give in the next Chapter. The sudden fall around 500 nm coincides with the bandgap energy of CdS, which is evident that the constructed system is reliable. The opposite sign between the total current (left panel in figure 2-16c) and photocurrent (right panel in figure 2-16 c) is because the preamplifier changes the polarity of the input signal, thus leading to the negative total current.

Figure 2-16 (a) The standard spectral response of a commercial Si photodiode S2387. (b) The spectral response of the commercial Si photodiode S2387 acquired by our home-built system. (c) The photoconductivity spectrum of a typical individual CdS nanobelt device. The left panel shows the total current while the right panel shows the photocurrent. The X-axis represents the wavelength with a unit of nm while the Y-

axis represents the total current (left panel) and photocurrent (right panel) with a unit of nA.

2.5 Photoluminescence and Raman Spectroscopy

2.5.1 Photoluminescence

Photoluminescence is a process in which a sample absorbs photons and then re-radiates photons. Depending on the excitation energy and temperature, a variety of transitions can occur in a photoluminescence process as shown in Figure 2-17. Those transitions include the free carrier recombination, free exciton emission, bound exciton emission, donor-acceptor pair emission and emission due to the deep defect levels. Therefore, Photoluminescence provides very rich information on both the intrinsic recombination processes and various radiative recombination processes associated with imperfections of a sample. From low temperature photoluminescence spectra, detailed information about the semiconductor properties could be obtained, such as exciton, phonon, and donor binding energy⁹¹.

Figure 2-17 The recombination processes in a direct bandgap semiconductor. (a) Band-to-band transition. (b) Conduction band-to-acceptor transition. (c) Donor-to-valence band transition. (d) Donor-to-acceptor transition. (e) Recombination via intermediate states. (f) Non-radiative recombination via intermediate states. (g) Band-to-band Auger recombination⁹¹.

Photoluminescence spectroscopy has been extensively used to study optical properties of semiconductors. As the change of the temperature, a shift of the band gap in semiconductors is present due to the thermal dilation of the crystal lattice and the electron-phonon interaction. The shift of the band gap can be described by an empirical Varshni equation or Bose–Einstein expression. Besides, the electron-

phonon coupling strength can be extracted from the temperature dependence of full width at half-maximum (FWHM). The shift of the bandgap of a semiconductor varies differently with the size and dimensionalities, which can be distinguished through the photoluminescence spectra. Furthermore, photoluminescence spectrum can provide information of the impurities and crystalline quality. Therefore, micro-photoluminescence spectroscopy is able to investigate the size effect, dimensionalities effect, temperature effect, and the impurities of the nanostructures in the individual nanowire and nanobelt.

While photoconductivity spectroscopy can provide information in the region above the band edge, photoluminescence spectroscopy would give information near and below the band edge. Combining those two approaches, the detailed information about both the band structures and impurities can be obtained. The information sheds light on the design and optimization of nanoscale optoelectronic devices.

2.5.2 Raman scattering spectroscopy

Raman scattering is the inelastic scattering of light, which was discovered by Raman and Krishnan in 1926. Since then, Raman spectroscopy has been extensively used to study phonons and other elemental excitations such as excitons, plasmons, polarons, polaritons and so on in condensed matter physics. Since it was discovered more than 80 years ago, Raman spectroscopy has become one of the most powerful spectroscopic tools with the advantages of non-destructive and high sensitive. It is capable of detecting objects in the order of nanometers and is able to be excited by a broad range of light from ultraviolet to near infrared.

Figure 2-18 Schematic of the Raman scattering processes: (a) Non-resonant Raman scattering and (b) Resonant Raman scattering.

When photons are scattered by atoms or molecules, a major part of the incident photons are elastically scattered (Rayleigh scattering), in which both the energy and momentum of the scattered photons are the same as those of the incident photons as schematically shown in Figure 2-18. In addition to the elastically scattered photons, a small fraction of the incident photons are inelastically scattered. The inelastic scattering is called Raman scattering. The first-order inelastic Raman scattering process involves the absorption of an incident photon and the subsequent emission of a photon via intermediate states which can be both real and virtual states.

The real intermediate states correspond to the resonant Raman scattering (Figure 2-18b) while the virtual ones correspond to the non-resonant Raman scattering (Figure 2-18a). Raman scattering has two possible outcomes: Stokes Raman scattering and anti-Stokes Raman scattering. During the Stokes Raman scattering, phonons are created and the emitted photons have lower energies, which corresponds to the scattering from ground vibrational states to excited vibrational states. In contrast, the process is completely reversed in anti-Stokes Raman scattering process, in which the phonons are annihilated corresponding to the scattering from excited vibrational states to ground vibrational states. The intensity of the Stokes Raman scattering and anti-Stokes Raman scattering depend on the temperature, which governs the population of the excited vibrational states.

During the Raman scattering processes, both the energy and momentum must be conserved:

$$h\nu_i = h\nu_f \pm h\nu_q \quad (2-3),$$

$$\mathbf{k}_i = \mathbf{k}_f \pm \mathbf{q} \quad (2-4),$$

where ν_i , ν_f and ν_q are the frequency of the incident photons, scattered photons and phonons, respectively; $\mathbf{k}_i$, $\mathbf{k}_f$ and $\mathbf{q}$ are the wave vector of incident photons, scattered photons and phonons. Equation (2-3) and (2-4) hold for both Stokes and anti-Stokes processes. '+' corresponds to the creation of phonons (Stokes process) while '-' represents the annihilation of phonons (anti-Stokes process). During the Raman scattering in the vibrational systems, the vibrational quantum number difference $\Delta\nu = \pm 1$ should be satisfied.

Many interesting phenomena in Raman scattering spectrum emerge or become more apparent in its nanoscale form. As the size of the nanostructure decreases to the quantum confinement regime, the phonon energy shows redshift. In addition to the quantum confined phonon states, the new modes such as breathing modes are present when the size of the structure is smaller than a critical size. Due to the large surface-to-volume ratio in nanostructures, surface phonons become significant. Besides, the electron-phonon coupling is greatly enhanced in nanoscale as well.

2.5.3 Instrumentation

Both Raman scattering and micro-photoluminescence measurements of individual nanostructures for this thesis were carried out in a Micro-Raman spectrometer (Horiba-JY T64000) in the backscattering configuration. The spectrometer is equipped with a 640 mm focal length double subtractive pre-monochromator followed by another 640 mm focal length spectrograph. With three 1800 mm^{-1} gratings, the spectral resolution can reach $\sim 0.5\text{ cm}^{-1}$. An Olympus U-5RE-2 confocal microscope is used to view the testing individual nanostructures and a liquid nitrogen cooled charge-coupled detector is used to collect the spectra.

Figure 2-19 The optical image of the Horiba-JY T64000 micro-Raman spectroscopy. All important components are labelled correspondingly.

A picture of the spectrometer is shown in Figure 2-19 with all important components labelled at side. The schematic image of the simplified spectrometer optics is displayed in Figure 2-20. More than ten laser lines in our lab are available to be selected. The excitation light beam is aligned and passes through a beam splitter (SB), which allows the excitation beam to pass through the objective to excite the scattering and at the same time allows the objective to collect the scattered photons. The confocal microscope defines the volume of scattering light being collected and

excludes the stray light. By adjusting the size of pinhole of the confocal microscope, the volume of light being collected can be adjusted according to the sample size and experimental requirements.

Figure 2-20 The schematic of the spectrometer optics.

Equipping with three gratings, the spectrometer has two available modes: single mode and subtractive mode. The single mode is applied for the Stokes photoluminescence measurement and high frequency phonon mode measurement while the subtractive mode is capable of detecting anti-Stokes photoluminescence and low frequency phonon mode ($\sim 5 \text{ cm}^{-1}$) by using the three gratings and effective filter. For the single mode, the scattered photons are directly directed to the third grating which disperses the spectrum onto the CCD detector. A notch filter is used in order to remove the Rayleigh scattering light which is quite strong and may damage the CCD detector if not removed. The subtractive double-grating acts like a filter, which

defines a spectral bandpass determined by the internal slit width for the subtractive mode. By coupling with a liquid helium continuous flow microscopy cryostat, the spectrometer is capable of measuring spectra from 4.2 K to 340 K.

Chapter 3 Photoconductivity of Individual CdS Nanobelt Devices

3.1 Introduction

3.1.1 Band structure of CdS

The photoluminescence and photoconductivity processes are closely related to the band structures of the materials and defect states. In a semiconductor, there are valence bands and conduction bands, between which a forbidden band gap is formed¹⁰. When a semiconductor is optically irradiated, the photons excite electrons from the valence band to the conduction band. If the electrostatic Coulombic interaction between electron and hole has to be taken into consideration, a quasi-particle called exciton is formed^{1,92}. The energy level of exciton is shown in Figure 3-1b. The dispersion relation of excitons can be expressed as $E_{ex}(n_B, \mathbf{K}) = E_g - Ry * \frac{1}{n_B^2} + \frac{\hbar^2 \mathbf{K}^2}{2M}$, where E_g is bandgap energy, Ry is exciton Rydberg energy, n_B is principle quantum number, M is translational mass and $\mathbf{K}$ is wave vector of exciton. Between the excitonic level $n_B = 1$ and the conduction band, there are many high-lying exciton energy levels such as $n_B = 2, 3, \dots$. Typical excitonic absorption spectra in GaAs crystals at various temperatures are shown in Figure 3-1c. A sharp peak at low temperature near the band edge corresponds to the excitonic absorption.

The energy difference between the excitonic level $n_B = 1$ and conduction band is defined as the exciton binding energy, which is 28 meV for CdS^{71,93} and it is larger than the thermal excitation energy of ~26 meV at room temperature. Compared with free carriers, excitons exhibit larger oscillation strength, narrower emission peaks and stronger coupling to phonons. Excitons can either move freely in the crystal lattice of a semiconductor or be bounded to certain defects including natural or ionized defects⁹¹. The free moving exciton is called a free exciton while the bound one called a bound exciton complex. Due to crystal field and spin-orbital interaction in group II-IV compound semiconductors, the valence band is split into three bands. The

corresponding excitons are named as free exciton A (FXA, Γ_9 , also refers to as heavy hole), free exciton B (FXB, Γ_7 or light hole) and free exciton C (FXC, or Γ_7 split-off (SO) band) as shown in Figure 3-1a^{1,94}. The selection rules of the polarization can be used to distinguish the excitonic transitions⁹⁵. Depending on the exciton binding energy, excitons may be ionized at a certain temperature. Besides, the excitons can be bound to acceptors and donors to form acceptor-bound excitons and donor-bound excitons, where the acceptors and donors can be either neutral or ionized¹. Low temperature absorption⁹⁶, reflection⁹⁷, and photoluminescence spectroscopy⁹⁸ techniques are capable of detecting the excitonic transition energies.

Figure 3-1 (a) The typical schematic band structure of the hexagonal II-IV compound semiconductors in the momentum space¹. (b) The schematic diagram of the excitonic energy levels for a direct bandgap semiconductor¹. (c) Exciton absorption spectra in GaAs crystal at different temperatures². (d) Summary of the band diagram of CdS in real space with intrinsic defect levels indicated, which are from the first principle calculation. The Coulombic interaction was not included during the calculation⁷⁸.

The characteristic energies of intrinsic FXA, FXB and FXC in CdS are 2.550 eV, 2.568 eV and 2.629 eV, respectively⁹⁹⁻¹⁰¹. The energy differences are 18 meV between FXA and FXB, and 79 meV between FXA and FXC. The characteristic energies may vary a little with sizes and dimensionalities of structures while the energy differences remain more or less the same, which is often used to assign peaks in photoconductivity and photoluminescence spectra. In addition to the intrinsic excitons, bound exciton complexes are present in CdS as well due to the presence of defects⁷⁸. Because of the different vapour pressure for Cd and S at certain temperatures, the stoichiometric defects can be unintentionally introduced during the synthesis. The stoichiometric defects include sulphur and cadmium vacancies, sulphur and cadmium interstitials and sulphur and cadmium anti-sites. The electrons, holes and excitons might be trapped to those defects forming the bound complexes. Excitons bounded to neutral acceptors and donors are labeled as I_1 and I_2 , respectively¹. Besides, the donor-acceptor pairs can combine and give rise to the emission peaks as long as the donor and acceptor levels are populated.

The summary of the energy levels including defects of interest is given in Figure 3-1d, which has been validated by first principle calculations. The exciton dynamics have been studied by steady-state and time-resolved photoluminescence spectroscopy⁷⁸. We can conclude that the sulphur vacancies mainly contribute to the shallow donors with an energy E_D of approximate 100 meV, while the cadmium vacancies mainly contribute to the acceptors with E_A of approximate 160 meV. The deep levels in CdS originate from the cadmium interstitials with an energy level of 1.68 eV above the valence band, the sulphur interstitials with 2.18 eV from the conduction band, and two anti-site defects with energy levels of 1.5 and 2.0 eV above the valence band⁷⁸.

3.1.2 Photoconductivity of nanostructure devices

Photoconductivity describes the phenomenon that the electric conductivity changes with light irradiation. Spectral response, switch characteristics and response speed are used to evaluate the photoconductivity of a semiconductor⁸⁸. Spectral response is defined as the photocurrent as a function of wavelength. However,

photocurrent depends on the incident light intensity and incident photon energy. To exclude the influence from the variation of the incident light intensity and photon energy, instead of photocurrent gain is a better physical quantity to be used in practice, which was defined as how many electrons are collected by electrodes for each incident photon ($G = \frac{I_{ph}/e}{\phi_{ph}}$, where I_{ph} is the photocurrent and ϕ_{ph} is the photon flux.)⁷¹. Alternatively, photoresponsivity has been used as well, which is defined as $R = \frac{I_{ph}}{P}$, where P is the light intensity illuminated on device. The switch characteristic is adopted to test the stability and reversibility of a device. The on-off ratio, defined as the ratio of the photocurrent under illumination to the photocurrent in dark, is used to describe the switch characteristic of a device, which is very crucial for the optical switch applications⁸⁸. The response speed is characterized by both the rise time and the fall time. The rise time (fall time) is the time required to increase (decrease) the photocurrent from 10% (90%) to 90% (10%) of its final value. In practice, short response time is preferred so that the dead time is minimized⁷⁹.

Nanomaterials have been shown to exhibit enhanced photoconductive properties compared to bulk. The scattering during the transport process is reduced due to the high crystalline quality of nanostructures, thus improving the carrier extraction efficiency. The great amount of surface states owing to the large surface-to-volume ratio in nanostructures enhances the recombination rate and thus lifting the response speed. Besides, the large surface-to-volume ratio creates a huge amount of surface states which could trap one type of carriers for a long time leading to the fact that other types of carriers can circulate many times before recombination¹⁰². As a result, the gain is greatly improved in nanostructures.

Yang and co-workers initiated the research on photoconductivity of II-VI nanowires by studying ZnO nanowires.¹⁰³ Since then, the photoconductive property of a wide variety of nanowires and nanobelts has been studied in great details. The photoconductivity of II-IV 1D nanostructures such as that from ZnO^{103,104}, CdS^{79,105-}

¹⁰⁷, CdSe¹⁰⁸, ZnSe¹⁰⁹, and ZnS¹¹⁰ have been intensively investigated. Various fascinating phenomena on the photoconducting properties of II-VI 1D nanostructures have also been studied, including the improvement of photosensitivity by exploiting a Fabry-Pérot cavity between a nanowire or a nanobelt photodetector with the associated substrate and a polarization-dependent sensitivity as was observed in CdSe¹⁰⁸ and CdTe¹¹¹ nanowires due to the high aspect ratio of nanowires.

There are two classes of photodetectors: photodiodes and photoconductors¹⁰². In a photodiode, a p-n junction is formed and the built-in electric field within the depletion region near the junction is established. The photogenerated electrons and holes move to the opposite electrodes driven by the built-in electric field. As a result, the external quantum efficiency of a photodiode cannot be higher than one provided that effects such as avalanche and carrier multiplication would not occur. In contrast to the photodiodes, the photoconductors can have very high gain because one type of photogenerated carriers may be trapped while the other type would circulate many times before recombination occurs under an external electric field.

3.1.3 Introduction to electroabsorption

Electroabsorption describes how the electric field influences the optical absorption in semiconductors. Electroabsorption near the optical band edge has been extensively investigated due to its promising applications in the electro-absorption modulators¹¹²⁻¹¹⁴. In general, an electric field applied to a semiconductor can lead to several modifications to the absorption spectrum including modulation of the absorption coefficient (Franz-Keldysh effect)^{115,116}, growth of the band-to-band absorption spectral weight¹¹⁷, shift of the spectral peak (Stark effect)¹¹⁸ and dissociation of exciton (exciton ionization)^{113,117,119}. The size, dimensionality and the crystalline quality of the semiconductors all play important roles in the electroabsorption⁷¹.

A plenty of studies on electro-absorption in bulk, 2D quantum wells and 0D quantum dots have been reported^{37,112,113,118,120-122}. However, investigations on the electro-absorption of 1D nanowires and nanobelts are rarely reported¹²³. The challenge is the technical difficulty to measure optical absorption on individual

nanowires or nanobelts. In this regards, photoconductivity spectroscopy is an ideal approach to shed light on electro-absorption on individual level. There has been considerable attention paid to the photodetection of semiconductor nanowires or nanobelts in the past decade^{35,56,79,91,108,124}, however, the electro-absorption of semiconductor nanowires or nanobelts in terms of their dependence on electric field strength, size and dimensionality remains elusive.

3.2 Photoconductivity of an individual CdS nanobelt device

Lee *et al.* systematically investigated the photoconductivity of an individual CdS nanobelt⁷⁹. The excitation-power dependent photocurrent, spectral response, response speed and the environmental influence on the photocurrent have been studied. The gain and response speed are ~ 100 and ~ 100 μs , respectively. Later, Golberg *et al.* reported the ultrahigh external quantum efficiency (10^7) and ultrafast response (20 μs) in CdS nanobelts³⁶. In this subsection, the photoconductivity measurement of individual CdS nanobelts is carried out in the home-built photoconductivity system.

Figure 3-2 The schematic of the photoconductivity measurement configuration.

The schematic of the photoconductivity measurement configuration is shown in Figure 3-2. The two-probe FET devices are used and the incident light illuminate on the device in the normal direction. By applying a source-drain voltage, the photocurrent is then measured. In this thesis, all of the photoconductivity measurements are carried out using the same configuration. The detailed procedure of the measurements can be found in Chapter 2.

The photocurrent as a function of applied source-drain voltage under different wavelength light irradiation is given in Figure 3-3a for an individual CdS nanobelt device. The thickness and the width of the nanobelt used are 50 nm and 2 μm , respectively. The channel of the device is around 4.5 μm . The nearly zero photocurrent for both 540 nm light irradiation and in dark suggests that the nanobelts have very high crystalline quality with a low carrier concentration without photon irradiation or with photon irradiation but the photon energy smaller than band gap energy of CdS at room temperature, which is around 2.5 eV corresponding to the wavelength of ~ 506 nm. The nearly zero photocurrent for the incident photon with energy smaller than band gap energy indicates the absence of the impurities and defects which would form intermediate states within the band gap. The photocurrent is no longer zero when the device is irradiated by photons with energy larger than the band gap energy. However, due to the different light intensity and absorption coefficient at different wavelength, the photocurrent varies.

Figure 3-3 Photoconductivity of CdS nanobelt FET devices. (a) The photocurrent versus the applied photocurrent under different wavelength light irradiation for a 50 nm CdS nanobelt device. The width of the nanobelt is 2 μm and the channel is around 4.5 μm . (b) The gain of a 50 nm CdS nanobelt device under various source-drain voltages. (c) The optical switch characteristic of a 50 nm nanobelt device under 475 nm light illumination. The applied source-drain voltage is 5 V. (d) The time response

of the CdS nanobelt device under 475 nm light illumination with a source-drain voltage of 1 V.

The spectral response of a 50 nm CdS belt device is shown in Figure 3-3b. The gain spectra under different applied source-drain voltage are shown rather than photocurrent spectra, since the gain is able to exclude the influence from the variation of the incident light intensity and incident photon energy at different wavelength as discussed previously. The gain of the nanobelt device is around several thousands, which is in an appropriate range as previously reported^{56,79}. The oscillations in the spectra are due to the interference between the nanobelt and the SiO₂ layer on the substrate, which will be discussed in detail below.

Figure 3-4 Temperature-dependent gain and photocurrent spectra of CdS nanobelt FET devices. (a) The temperature dependence gain of a 230 nm CdS belt device from 90 K to room temperature. The photocurrent spectra of 230 nm (b), 50 nm (c) and 65 nm (d) CdS belt devices from liquid nitrogen temperature to room temperature.

The optical switching characteristic of the 50 nm nanobelt device obtained via time scanning is shown in Figure 3-3c. As we can see from the curve, the photocurrent changes rapidly with the light on and off. The on/off photocurrent maintains the same for all measured cycles indicating the excellent stability and reversibility of the used device. The on-off ratio is ~ 104 , which is much larger than the reported value^{36,106}. This large on-off ratio indicates that our samples are ideal candidates for the optical switch applications.

The response speed is important for the photodetectors and optical switches. In this thesis, the respond speed is measured by using oscilloscope as shown in Figure 3-3d for a 50 nm CdS nanobelt device. The wavelength and the applied source-drain voltage are set to be 475 nm and 1 V, respectively. The rise time and fall time are 500 μ s and 700 μ s, respectively, which are comparable with the previous reported value⁷⁹.

The temperature dependent photoconductivity spectra can provide information on the exciton energy, electron-phonon coupling and transport properties of semiconductors¹²⁵⁻¹²⁷. The temperature evolution of the photoconductivity spectra of CdS nanobelt devices was carried out by mounting the devices into a microscopy cryostat. Figure 3-4a displays the temperature dependent gain spectra of a 230 nm CdS belt from 90 K to 293 K under the applied source-drain voltage of 1 V. As the temperature decreases, the band edge gradually shifts toward higher energy. The gain continuously decreases with temperature as well. The blue shift of the band edge and the decrease of the photocurrent have been also observed for 50 nm and 65 nm CdS nanobelt devices (Figure 3-4 c-d). The band edge blueshift is due to the lattice thermal expansion and the change of the electron phonon coupling strength with the temperature as well described by Varshni equation¹²⁸. Since the light intensity we used to measurement those three devices maintains the same, the gain for all those devices should decrease with temperature. The decrease of the gain with temperature is somewhat unexpected.

In general, the extraction efficiency of the photogenerated carriers will increase due to the reduction of the carrier scattering by phonons at a low temperature¹²⁹. The reduction of the thermal excited carriers is one possible reason for the higher resistance, thus smaller current in semiconductors at low temperatures. However, what we measured here was photocurrent acquired by lock-in amplifiers,

through which the dark current can be eliminated from the photocurrent spectra. The thermal excited carriers would not contribute to the photocurrent, thus should not be the origin of the decrease of gain. Other two reasons may be responsible for the reduction of the gain with temperature: the space charge limited photocurrent and the shorter lifetime of the photogenerated carriers at low temperature. The first one is the surface depletion induced electric field, which would lead to a depletion region near the surfaces or interfaces. The electric conduction becomes space charge limited at those regions, leading to a smaller electric conductivity. In nanostructures, the larger surface-to-volume ratio gives rise to a huge amount of surface states within bandgap region, which will trap one type of carriers. For example, in n-type CdS nanobelts under thermodynamic equilibrium, the electrons will flow to the surface to fill up the surface states creating a negative surface charge. A depletion region is formed near the surface induced by the surface charge. As the temperature decreases, the density of thermal excited carriers reduces leading to a larger surface depletion region but a smaller confinement potential (see next chapter)³³. As a result, the neutral bulk region becomes smaller leading to a smaller conductivity, which can result in a smaller photocurrent. Another one is the shorter of the carrier lifetime at low temperatures. As aforementioned, the huge amount of surface states would trap one type of carriers for a long time while the other type of carriers can circulate many times before recombination leading to the large gain¹⁰². As the temperature decreases, the smaller confinement potential makes both holes inside the CdS nanobelts and electrons trapped at surfaces tunnel through the potential barrier easier, resulting in a larger recombination probability of the photogenerated electrons and holes and thus a shorter lifetime of the photogenerated carriers, which would further reduce the photocurrent as well.

Besides, as seen from Figure 3-4b, c, d, another distinct feature is that two distinguished peaks can be viewed in the 50 nm and 60 nm belt devices while only one broad band edge transition is present in the 230 nm belt. The peak at 2.525 eV (2.562) for 50 nm (65 nm) belt device can be attributed to FXB while the peaks located at 2.599 eV (2.633 eV) for 50 nm (65 nm) is due to the FXC, respectively (see section 3.4.2)^{71,78}. It should be noted that excitons are initially bounded together *via* Coulomb interactions which will not contribute to the photocurrent unless they are ionized through interactions either with optical phonons¹²⁵ or by field ionization^{71,130}

(including the internal electric field due to the surface depletion or the external electric field exerted through electrodes) in a time scale smaller than their lifetime¹³¹. In our CdS samples, the electron-phonon coupling is significant⁴¹, which has been confirmed by the resonant Raman scattering experiments in similar II-VI nanostructures⁴⁰. The strong electron-phonon coupling would dissociate the excitons leading to an increased photocurrent at the exciton peak positions. Besides, the strong surface electric field in low dimensional nanomaterials (nanowire or nanobelt) and applied source-drain electric field can also cause the dissociation of the excitons. The exciton ionization has been observed in CdS crystal, where the correlation measurements between exciton absorption and photoconductivity have been conducted. Those two spectra give the same spectral configuration, which manifests that excitons are ionized and contribute to the photocurrent¹²⁵.

Figure 3-5 The photocurrent (a) and gain (b) spectra of a 46 nm CdS belt device below liquid nitrogen temperature under an applied source-drain voltage of 1 V. The photocurrent spectra have been normalized and shifted vertically for clarity. The gain spectra are shifted vertically by 1500 in order to compare the features near the band edge among each other.

The photoconductivity measurement of a 46 nm CdS nanobelt device below liquid nitrogen temperature has also been performed with applied source-drain voltage of 1 V as shown in Figure 3-4b. Since the gain at three different temperatures is almost same at all wavelengths, the spectra are shifted vertically by 1500 in order to compare among each other. In contrast to the temperature dependent gain above 77 K,

the gain for all three temperatures is almost the same with a maximum value of 6000. The peak at 2.568 eV can be assigned to FXB while the peak at 2.637 eV is due to FXC. The FXB and FXC peaks show a very small blueshift as the temperature decreases. The large oscillations is due to the the interference effect, which will be discussed in detail below.

3.3 Interference effect due to the SiO₂ on the substrate

The incident light would not be completely absorbed by the nanobelts if the thickness of those nanobelts is not large enough. The thickness required for the complete absorption of the incident light is around 200 nm evaluated by the Beer-Lambert law using the optical absorption coefficient obtained from Landolt-Bornstein handbook⁹³. The light passed though the nanobelts will be reflected back by the substrate and be absorbed by the nanobelts again as shown in Figure 3-6a. The reflectivity spectrum of a bare 500 nm SiO₂/Si substrate shows oscillations, which can be attributed to the Fabry-Pérot modes formed due to the silicon oxide cavity on the substrate, as shown in Figure 3-6b. Those oscillations appeared on the reflectivity spectrum of the substrate are also shown in the spectral response of the thinner nanobelts (labelled as red arrows) in Figure 3-7a, which has been previously observed in CdSe nanowires¹⁰⁸.

Figure 3-6 (a) The schametic of the Fabry-Pérot modes formed due to the silicon oxide cavity on the substrate and nanobelts themselves. (b) The reflectivity spectrum of a bare 500 nm SiO₂/Si substrate.

Assuming that the reflected light from the substrate only undergoes one time more absorption, the total energy deposits to the nanobelts can be expressed

$$I = I_0(1 - R_0)(1 - \exp(-\alpha L)) + I_0(1 - R_0)\exp(-\alpha L)R(1 - \exp(-\alpha L)) \quad (3-1),$$

where I_0 is the intensity of the incident light, L is the thickness of the nanobelt, R is the reflectivity of the substrate, R_0 is the reflectivity from the top surface of the CdS nanobelt and α is the absorption coefficient. The first term of the (3-1) indicates the first time absorption of the incident light and the second term shows the absorption of the reflected light from the substrate. The ratio of the energy deposited to the CdS nanobelt to the incident light can be calculated by using the optical absorption coefficient taken from the Landolt-Bornstein handbook⁹³. The calculated results are given in Figure 3-7b. The oscillations appear at the same energy position as the experimental results (labelled as P1 and P2 in Figure 3-7a), which verifies that the oscillations originate from the Fabry-Pérot modes formed due to the silicon oxide cavity on the substrate. No oscillation is observed from the thick belt (230 nm) because its thickness is comparable to the penetration depth using the optical absorption coefficient $5 \mu\text{m}^{-1}$ ⁹³.

Figure 3-7 (a) Gain spectra of various thickness CdS nanobelt devices at room temperature. All spectra have been normalized and vertically shifted in order to compare among each other. P1, P2 and P3 are used to label oscillation peaks while V1 represents the oscillation valley. (b) The calculated ratio of the absorbed photon number to the incident photon number provided the reflected light from substrate undergoes one time more absorption by the CdS nanobelts.

Further, the Fabry-Pérot modes can also form inside the nanobelts themselves if the thicknesses of them satisfy the condition

$$L = \frac{m\lambda}{2n} \quad (3-2),$$

where L is the thickness of the belts, m is a positive integer, n is the refractive index at certain wavelength λ . The P3 peak for the 65 nm nanobelt device in the Figure 3-7a locates around 330 nm (corresponding to an energy of 3.76 eV), at which wavelength the refractive index n is around 2.5. By inserting $m=1$, $n=2.5$ and $\lambda=330$ nm into equation (3-2), the thickness obtained is around 66 nm, which is consistent with the thickness measured by AFM. Therefore, the peaks around 3.76 eV (labelled as P3 in Figure 3-7a) can be ascribed to the Fabry-Pérot modes formed inside the nanobelts. The P3 peak of the 57 nm belt device can be attributed to the Fabry-Pérot modes formed inside the nanobelts as well. For the 230 nm belt, the thickness is large enough to completely absorb the incident light so that no reflection light contributes to the photocurrent. For the 50nm belt, the Fabry-Pérot mode forms below 300 nm, which is out of the measuring range of our setup.

Figure 3-8 (a) The intensity ratio of the P2 peak to V1 valley as a function of the nanobelt thickness extracted from Figure 3-7a. The horizontal red line indicates the intensity ratio for 230 nm belt device. (b) The measured reflection spectrum of a Si substrate with 100 nm SiO₂ (blue curve) and the gain spectrum of a 54 nm nanobelt device (red curve) at room temperature.

In order to evaluate the extent how much the substrate influences the gain spectrum, we extract the intensity ratio of the P2 peak to V1 valley since both of P2 peak and V1 valley originates from the reabsorption the substrate reflected photons. The intensity ratios are extracted from Figure 3-7a and plotted against the nanobelt thickness shown in Figure 3-8a. Since there is no oscillation for 230 nm belt, the intensity ratio of P2 to V1 was set to unity. As the thickness increases, the intensity ratio monotonously decreases, indicating the influence from the substrate becomes weaker in thick nanobelts. Furthermore, it is expected that the P1, P2 peaks and V1 valley should be absent if we select a Si substrate with a 100 nm SiO₂, because 100 nm SiO₂ is too thin to support Fabry-Pérot modes in the wavelength range of interesting (from 300 nm to 600 nm). The reflectivity spectrum of a Si substrate with 100 nm SiO₂ indeed shows no oscillation in the range of interesting as shown in Figure 3-8b (blue curve). In contrast to the oscillations observed in Figure 3-7a where substrates with a 500 nm SiO₂ are used, the gain spectrum of a 54 nm CdS belt device on a 100 nm SiO₂ substrate (red curve in Figure 3-8b) shows monotonously decreases as the photon energy increases. The absence of oscillation in Figure 3-8b further proves that the oscillations appeared in Figure 3-7a originate from the Fabry-Pérot modes due to the silicon oxide cavity on the substrate.

The observations implies that the cavity-resonance effect can be exploited for photodetectors based on such nanobelt for enhancing the sensitivity at certain wavelengths or suppressing unwanted ones by properly selecting the thickness of the nanobelts and the substrates¹⁰⁸. This cavity-resonance effect can also be used to enhance the energy conversion efficiency for the energy-harvesting applications.

3.4 Thickness and dimensionality dependence of the spectral response

As previously mentioned, the electroabsorption varies with the features near the band edge, thus it depends on both the size and dimensionalities of the structures. In this section, the size and dimensionality dependence of the photocurrent and gain would be discussed first. Then the peaks and bumps near the band region will be assigned since they are crucial for investigations on the electroabsorption which would be present in the next section.

3.4.1 Spectral response

Figure 3-9 (a) The photocurrent spectra and (b) the gain of the nanowire and nanobelt devices at room temperature. The applied source-drain electric field is 2 kV/cm.

The photocurrent spectra of a nanowire (the diameter of the nanowire is 120 nm) and nanobelts with different thicknesses ranging from 50-230 nm at room temperature are shown in Figure 3-9a. The applied source-drain electric field is defined as the ratio of the source-drain voltage to the channel length of the devices. Here the applied source-drain electric field is 2 kV/cm. The diameter of the nanowire is around 120 nm. A few broad oscillation peaks appearing on the nanowire and thin nanobelt (50 and 65 nm) devices can be attributed to the Fabry-Pérot modes formed due to the silicon oxide cavity on the substrate and the nanobelts themselves as discussed previously. The apparent decreasing of photocurrent at the higher energy side is due to the low incident light intensity in UV regime for a quartz tungsten halogen lamp. As previously mentioned, to exclude the influence from the variation of the incident photon flux on the photocurrent, gain spectra are given as well in Figure 3-9b. The gain of all devices is around several thousands, which is in an appropriate range as previously reported^{56,79}.

Figure 3-10 The gain of the nanowire and nanobelt devices near the band edge region at room temperature.

The spectral response near the band edge region at room temperature exhibits a noticeable dimensionality and size dependence as shown in Figure 3-10. The gain spectra have been normalized by the maximum in order to compare among each other. A distinct sharp peak around 2.43 eV can be resolved from the nanowire device, while a small peak near 2.48 eV and another rather broad bump close to 2.56 eV are identified for those thinner nanobelts (50 and 60 nm). For the thick nanobelt (230 nm), only a broad band edge transition is resolved at ~ 2.45 eV, which exhibits a very long tail at the lower energy side. The long tail has various possible origins including phonon-assisted transition, excitonic effect, impurities and Franz-Keldysh effect^{123,132}. Away from the band edge at the higher energy side, oscillations are observed for all devices but more pronounced for the nanowire and thicker nanobelt. The band edge exhibits a gradual red shift as the thickness of the nanobelts increases, which has also been observed in photoluminescence spectra³³ and will be discussed in the next section.

3.4.2 Peak assignment

The information about those peaks and bumps near the band edge region in photoconductivity spectrum is indispensable for examining how those features evolve with the applied field. In order to assign those peaks and bumps nearby the band edge unambiguously, the photoluminescence spectra have been taken at room temperature and low temperatures as shown in the comparisons of photoluminescence and

photoconductivity spectra except for nanowire, where only photoluminescence and photoconductivity spectra at room temperature are present (Figure 3-11).

In the nanowire, the emission peak energy is higher than the sharp peak of photoconductivity spectrum with a blue shift of 45 meV, larger than the exciton binding energy of 28 meV^{50, 61, 128,133}. Therefore, the sharp peak of photoconductivity spectrum can be tentatively attributed to FXB, while the photoluminescence emission is due to the free carrier recombination. The small bump ~ 14 meV below the sharp FXB peak can be assigned as FXA as labelled in Figure 3-11a. The considerably large energy difference (~ 59 meV) between FXA and photoluminescence peak is due to a Stark effect in nanowire, which introduces a strong red shift in the photoconductivity spectrum as will be explained in detail later. We can assign the peak in the photoconductivity spectrum from 65 nm nanobelt as FXB and the small transition just below FXB as FXA (as indicated in the Figure 3-11c) by comparison of the photoluminescence and photoconductivity spectra at 77 K. Similarly, FXA and FXB for the 50 nm belt are assigned at 180 K as labelled in Figure 3-11b. The 50 nm belt device is broken down below 180 K so we do not show the photoconductivity spectrum at 77 K.

Based on the temperature dependent photoluminescence and photoconductivity spectra, the peaks and bumps at room temperature are properly and unambiguously assigned. It is not surprising that exciton peaks can be identified in photoconductivity spectrum at room temperature, as it has been demonstrated that the FXA emission is dominated in CdS nanobelts at the room temperature^{128,134}. For the 230 nm nanobelt, the thickness is larger than the half of the wavelength of emitted photons inside the belt, which is around 97 nm^{71,135}. The internal reflection can occur at the surfaces or interfaces of the nanobelts which will trap the emitted photons causing the reabsorption of the emitted photons. As a result, the reabsorption effect must be taken into account which leads to the redshift of the luminescence spectrum. From a detailed thickness dependent photoluminescence spectroscopy investigation discussed in the next chapter³³, the emission peak position without reabsorption can be deduced by the extrapolation of the photoluminescence peak position versus thickness, which exactly coincides with the broad band edge transition position of the photoconductivity spectrum³³. Therefore, the broad band edge transition corresponds to the mixture of FXA and FXB. As the temperature increases, the increase of the

redshift due to the reabsorption leads to the larger difference between the emission peaks and the broad band edge transition as seen from the Figure 3-11d. Once the positions of FXA and FXB are confirmed, the position of FXC can be assigned correspondingly according to the energy difference for different temperatures as shown in Figure 3-11a-d. The agreement of exciton peaks in photoluminescence and photoconductivity spectra shows negligible Stokes shift, which proves the crystalline quality of our samples⁷⁹, consistent with recent reports of n-type CdSe nanowires studied by our group^{81,136}.

Figure 3-11 The photoluminescence (solid lines) and gain spectra (symbol lines) of (a) the 120 nm nanowire, (b) the 50 nm nanobelt, (c) the 65 nm nanobelt and (d) the 230 nm nanobelt at room temperature and low temperatures. The applied source-drain field is 2 kV/cm.

3.5 Electroabsorption

Once we have assigned the peaks and bumps near the band edge region at room temperature, the peaks and bumps of interesting are selected to investigate the electroabsorption. Since all photoconductivity measurements are performed using the floating back-gate configuration, any effect from the floating back-gate should be excluded or clarified. In this section, how the floating back-gate effect influences gain near the band edge region will be examined first. The Franz-Keldysh effect will be verified through the quasi-periodic oscillations right above the band edge and exponential decay tail. The Stark effect and field induced exciton ionization will be discussed finally.

3.5.1 Floating back-gate effect

The floating back-gate electrode in photoconductivity measurements can have any arbitrary potential. The applied electric field between the source and drain electrodes on the nanowire/nanobelt was a few kV/cm. Under such conditions, there can be a much more significant electric field along the plane normal of substrate due to the potential difference between the gate and those two top electrodes in view of the thinner dielectric layer (500 nm) compared to the length of the nanowire/nanobelt (a few micrometers). How the floating back-gate electrode influences the electroabsorption can be examined via three methods. The first one is to fabricate devices in which the nanowire/nanobelt is suspended such that it is decoupled capacitively from the gate as much as possible. The other two are to provide simulation of electric field situation with grounded gate and a bias applied between two source-drain contacts and to compare the spectra with and without grounding the gate electrode.

Figure 3-12 The photoconductivity gain and their second derivative for a 60 nm nanobelt with and without grounding the back-gate electrode. The applied source-drain electric field is 2 kV/cm.

If the device can be suspended, we can certainly eliminate the influence from the floating gate. However, on one hand it is quite difficult to fabricate the suspended devices. On the other hand, suspending belts will possibly introduce strain, which will shift the excitonic peaks. The strain induced peak shift on CdS nanobelts has been observed by photoluminescence spectroscopy. Simulating the electric field between the source and drain electrodes can indeed shed light on how the electric field

distributes with grounding the gate electrode. For the simulation, we have to assume that the contacts are Ohmic, which is not all the case in real devices. Besides, the surface depletion associated electric field has to be taken into account¹²³. To describe the surface depletion associated electric field, we need to obtain the surface state density, the electron concentration and the surface neutral level¹³⁷. However, those values cannot be determined experimentally. The most straightforward way is to compare the spectra with and without grounding the back-gate electrode.

The photoconductivity measurements with and without grounding the gate electrode have been conducted for a 60 nm CdS nanobelt device. The photoconductivity gain spectra and their second derivative near the band edge region are shown in Figure 3-12. Comparing the spectra with and without grounding the gate electrode, we found that the difference between spectra is negligible within the experimental uncertainties, meaning the floating gate will exert negligible influence on the photoconductivity spectra. Although the floating back-gate can have arbitrary potential, both source and drain electrodes are floated by the same gate potential. When we apply the source-drain electric field, one electrode is grounded. Therefore, all measured voltage is relative to the ground. Because the arbitrary potential on the gate electrode is static, we expect it would pose negligible influence on the distribution of the source-drain electric field due to the presence of the dielectric layer (500 nm SiO₂).

3.5.2 Franz-Keldysh effect

The Franz-Keldysh effect was independently discovered by Franz and Keldysh in 1958^{115,116} and this effect was named after them. The Franz-Keldysh effect deals with how the electric field affects the absorption spectra in semiconductors. When an electric field is applied to bulk semiconductors, the energy band in the real space will be tilted. For the incident photons with energies smaller than the band gap energy of a semiconductor, an electric field leads to the leakage of the electrons and holes wavefunction into the band gap region¹⁰. The overlap integral of electrons and holes wavefunction is not zero any more, which introduces an exponential decay absorption tail below the bandgap $\exp[-\sigma(h\nu - E_0)^{3/2}]$, where $h\nu$ is the photon energy, E_0 is a fitting parameter and σ is related to the material and the electric field, and quasi-

periodic oscillations above the bandgap¹²³. This effect is known as Franz-Keldysh effect. When the exciton formation due to Columbic interaction is included, the absorption tail below the bandgap exhibits a simpler exponential dependence of $\exp[-\sigma(h\nu - E_0)]$ ^{114,123}. For the incident photons with energies larger than the band gap of a semiconductor, both the electron wave and hole wave are consisted of an incident wave and a reflected wave. An electric field will change the relative phase between the incident and reflected waves, which leads to an interference effect¹³⁸. As a result, quasi-periodic oscillations are introduced right above the band edge in the absorption spectra. The extrema of the oscillations (E_n) as a function of the oscillation index (n) can be expressed as $E_n \propto n^{2/3}$ ^{139,140}. Far away from the band edge at the higher energy side, the oscillations average out¹¹². In summary, the exponential decay tail below the bandgap and the quasi-periodic oscillations above the band gap are two characteristic fingerprints of Franz-Keldysh effect. To handle the low dimensional nanostructures such as quantum well structures, the quantum-confined Franz-Keldysh effect has been proposed in which absorption at the band edge region exhibits small and closely spaced step-like behaviour due to the quantum confinement effect. The normal Franz-Keldysh effect is recovered when the confinement diminishes.

When an electric field is applied to a semiconductor, one additional term is added to the Hamiltonian. If one ignores the Coulomb interaction and assumes the applied electric field along z -direction, the Hamiltonian for an electron can be expressed as^{113,138}

$$H = \frac{p^2}{2m_0} + V_c(\mathbf{r}) - eFz \quad (3-3),$$

where p is the momentum of the electron, m_0 is the mass of electron, $V_c(\mathbf{r})$ is the crystal field potential, e is the electron charge, F is the applied electric field and z is z coordinate. The corresponding Schrodinger's equation can be written as

$$\left(\frac{p^2}{2m_0} + V_c(\mathbf{r}) - eFz\right)\varphi(r) = E\varphi(r) \quad (3-4).$$

The solution for equation (3-4) changes from Bloch functions for electric field free equation into Airy functions. Once the wavefunction for electrons and holes in an electric field are obtained, the absorption coefficient under an electric field can be estimated as¹⁰

$$\alpha(\hbar\omega) = \frac{2\pi \langle |p_{cv}|^2 \rangle}{n\varepsilon_0\omega c} \left(\frac{e}{m_0} \right)^2 \sum_m |\varphi_m(0)|^2 \delta(E_m - \hbar\omega) \quad (3-5).$$

Where n is the refractive index, ε_0 is the electric permittivity, $\hbar\omega$ is photon energy, c is light speed in vacuum and p_{cv} is transition matrix element between Bloch states in the valence and conduction bands. After inserting the wavefunction $|\varphi_m(0)|$ and conduct the summation, the expression can be rewritten as¹⁰

$$\alpha(\hbar\omega) = \frac{\alpha_b \mu f^{1/3}}{2\pi\hbar^2} \left\{ -\beta \text{Ai}^2(\beta) + |\text{Ai}'(\beta)|^2 \right\} \quad (3-6),$$

where $\alpha_b = \frac{2\pi \langle |p_{cv}|^2 \rangle}{n\varepsilon_0\omega c} \left(\frac{e}{m_0} \right)^2$, μ is reduced effect mass defined as $\mu^{-1} = m_e^{-1} + m_h^{-1}$

where m_e and m_h are electron effective mass and hole effective mass respectively,

$f = \frac{eF}{R_x a_B^2}$ (where $R_x = \frac{\hbar^2}{2\mu a_B^2}$ and a_B is bulk exciton Bohr radius), $\text{Ai}(\beta)$ is Airy

function and β is defined as $\beta = \frac{2\mu(E_g - \hbar\omega)}{\hbar^2 f^{2/3}}$ where E_g is the band gap energy.

The asymptotic expansion of the Airy function and the relation between Airy function and its second differentiation are used to examine the absorption coefficient for the incident photon energies well below and above the band gap region. After some simplification, the absorption below the band gap can be expressed as

$$\alpha(\hbar\omega) = \frac{\alpha_b}{32\pi^2} \frac{f}{E_g - \hbar\omega} \exp \left[-\frac{4}{3f} \left(\frac{2\mu(E_g - \hbar\omega)}{\hbar^2} \right)^{3/2} \right] \quad (3-7).$$

And above the band gap can be written as

$$\alpha(\hbar\omega) = \frac{\alpha_b}{(2\pi)^2} \left(\frac{2\mu}{\hbar} \right)^{3/2} (E_g - \hbar\omega) \left[1 - \frac{3/2}{(\hbar\omega - E_g)^{3/2}} \cos \left\{ \frac{4}{3} \left(\frac{\hbar\omega - E_g}{E_0} \right)^{3/2} \right\} \right] \quad (3-8),$$

where $E_0 = R_x \left(\frac{ea_B F}{R_x} \right)^{3/2}$. As seen from expressions (3-7) and (3-8), an exponential tail indeed appears in the absorption tail and a quasi-periodic oscillations presents right above the band edge region. Since the expression (3-8) is not strictly periodic, the oscillations fade out far away from the band edge at the higher energy side.

In bulk materials, the Franz-Keldysh effect was first observed in CdS crystals in 1960¹⁴¹. Later, this effect was found in Ge¹⁴² and GaAs¹⁴³ as well. In GaAs quantum well structures, the presence of quantum confinement gives rise to different features for the Franz-Keldysh effect which finally leads to the appearance of the quantum confined Franz-Keldysh effect^{112,118}. The exponential tail has been observed in photoconductivity of GaN nanowire, which was attributed to the Franz-Keldysh effect induced by surface electric field.¹²³ Nonetheless, a few other underlying processes may also give rise to the exponential tail, such as electron-phonon interaction,¹³² structural disorders,¹⁴⁴ and impurities.¹⁴⁵ Therefore, both exponential tail and the oscillation extrema scaling must be taken into account to pin down the possible Franz-Keldysh effect.

Figure 3-13 (a-d) The normalized gain spectra (red curves) and their corresponding second derivative (blue curves) for the nanowire and nanobelts with an applied source-drain electric field of 2 kV/cm near the band edge region at the higher energy

side. The numbers labelled in each figure indicate the index of the oscillations. Spectra are offset vertically for clarity.

The normalized gain of photoconductivity spectra of the CdS nanowire and nanobelts near the band edge region at the higher energy side are shown in Figure 3-13a-d. The second derivative of gain versus energy for the nanowire and nanobelts are given in Figure 3-13a-d as well in blue dot-lines in order to extract the extrema of the oscillations versus the oscillation index. The quasi-periodic oscillations have been unambiguously identified in all spectra. The extrema energies E_n can be well fitted by the function $E_n \propto n^{2/3}$ shown in Figure 3-14. Therefore, the quasi-periodic oscillations at higher energy side of the band edge can be attributed to the Franz-Keldysh effect. The oscillations in the nanowire and thicker nanobelt devices are more pronounced than those in thinner belt devices. This is probably due to the transition from a bulk Franz-Keldysh effect to a quantum-confined Franz-Keldysh effect, as proposed in 2D quantum well structures¹¹⁸. In addition, the exponential decay tails have been observed in our measurements as well. However, we cannot attribute them to purely Franz-Keldysh effect due to the strong electron phonon interaction in CdS nanobelts as will discussed in Chapter 5.

Figure 3-14 The extrema of the oscillation versus the index of the oscillations (solid dots) extracted from Figure 3-13. The experimental data are well fitted by the function $E_n \propto n^{2/3}$ shown in solid lines.

The Franz-Keldysh effect can be harnessed in Franz-Keldysh-effect modulators¹³⁸. A Schottky contact and an Ohmic contact should be first deposited on a semiconductor waveguide. By applying a voltage between the Schottky contact and

Ohmic contact, an electric field will be introduced to the semiconductor waveguide. As a result, the waveguided photons with energy smaller than the bandgap energy will be absorbed much larger than that under zero-field conditions. The Franz-Keldysh-effect modulators operate quite fast (in tens of GHz range) since they donot require the bulk displacement of electrical charges.

3.5.3 Stark effect

The Stark effect was first discovered by Johannes Stark in 1913¹⁴⁶. The Stark effect describes the shifting and splitting of the spectral lines of atoms and molecules under an applied electric field. The amount of the energy level shifting is called Stark shift. The Stark effect originates from the interaction between the electrons and an external static electric field. When an electric field $\mathbf{F}$ applies to atoms or molecules, the interaction energy can be expressed as the dot production between the field $\mathbf{F}$ and the dipole moment $\boldsymbol{\mu}$

$$E_{\text{int}} = -\mathbf{F} \bullet \boldsymbol{\mu} \quad (3-9).$$

The interaction energy can be either positive or negative depending on the direction of the applied electric field and direction of the dipole moment. Applying the perturbation theory, the Stark shifting can be obtained. There are linear Stark effect and quadratic Stark effect. Based on the first-order perturbation theory, the Stark shifting for linear Stark effect can be written as

$$E^{(1)} = -\mathbf{F} \bullet \boldsymbol{\mu} \quad (3-10),$$

For the quadratic Stark effect, based on thesecond-order perturbation theory the Stark shifting can be expressed as

$$E^{(2)} = -\frac{1}{2}\alpha_0 F^2 \quad (3-11),$$

where α_0 is the polarizability. The total Stark shifting is the sum of the linear term and quadratic term³⁷:

$$E_{\text{Stark}} = -\mathbf{F} \bullet \boldsymbol{\mu} - \frac{1}{2}\alpha_0 F^2 \quad (3-12).$$

In general, the linear Stark effect dominates and the quadratic Stark effect is negligible unless the linear Stark effect is absent due to the zero dipole moment such as in systems with inverse centres.

Since the excitonic energy levels are much like the discrete energy levels in hydrogen atomic systems, the Stark effect has been observed in high quality direct-gap semiconductors, where the absorption edge is dominated by the exciton absorption resonance especially at low temperature. In this case, excitonic effect has to be taken into consideration during modeling the electroabsorption. Applying a relative electric field would lead to a red shift of the exciton peak which is quite similar to the Stark effect in the hydrogen atoms and is thus refer as Stark effect as well.

In semiconductors, the Stark shifting can be described by the equation (3-12) as well. The linear term originates from the dipole moment while the quadratic term comes from the polarizability³⁷. In general, the surface trap states should have a strong dipole character, thus contributing to the dipole moment while the delocalized bulk excitonic states should be highly polarizable which gives rise to the polarizability. In the semiconducting nanostructures, the large surface-to-volume ratio leads to the fact that both the linear and quadratic Stark effects are present.

The Stark effect is seldom observed in bulk semiconductors due to the small magnitude of the Stark shifting and severe peak broadening under an electric field, which is resulted from the reduction of lifetime of the exciton due to the field induced exciton ionization by the applied electric field. However, in quantum size regime, the magnitude of Stark shifting increases dramatically due to the change of density of states (DOS) and the increasing of the exciton binding energy²⁸. The Stark effect in quantum size regime is usually called quantum-confined Stark effect to distinguish from its bulk counterpart in semiconductors^{113,131}. A requirement for the quantum-confined Stark effect to be observed is that the size of the nanostructures in at least one dimension should be comparable or smaller with their bulk exciton Bohr radius. As a result, the exciton binding energy increases significantly compared to bulk which suggests that a larger electric field is required for exciton ionization, thus leading to a larger Stark shifting. Nevertheless, the enhanced electron-LO phonon interaction at nanoscale may promote the rate of the exciton dissociation verified by

the appearance of exciton contribution in photoconductivity spectrum¹⁴⁷. A large Stark shift (more than 2.5 times of bulk exciton binding energy) has been observed in quantum wells, at an electric field of 50 times larger than the ionization field which is defined as $\frac{E_b}{a_B}$, where E_b is the bulk exciton binding energy and a_B is the bulk exciton Bohr radius¹³¹. The quantum-confined Stark effect has also been observed in nanocrystalline quantum dots by photoluminescence spectroscopy³⁷.

Figure 3-15 The electric field dependence of the normalized gain (a-c) and their corresponding second derivative (d-f) of nanowire and the thin nanobelts with various sizes near the band edge region: (a, e) 120 nm nanowire, (b, f) 50 nm nanobelt and (c, g) 65 nm nanobelt. The red arrows in (a) and thin lines in (b, c) indicate the positions of excitons of interest. All spectra are offset vertically for clarity except (d).

The electric field dependence of photoconductivity gain spectra and their corresponding second derivative near the band edge are shown in Figure 3-15. The spectra have been normalized by the maximum value of each spectrum and offset vertically except (d) in order to compare the field dependence and the second derivatives help to trace the shifting trends and extract the peak positions. Based on the previous assignments, FXB in the nanowire and 65 nm nanobelt, FXC in the 50

nm nanobelt and the broad band edge transition in the 230 nm nanobelt are selected to examine the trends versus field strength. Due to the strong surface electric field broadening and small energy difference of 17 meV between FXA and FXB, the FXA and FXB are not well resolved at room temperature. Therefore, we select FXC for 50 nm belt. For the nanowire and thinner nanobelt devices, FXB and FXC peaks exhibit a gradual red shift and a considerable broadening as the electric field is increased. At certain electric field strength, the broadening is so significant such that those exciton peaks in photoconductivity can no longer be resolved; for instance, 4 kV/cm for the nanowire and 65 nm nanobelt and 6 kV/cm for the 50 nm nanobelt.

The possible heating effect due to incident photons, which usually gives rise to a red shift of band-edge emission in semiconductors, can be ruled out since the power density of the incident collimated photons in our photoconductivity experiments is very small around tens of $\mu\text{W}/\text{mm}^2$. The heating effect due to photocurrent itself can also be ruled out. To confirm this, the photoluminescence spectra and the photocurrent spectra have been taken simultaneously excited by a 457 nm laser (Ar ion laser) with a power density of $5 \text{ W}/\text{mm}^2$, several orders higher than the power density of the broad band light source used in our photoconductivity experiments. Therefore, the photocurrent is expected to be much higher than in photoconductivity spectroscopy. During a continuous two hours running, the photoluminescence spectra do not show any noticeable red shift, suggesting no Joule heating effect due to photocurrent itself.

Figure 3-16 The field dependence of the FXB position in the nanowire and in the 65 nm nanobelt, and the FXC in the 50 nm nanobelt (right axis) extracted from Figure 3-15. The curves are the fittings as described in the text.

From the second derivative of the gain spectra, the peak positions of interest can be readily extracted. A plot of the FXB peak position as a function of the applied electric field in the nanowire is shown in Figure 3-16. The plot can be well fitted by the sum of linear and quadratic functions of the field

$$E(F) = E(0) + \mu F + \frac{1}{2} \alpha F^2 \quad (3-13),$$

where $E(F)$ is the peak positions with an applied electric field F , $E(0)$ is the peak position without the electric field, F is the field applied, and μ and α are the projections of the excited-state dipole and polarizability along the applied field, respectively. The presence of the linear and quadratic terms in the fitting function indicates that both polar characters originated from the localized surface trap states¹⁴⁸ and polarizable character due to the delocalized bulk exciton states¹⁴⁹ contribute to the Stark effect in the nanowire. The fitting result of the coefficient of the quadratic term is quite small meaning that the localized surface state contribution is dominating. The zero-field peak position extrapolated ($E(0)=2.443$ eV) differs from the peaks of photoluminescence spectrum (2.466 eV, Figure 3-11a) by 23 meV, consistent with the exciton binding energy of 28 meV within the experimental uncertainty, which verifies the aforementioned assignment.

In the thinner nanobelts, peak positions versus the applied field can be well fitted by a linear function alone (Figure 3-16) indicating that only the dipole component plays a major role, which illustrates that the localized surface trap states mainly contributes to the Stark effect and the contribution from delocalized bulk exciton states is negligible, consistent with the large surface-to-volume ratio in those thinner nanobelts. The thickness of the nanobelts (50 nm and 65 nm respectively) is less than the diameter of the nanowire of 120 nm. Therefore, it is expected that only surface trap states play a major role in the nanobelts, while both surface trap states and delocalized bulk exciton states contribute to Stark effect in the nanowire.

Up to 48 meV Stark shift was observed in the nanowire which is two times larger than the exciton binding energy. This contradicts to the bulk case where the Stark shift can only shifts ~10% of the exciton binding energy before the exciton peaks become unresolvable caused by broadening¹¹⁸. The Stark shifts are 12 meV and

6 meV for 50 nm and 65 nm nanobelts, respectively, both of which are also larger than 10% of the exciton binding energy. Those shifts are larger than the values observed in CdS single crystal and the electric field applied here is also one order of magnitude smaller¹⁵⁰. The reason for the observation of the large Stark shifts under such a small applied electric field is not clear yet. However, there are some clues that the large Stark shifts might be due to the confinement induced by the surface depletion³³. For instance, the Stark shift in 50 nm nanobelt is larger than that observed in 65 nm nanobelt, and no Stark shift was observed in 230 nm thick nanobelt (Figure 3-17), which implies that the size effect indeed plays a significant role. Regarding the nanowire, one more dimensional confinement may lead to a much larger shift. However, the size of our samples (both for nanowire and nanobelts) is much larger than the bulk exciton Bohr radius required for the presence of the quantum confined Stark effect unless the surface depletion poses a very important influence to the confinement. However, it is required the electric field should be along with the confinement orientations for the quantum confined Stark effect to occur. In our case, the applied source-drain electric field between the top metal contacts has the perpendicular component, which probably contributes to the large Stark shift¹⁵¹. With respect to the small applied electric field, possible reasons include the surface electric field and non-uniform distribution of the applied electric field¹⁵².

3.5.4 Field induced exciton ionization

Exciton in semiconductors can be ionized in an electric field, apart from the exciton ionization due to electron phonon interaction. When the applied electric field larger than the ionization field, which is defined as the ratio of the exciton binding energy to the bulk exciton Bohr radius, the bound electron-hole pairs (exciton) can be directly separated and prompted to the conduction band, thus can be detected by the photoconductivity measurement. If the applied electric field smaller than the ionization field, the energy band in real space will be tilted as shown in Figure 3-17d. In this case, the applied electric field enables the electrons lying in exciton energy levels tunnel to the conduction more easily leading to the photocurrent. Photoconductivity^{119,153} and photoluminescence¹⁵⁴ spectroscopy can be used to investigate the field ionization of excitons. The photoconductivity spectroscopy provides an indirect way to measure the field ionization of exciton by checking the

exciton peaks in spectral response¹¹⁷ while the photoluminescence spectroscopy can detect the field ionization by monitoring the suppression of the exciton emission peaks¹⁵⁴.

Figure 3-17 The electric field dependence of the normalized gain (a) and its corresponding second derivative (b) of a 230 nm CdS belt device. (c) The field dependence of the band edge transition in the 230 nm nanobelt extracted from (b). The curve is the exponential function fittings as described in the text. (d) The schematic of the field induced exciton ionization process.

In contrast to the Stark effect mentioned in previous section where the exciton peaks show redshift with the increase of the applied field, the broad band edge transition in photoconductivity for a 230 nm nanobelt as shown in Figure 3-16a exhibits significant blue shift and the band tail of the photoconductivity spectra becomes steeper and steeper as the electric field is increased. The second derivative of the gain spectra is given in Figure 3-17b as well to extract the band edge transition energies. The energy of transition extracted from Figure 3-17c versus applied electric

field can also be fitted by an exponential function $E(\xi) = A \exp \left[-\frac{(E_m - e\xi a_B)}{B} \right] + E(0)$, where A and B are constants, E_m is exciton binding energy, m is the exciton energy level index, a_B is the bulk exciton Bohr radius, ξ is the applied field and $E(0)$ is the photon energy without field applied. This blue shift trend might be explained by field enhanced exciton ionization¹³⁰.

Figure 3-18 The source-drain electric field dependent gain for a given wavelength around the FXA and FXB for the 230 nm belt device at room temperature.

Between the exciton ground level ($m=1$) and conduction band, a great amount of high-lying exciton levels ($m>1$) exists as shown in Figure 3-17a. The electrons resonantly excited from the valence band to those high-lying exciton levels ($m>1$) should have much larger possibilities to be ionized by tunnelling due to both the smaller exciton binding energy ($E_m = \frac{E_1}{m^2}$) and the reduction of barrier height ($E_m - eFa_B$) induced by the electric field F ¹¹⁹. Hence, the larger the applied electric field is, the larger the tunnelling possibility ($\exp \left[-\frac{(E_m - eFa_B)}{B} \right]$) is, which reflects the probability that the excitons in those high-lying levels ($m>1$) can be ionized before decay to the ground level (hence no contribution to photocurrent). It should be noted that the applied electric field here is much smaller than the ionization field for CdS, which is on the order of 10^5 V/cm¹⁵⁰. Therefore, the exciton ionization induced by the electric field is mainly through the tunnelling rather than direct ionization. The ionization for those high-lying excitons gradually changes from tunnelling to direct

ionization as the applied field increases further. As a result, the band edge transition shows a blue shift. In addition, the band tail of the photoconductivity spectra becomes steeper and steeper as the increase of the electric field, which also indicates the larger probabilities for those high-lying excitons to be ionized at higher fields.

We have conducted the photoconductivity gain magnitude verses electric field for a given wavelength both near the band edge region and above the band gap to identify field induced exciton ionization. As previously mentioned, gain is defined as how many electrons collect by electrodes for each incident photon. For two-probe configuration like ours, gain can be written as $G = \frac{V\mu\tau}{l^2}$, where V is the applied source-drain voltage, τ is the lifetime of photogenerated carriers, μ is the mobility and l is the channel length between the source and drain electrodes³⁵. Because we adopted two-probe configuration to measure the spectral response, the photoconductivity gain should be proportional to the applied source-drain electric field provided that the field ionization is absent. However, as shown in Figure 3-18, gain shows a significant increase with the applied field and deviates from the linear dependence, indicating the presence of the field induced exciton ionization.

Figure 3-19 (a) The photoluminescence (red curve) and photoconductivity spectra (blue curve) of the 65 nm thick nanobelt at 77 K. (b) The electric field dependence of normalized photocurrent spectra at 77 K. The vertical lines indicate the positions of FXB and FXC. The spectra are offset vertically for clarity.

Furthermore, in order to further understand how Stark effect and exciton ionization compete in nanobelts, photoluminescence measurements have been conducted at 77 K on the 65 nm nanobelt. Electron-longitudinal phonon coupling has been shown to be considerably weak below in CdS 100 K¹²⁶. Therefore, the exciton ionization is presumably not very significant at 77 K. As shown in Figure 3-19a, the peak assignment in photoconductivity spectrum can be supported by photoluminescence spectrum taken from the same belt at 77 K. Accordingly, FXA, FXB and FXC are assigned in photoconductivity spectrum as labelled in Figure 3-19a. The broad emission band at the lower energy side is due to donor-acceptor pair recombination formed between sulphur and cadmium vacancies⁷⁸. Both FXB and FXC show noticeable blue shifts with the increase of the applied field as shown in Figure 3-19b, a strong evidence of the field enhanced exciton ionization. The completely opposite shifts here compared to Figure 3-15c indicate that field induced exciton ionization dominates over Stark effect. At room temperature, the exciton ionization is dominated by electron- longitudinal phonon coupling thus the electric field induced ionization is negligible in those thin belts and nanowires.

3.6 Summary

The photoconductivity measurement of individual CdS nanobelt devices has been carried out both at room temperature and low temperatures. The high photoconductivity gain, large on-off ratio and fast response speed are obtained in CdS nanobelt devices. The oscillations in the thin nanobelt devices are present as a consequence of the interference patterns due to the silicon dioxide layer on the top of the substrate. As the temperature decreases, the band edge of the photoconductivity spectra shows gradually blue shifting and exciton peaks become visible for the thin belts.

The source-drain electric field dependence of the electro-absorption near the band edge region of individual CdS nanowires and nanobelts has been investigated. Franz-Keldysh effect has been demonstrated by the quasi-oscillation above the band edge of photoconductivity spectra. As the applied field increases, a pronounced red shift and broadening of exciton peaks are identified in the nanowires and thinner nanobelts. The exciton peak position as a function of the electric field can be well

fitted by the sum of a linear and a quadratic function of the electric field in the nanowire, indicating that both delocalized exciton states and localized surface trap states contribute to the red shift. In comparison, surface trap states alone play a major role to the redshift of the exciton peaks in thinner nanobelts supported by the linear field dependence of exciton peaks in photoconductivity spectra. In the thicker nanobelt, the band edge transition shifts toward higher energy side with the increase of the applied electric field, which might be due to the field enhanced exciton ionization. From the blue shift of the exciton peaks with the applied electric field at 77 K when the electron-longitudinal phonon coupling is considerably weaker, we deduce that the exciton ionization at room temperature is dominated by the strong electron-longitudinal phonon coupling. The strong electric field dependent band edge in photoconductivity spectra can find promising applications in the electro-absorption modulators.

Chapter 4 Surface Depletion Induced Confinement Effect beyond the Quantum Confinement Regime

4.1 Introduction

In the past decade, zero- and one-dimensional semiconductor nanomaterials and heterostructures (quantum dots, nanowires or nanobelts) have attracted tremendous attention due to their unprecedented properties derived from their quantum size in at least one dimension or strong anisotropy (*e.g.*, antenna effect in 1D cases)¹⁵⁵⁻¹⁵⁷. When the physical dimension of nanomaterials (for instance, the diameter of quantum dots or nanowires or the thickness of nanobelt) becomes comparable to or smaller than the characteristic lengths of elemental excitations, such as the mean free path of electron or phonon, the Bohr radius of exciton, *etc.*, at finite temperature, quantum confinement effect is anticipated, giving rise to the blue shift of bandgap in term of electronic states¹⁵⁸ and the red shift of confined phonon states^{157,159}. One particular exciting achievement in direct bandgap semiconductor quantum dots and nanowires is the tenable emission based on quantum confinement^{32,160-162}.

It is generally believed that the bulk exciton Bohr radius (a_B) is the approximate dimension for the onset of the quantum confinement effect¹⁵⁶. Base on the size l in the confinement direction, three regions can be identified: strong quantum confinement regime, weak confinement regime and beyond the quantum confinement regime¹⁶³. In the strong quantum confinement regime ($l < a_B$), the quantum confinement originates from the geometric confinements of electrons and holes as independent particles¹⁶³. The small geometric size d deforms the wavefunctions of the electrons and holes leading to the increase of the bandgap and the exciton binding energy¹⁵⁶. The particle-in-a-box model has been used most frequently to describe the confinement effect, *i.e.*, $\Delta E = \frac{\hbar^2 \pi^2}{2\mu l^2}$, where $\hbar$ is the reduced Planck constant,

$\mu = \frac{m_e m_h}{m_e + m_h}$ is the reduced mass of electron and hole. m_e and m_h are the effective

mass of electron and hole, respectively. Experimental reports in the strong confinement regime have proved the linear $1/l^2$ dependence of bandgap shift predicted by the particle-in-a-box model¹⁶². Deviation from linear $1/l^2$ dependence has also been observed. For instance, the band gap energy scales linearly versus $1/l^{1.36}$ in CdSe nanowire¹⁵⁸ and $1/l^{1.46}$ in InP nanowires¹⁶⁴. In the weak confinement region ($l > a_B$), the confinements on electrons and holes are small and Coulomb interaction is dominant. As a consequence, there occurs a size quantization of the motion of the exciton in the confinement dimensions¹⁶³. By applying the particle-in-a-box model, the shift of bandgap energy follows the linear $1/l^2$ as well but with a different energy shift ($\Delta E = \frac{\hbar^2 \pi^2}{2Ml^2}$, where $M = m_e + m_h$ is the mass of the exciton.). The peak shift of exciton emission caused by the quantization of the motion of the exciton has been observed in CdS slabs¹⁶⁵. Beyond the quantum confinement regime ($l \gg a_B$), the band gap energy also shows an anomalous blueshift as the size decreases. The size dependent phenomena can mainly attribute to the surface effect due to the large surface-to-volume ratio¹⁶⁶⁻¹⁶⁸.

The blueshift of the bandgap versus size parameter has also been observed in CdS¹⁶⁵ and WSe₂ slabs¹⁶⁹, CdSe¹⁶⁶ and InP¹⁷⁰ nanowires, ZnO nanowires¹⁶⁷ and nanopencils¹⁶⁸ beyond the quantum confinement regime, *i.e.*, when the size parameter is larger than a_B . For instance, Buhro *et al.* investigated the transition from 3D to 2D confinement in CdSe nanorods and found that the minimum length of the nanorods exhibited 2D confinement is as large as 30 nm, six times larger than a_B (~ 5 nm)¹⁵⁸. The blueshift of photoluminescence peak compared with their bulk counterpart was also found in InP nanowires with a diameter of 50 nm ($a_B \sim 19$ nm)¹⁷⁰. Recently, Yu *et al.*¹⁶⁶ reported that the blue shift of the emission peak exhibits $1/l^{2/3}$ dependence in the CdSe nanowires with diameters range from 50 nm to 700 nm. They attributed this blue shift to the Burstein-Moss (B-M) effect due to high carrier concentration induced by surface vacancy and laser excitation.

Although surface emission¹⁶⁷ and B-M effect have been proposed to explain the anomalous blueshift of the emission spectra of nanowires and nanobelts with the size far beyond the quantum confinement regime, the physical mechanism behind is still not well understood. Further investigations are demanded.

CdS is a direct wide bandgap (2.54 eV) compound semiconductor with an exciton binding energy of 28 meV⁹³ with a Bohr radius of 3.2 nm¹⁶⁵. CdS nanowires and nanobelts have been demonstrated to have potential applications in nano-optoelectronic devices^{106,171,172}, such as visible range photodetection^{36,65,71,79}, electro-absorption modulators^{71,173}, optical switch⁶⁸ and laser devices^{69,174,175}. In terms of the nano-optoelectronic applications, a profound understanding of the influence of nanoscale size on the emission properties beyond the quantum confinement regime is essential for the device optimization and integration. In this chapter, we will address how the photoluminescence peaks evolve with the thickness of the CdS nanobelts beyond the quantum confinement region and elucidate the physical mechanism using temperature and power dependent photoluminescence spectroscopy, which is supported by photoconductivity measurements. Part of the results in this chapter has been published on ACS Nano³³.

4.2 Temperature dependent photoluminescence spectroscopy

4.2.1 Photoluminescence emission peak assignment

Figure 4-1 The photoluminescence (PL) spectra of a 31 nm and a 230 nm CdS nanobelt at 5 K excited by a 457 nm laser with a power intensity of 5 W/mm² at 5K. The peak assignments are labelled and explained in detail in the text.

To investigate the thickness dependent photoluminescence emission properties, the peaks need to be assigned first. The typical photoluminescence spectra of a 31 nm and a 230 nm nanobelts at 5 K are shown in Figure 4-1. The absence of surface state related emission and rich distinct exciton emission-related features indicate the high crystalline quality of our samples. According to the photoluminescence spectrum of the ensemble CdS nanobelts,^{78,128} the emission peaks can be assigned as labelled in Figure 1a. As mentioned in the previous chapter, due to the crystal field and spin-orbit interactions, the valence band splits into three bands. The corresponding excitons are labelled as free exciton A (FXA), free exciton B (FXB) and free exciton C (FXC). The emission peaks can be assigned from high to low energy as: heavy-hole free exciton B (FXB, ~2.568 eV), light-hole free exciton A (FXA, ~2.552 eV), neutral donor bound exciton I₂ (~2.545 eV), neutral acceptor bound exciton I₁ (~2.528 eV), single LO-phonon replica of I₂ (I₂-LO, ~2.506 eV), single LO-phonon replica of I₁ (I₁-LO, ~2.491 eV), donors bound to holes (D-h, ~2.477 eV), donor-acceptor pair (DAP, ~2.418 eV) and LO-phonon replicas of DAP (from DAP-1LO to DAP-4LO), as we previously discussed involving cadmium and sulphur vacancies. The FXA and FXB peaks can be clearly distinguished in the 31 nm belt, while they are smeared into one broad peak in the 230 nm belt. This smearing in the 230 nm nanobelt is probably due to the presence of reabsorption in the thick belts, which will be discussed below in detail^{33,71}.

4.2.2 Temperature-dependent exciton emission

Figure 4-2a and b show the temperature dependent photoluminescence spectra from 5 K to room temperature for a 31 nm and 230 nm CdS nanobelt, respectively. A 457 nm Ar ion laser was used as the excitation source. During the measurement, the power density of excitation light kept as low as 5 W/mm² in order to eliminate the heating effect due to the excitation laser. The thickness of the nanobelts was measured by AFM relative to the Si substrate.

Figure 4-2 The temperature evolution of photoluminescence spectra for a 31 nm (a) and a 230 nm (b) CdS nanobelt excited by a 457 nm laser with a power intensity of 5 W/mm² from 5K to room temperature. The dash lines in (a) indicates the FXA and FXB peak evolution. Spectra have been vertically shifted for clarity. The temperature dependence of the FXA and FXB for a 31 nm (c) and a 230 nm (d) CdS nanobelt. The discrete data points were extracted from (a) and (b) respectively. The solid lines are Varshni fitting curves.

Based on the previous peak assignment, the FXA and FXB peaks are labelled in Figure 4-2a. Both FXA and FXB emission appears even at room temperature because of the large exciton binding energy of 28 meV, larger than the thermal energy of 26 meV at room temperature¹²⁸. As the temperature decreases, more features appear as a result of the smaller thermal excitation energy at low temperature. Because the donor and acceptor energy levels start to be populated below 180 K, DAP emission appears and becomes stronger with a further decrease of the temperature as show in Figure 4-3a. A close look at the trend of the DAP emission shows that the intensity of DAP emission almost maintains constant below 90 K, decreases rapidly with the increase of the temperature and completely disappears above 180 K, suggesting that the donor and acceptor energy levels are ionized¹²⁸. The longitudinal optical (LO) phonon replicas of DAP can be resolved below 77 K and up to 4th order LO phonon replicas of DAP is able to be observed indicating the strong electron phonon interaction⁷⁸.

As the temperature decreases, the FXA and FXB peaks can be resolved around 90 K. With a further decrease of the temperature, the intensity of the free exciton greatly decreases and there appears emission from recombination of the bound exciton complexes such as I_2 and I_1 . Below liquid nitrogen temperature, the bound exciton complex emission dominates the emission spectra. Due to the strong electron LO phonon interaction, the phonon replicas of I_2 and I_1 can be observed as well.

Figure 4-3 The temperature dependent photoluminescence spectra of a 65 nm (a) and a 50 nm (b) CdS nanobelt above liquid nitrogen temperature. Spectra in (a) have been normalized and shifted vertically for clarity.

The FXA and FXB emission energies at different temperatures were extracted by Voigt fitting¹⁷⁶ and plotted versus temperature as shown in Figure 4-2c and d for 31 nm and 230 nm, respectively. Both the FXA and FXB emission energies gradually move to higher energy as the temperature goes down due to the thermal dilation of the crystal lattice and the electron phonon interaction¹⁷⁷. Those plots can be well fitted by an empirical Varshni equation¹⁷⁸

$$E(T) = E(0) - \frac{\alpha T^2}{T + \beta}, \quad (4-1),$$

where $E(0)$ is the energy of FXA at 0 K, α and β are constants related to the certain materials. The fitting results were given in Table 4-1, which agrees well with the literature^{99,128}.

Table 4-1 The Varshni function fitting results for a 31 nm and a 230 nm CdS nanobelt obtained from Figure 4-2c and d.

		$E(0)$ (eV)	α (eV/K)	β (K)
31 nm	FXA	2.553	4.871E-4	126.952
	FXB	2.567	4.148E-4	91.591
230 nm	FXA	2.545	5.005E-4	106.903
	FXB	2.564	5.558E-4	195.911

Both the radiative and non-radiative recombination rate in semiconductors relies on the temperature¹⁷⁹, thus the integrated emission intensity of free excitons depends on temperature. In general, as the temperature decreases, the radiative recombination rate increases while the non-radiative recombination rate decreases. As a result, a larger integrated emission intensity of free excitons should be observed at low temperature. As shown in Figure 4-3b, the integrated emission intensity for a 50 nm CdS belt greatly increases as the temperature lowers from 290 K to 120 K. With further lowering the temperature, other decay channels such as DAP recombination and recombination of bound exciton complex start to play a role such that the integrated emission intensity of free exciton reduces again. Therefore, we only show the photoluminescence spectra above 120 K in Figure 4-3b because the photoluminescence spectra split into many peaks below 120 K, and it is no longer appropriate and irrelevant to compare the intensities.

4.3 Surface depletion induced confinement effect

4.3.1 Reabsorption

Reabsorption is a process that the emitted photons are absorbed again during their propagation inside the samples or if the emitted photons are trapped inside the samples⁹³. Therefore, a prerequisite for reabsorption occurs in nanobelts is that the thickness of the nanobelts should be larger than the half wavelength of the emitted light inside the sample. For CdS nanobelts, the wavelength of the emitted light in the nanobelts is ~ 100 nm at room temperature if we take the emission peak as 500 nm

and the refractive index as 2.5 at 500 nm. The thermal broadening of the energy band is the origin of the reabsorption. Due to the finite width of the energy band, the higher energy photon would be emitted from the electron transiting from the high energy level of the conduction band to the valance band. The emitted photon with higher energy would be reabsorbed and excited an electron from the valance band to the low energy level of the conduction band¹⁸⁰. Afterward, a lower energy photon is emitted. This process repeats many times during the emitted photon propagation inside sample and a certain amount of energy will be lost at each step. As a result, the reabsorption leads to a red shift, a broadening of the emission peak and a long tail at the longer wavelength side at higher temperatures^{67,181,182}. As the temperature decreases, the narrowing of the thermal broadening diminishes the redshift gradually¹⁸¹. However, the reabsorption can still give rise to the peak broadening at 5 K which makes the free exciton emission peaks not resolvable in the 230 nm belt (Figure 4-1)³³.

Figure 4-4 (a) The schematic of the reabsorption processes. (b) The photoluminescence spectra of a 31 nm and a 230 nm CdS nanobelt 294 K. The spectrum of the 230 nm belt is shifted to the higher energy side by 40 meV shown as the dotted red line in order to compare the lineshape between each other.

In general, the absorption coefficient does not suddenly approach to zero below the band gap. Due to the presence of defects and impurities, the electron phonon interaction, excitonic effect and Franz-Keldysh effect, a long exponential decay absorption tail always presents, which is called Urbach tail¹⁸³. Therefore, there are two absorption regions: Urbach tail and absorption above the band gap, which

depends on the joint density of states between the conduction band and valance band¹²⁹. At the boundary of those two regions, the absorption coefficient should be continuous which leads to a crossover energy $E_{cr} = E_g + \frac{k_B T}{2\sigma}$, where E_g is the band gap energy, T is the temperature, k_B is Boltzmann constant and σ is a dimensionless phenomenological parameter depending on the Urbach tail¹⁸². The absorption coefficient can be expressed as¹⁸⁴

$$\alpha(h\nu) = \begin{cases} A\sqrt{h\nu - E_g} & h\nu \geq E_{cr} \\ A\sqrt{\frac{k_B T}{2\sigma}} \exp\left(\frac{\sigma}{k_B T}(h\nu - E_{cr})\right) & h\nu \leq E_{cr} \end{cases} \quad (4-2),$$

where A is a constant related to materials. Based on the principle of detailed balance, the emission intensity relates the absorption coefficient via the Roosbroeck-Shockley equation, which can be written as^{10,41}

$$I(h\nu) = \frac{\alpha(h\nu)(\kappa h\nu)^2}{(\pi c)^2 \hbar^3 [\exp(\frac{h\nu}{k_B T}) - 1]} \quad (4-3),$$

where $I(h\nu)$ is the emission intensity and κ is the refractive index. By inserting equation (4-2) to (4-3), a long emission tail at the lower energy side automatically appears due to the presence of the Urbach tail. As the temperature decreases, the negligible thermal energy leads to the absence of the Urbach tail and emission tail at lower energy side, indicating that the reabsorption diminishes at low temperature.

Since the reabsorption occurs during the propagation of the emitted photons, it depends on the propagation length. In CdS nanobelts, the reabsorption closely relates to the thickness of the nanobelts. The emission intensity suffering reabsorption $I(h\nu)$ relates to the original emission intensity $I_0(h\nu)$ by¹⁸²

$$I_0(h\nu) = \frac{\alpha(h\nu)tI(h\nu)}{(1-R)[1 - \exp(-\alpha(h\nu)t)]} \quad (4-4),$$

where R is the reflection coefficient and t is the thickness of the sample. For the very thinner nanobelts, $\alpha(h\nu)t$ is quite small and $[1 - \exp(-\alpha(h\nu)t)]$ is proximately equal

to $1 - \alpha(h\nu)t$ derived using Taylor expansion. Under this condition, the equation (4-4) can be approximately written as

$$I_0(h\nu) = \frac{I(h\nu)}{(1-R)} \quad (4-5).$$

For the nanobelts with thickness smaller than the half wavelength of the emitted light inside the nanobelts, the emitted photons will directly escape the belts, thus leading to the zero internal reflection at the interfaces. In this case, the reflectivity can be ignored and no reabsorption will occur.

The reabsorption effect in the 230 nm belt is demonstrated by the lineshape of the room temperature photoluminescence spectra as shown in Figure 4-4b. In order to compare the lineshape between those two spectra, the spectrum of the 230 nm nanobelt has been shifted horizontally toward the higher energy side by 40 meV shown as a dotted curve in Figure 4-4b. In contrast to the symmetric lineshape of the photoluminescence spectrum of the 31 nm nanobelt where no reabsorption is present due to the small thickness, the asymmetric lineshape of the photoluminescence spectrum of the 230 nm nanobelt with a long tail at the longer wavelength side confirms the presence of the reabsorption.

Figure 4-5 The photoluminescence and photoconductivity spectra of a 230 nm belt at 294 K (a), 240 K (b), 180 K (c) and 77 K (d). The broad emission at the lower energy side in (c) and (d) is due to the recombination of DAP.

The comparisons of photoluminescence and photoconductivity spectra of a 230 nm belt at various temperatures above the liquid nitrogen temperature are given in Figure 4-5. The FXA emission peak almost coincides with the band edge transition at 77 K while the emission peak red shifts significantly compared with the band edge transition of photoconductivity spectra at room temperature. As the temperature decreases, the FXA position of the photoluminescence spectra gradually shifts to the band edge of the photoconductivity spectrum, consistent with the results predicated by the reabsorption. With lowering the temperature, the band broadening due to thermal excitation reduces leading to the reduction of the redshift of photoluminescence emission peaks. Finally, the redshift of emission peaks is absent below 77 K indicating that no reabsorption presents below 77 K.

4.3.2 Thickness dependent emission at various temperatures

The thickness (L)-dependent photoluminescence spectra at 294 K, 240 K and 180 K are shown in Figure 4-6 a, b and c. As the thickness decreases, the emission peak continuously blue shifts and the lineshape of the emission peak gradually evolves from asymmetric shape with a long tail at the lower energy side to symmetric shape at the thickness less than 100 nm. At 77 K, for the belts with a thickness larger than 60 nm, only one broad peak can be resolved, which shows a slight blue shift as the thickness decreases as shown in Figure 4-6d. Strikingly, two distinct peaks appear in the thinner belts as shown noticeably for thickness of 50, 40 and 31 nm at 77 K. Negligible shift of those two distinct peaks is observed for L less than 60 nm (Figure 4-6e). When the samples are further cooled down to 5 K, no peak shift of the corresponding excitons among the different thickness belts is exhibited as shown in Figure 4-6f. The free exciton and bound exciton emission peaks show narrow lineshape in the thin belts. As a result, those peaks are well separated from each other. However, due to the large linewidth of those peaks in the thicker belts, they are smeared into a broad peak (*e.g.*, 80 nm and 230 nm).

Figure 4-6 The photoluminescence spectra of belts with various thickness at 294K (a), 240 K (b), 180 K (c), 77 K (d) and 5 K (f). (b) The photoluminescence (PL) spectra of nanobelts with thickness less than 60 nm at 77 K. All spectra are offset vertically for clarity.

Based on the Voigt function fitting, the energies of FXA and FXB emission peaks can be extracted. The energy of FXA emission peak is plotted versus $1/L^2$ at various temperatures in Figure 4-7a. The following information can be extracted from Figure 4-7a: (1) at 77 K and above, the FXA emission peak scales linearly in $1/L^2$ up to a thickness of 100 nm. The intercept at vertical axis corresponds to the FXA emission energy in bulk (*i.e.*, when L approaches infinite). We can define a quantity of energy shift $\Delta E = E(L) - E(L \rightarrow \infty)$. When the thickness is 31 nm, we can obtain a maximum energy shift ΔE of 38 meV at 294 K, 24 meV at 240 K, 18 meV at 180 K and 8 meV at 77 K, respectively. The FXA emission is no longer dependent on thickness at 5 K. (2) when the thickness L is more than 100 nm, the energy shift ΔE

deviates from the linear dependence of $1/L^2$. The deviation becomes smaller and smaller as the temperature decreases, and completely disappears at 5 K. (3) at 77 K, the FXA emission peak also exhibits linearly shifting with $1/L^2$ for the thickness L ranging from 60 nm to 100 nm, but no shift is observed when the L is less than 60 nm. The maximum energy shift is around 8 meV, much smaller than that obtained at 294 K.

The extracted FXA energy in bulk $E(L \rightarrow \infty)$ versus temperature is plotted in Figure 4-7b. The energy of FXA emission peak shows a redshift as the temperature increases due to the enhanced electron-phonon interactions and the lattice expansion. The energy of FXA as a function of temperature can be described by the empirical equation Varshni equation (4-1). Our result can be well fitted by Varshni equation, with fitting parameters $E(0)=2.550\pm0.002$ eV, $\alpha=0.38\pm0.04$ meV K⁻¹ and $\beta=43\pm30$ K, in good agreement with the previous reports^{99,128}.

Figure 4-7 (a) The photon energy of FXA emission versus the thickness of nanobelts at various temperatures. (b) Extrapolating the linear fitting of (a) to infinite thickness, the energy of FXA in bulk can be extracted. The extrapolated photon energy of FXA is plotted against temperature. The dots represent the extrapolated data and the solid line is the Varshni fitting.

The deviation from the linear $1/L^2$ dependence of FXA emission energy for those belts with the thickness more than 100 nm can be ascribed to the reabsorption as mentioned previously. The reabsorption leads to a redshift of the emission peak. Because the thermal broadening is reduced as the temperature decreases, the deviation becomes smaller and smaller and completely disappears at 5 K¹⁸¹.

Our results can be explained by neither exciton confinement nor B-M effect. Taking a 31 nm belt at 294 K as an example to do a rough estimation, using $m_e = 0.2m_0$ and $m_h = 1.35m_0$ (m_0 is the mass of electron)¹⁸⁵, the energy shift ΔE is estimated to be ~ 1.25 meV for the confinement of the electron and hole and ~ 0.25 meV for the confinement of the exciton. Our experimental energy shift of the 31 nm nanobelt is 38 meV, which is much larger than either of the calculated values. Besides, the temperature dependence of the energy shift ΔE cannot be explained by the particle-in-a-box model as well, unless the confinement length d is able to change with the temperature because the effective masses of both electron and hole are insensitive to the temperature, supported by parabolic band approximation.

Figure 4-8 (a) The power dependence of photoluminescence spectra of a 40 nm belt at 77 K excited by a 457 nm laser. The vertical lines indicate the positions of FXA and FXB emission. The broaden peak at the longer wavelength side is DAP emission. The spectra are vertically offset for clarify. (b) The photoconductivity gain spectra of a 50 nm, a 65 nm and a 230 nm CdS nanobelts at 77 K.

Furthermore, the B-M effect induced by laser excitation is not applicable to our experimental results. The B-M effect is an important phenomenon in degenerate semiconductors which causes the blue shift of the optical gap in the absorption and photoluminescence spectra¹⁸⁶. Taking an n-type degenerate semiconductor as an example, the Fermi level is positioned inside the conduction band due to the filling of the conduction band by electrons. As such the absorption can only be contributed by the optical transition between the valence band and the unoccupied conduction band

above Fermi level, which gives rise to the apparent increasing of the optical gap. Therefore, the B-M shift would increase with the excitation power as a higher excitation power increases electron concentration. The excitation power-dependent photoluminescence spectra of a 40 nm CdS belt at 77 K are given in Figure 4-8a. The two vertical dashed lines indicate the positions of FXA and FXB emission and the broad band at the longer wavelength side is DAP emission. With the increase of the excitation power, the DAP emission is saturated suggesting that the cadmium vacancy levels become fully populated⁷⁸. However, no noticeable shifts of FXA and FXB emission peaks are observed by varying the excitation power from 16 μ W to 1 mW, which suggests that the carrier concentration is not high enough to give rise to the B-M effect at those excitation powers. The excitation power used in Figure 4-6 falls into this range. Besides, as the thickness decreases, the blue shift of the exciton peaks has also been observed in the photoconductivity spectra of individual CdS nanobelt devices both at room temperature (see chapter 3) and at 77 K as shown in Figure 4-8b. The photon excitation in photoconductivity measurements is provided by a tungsten halogen lamp, whose intensity magnitude is five orders of magnitude smaller than the laser power intensity used here for photoluminescence studies. This is an additional strong evidence that the B-M effect cannot explain the thickness dependence of the anomalous blue shift in our samples.

4.3.3 Surface depletion effect

The linear $1/L^2$ dependence of the FXA emission energy in CdS nanobelts can be ascribed to the surface depletion induced quantum confinement effect. The surface depletion induced quantum confinement can only occur in the thickness direction because of the much larger size in the width and length direction. The breaking of the translational symmetry of the crystal potential at the semiconductor surface leads to the formation of the surface states within the gap near the surface¹⁸⁷. The distribution of the surface states forms a continuum within the bandgap. A neutral level ϕ_0 is introduced to characterize this continuum as shown in Figure 4-9. When the surface states are occupied up to the neutral level ϕ_0 , the surface is electrically neutral. At thermodynamic equilibrium, electrons flow to the surface of an n-type semiconductor thereby creating a layer of negative surface charge, which produces two depletion

layers near both surfaces of the nanobelts as shown in Figure 4-9a, b and c. The existence of the depletion regions effectively generates modified potential wells that confine carriers into a region smaller than the geometrical size of the structure, *e.g.*, thickness of the nanobelt¹⁸⁸⁻¹⁹⁰. The as-grown CdS nanobelts synthesized by the physical vapour transport method are usually n-type due to the sulphur vacancies⁷⁹. According previous report¹⁹¹, the surface neutral level ϕ_0 lies 0.46 eV below the conduction band, which is much large than the thermal energy (5 K-294 K). Therefore, it is reasonable for us to assume that the surface neutral level maintains constant with the variation of the temperature.

Figure 4-9 The schematic diagrams of the energy band of CdS nanobelts at a temperature T_0 (a), at a lower temperature T_1 (b) and after surface passivation at T_0 (c). E_c and E_v represent the conduction band and the valence band, respectively. E_F is the Fermi level and ϕ_0 is the neutral level. V_d is the electrostatic potential drop due to the surface depletion. (d) The graphical solutions of the finite square potential well. V_1 and V_2 are the height of the potential well. The eigen energy is proportional to k^2 .

The width of the depletion region d is related to the electrostatic potential drop V_d in the depletion region and the electron concentration N_d by the expression¹⁸⁷

$$d = \sqrt{\frac{2\varepsilon V_d}{eN_d}} \quad (4-6),$$

where ε is the dielectric constant which is 8.87 for CdS¹⁸⁵ and e is the elementary charge. The electrostatic potential drop V_d is the difference between the neutral level ϕ_0 at the surface and the Fermi level (E_F) inside the bulk. The Fermi level E_F will be lowered and the electron concentration N_d would be also decreased as the temperature T decreases¹⁹². Therefore, the width of the depletion region d is also a function of the temperature T . On the other hand, according to the charge neutrality, the depletion region d should increase due to the reduction of the electron concentration N_d at a low temperature.

For an n-type semiconductor neglecting the acceptor concentration, the electron concentration is given by¹⁹³

$$N_d = \sqrt{\frac{N_D N_C}{2}} \exp\left(-\frac{E_C - E_D}{2k_B T}\right) \quad (4-7),$$

where N_D is the donor concentration, N_C is the effective density of states in the conduction band, E_D is the donor energy level and k_B is the Boltzmann's constant. The effective density of states in the conduction band N_C is around $2.28 \times 10^{18} \text{ cm}^{-3}$ at 300 K¹⁹³ and $E_C - E_D$ is around 35 meV for CdS⁷⁸.

We assume that the confinement potential is a finite square potential well with a depth of $V_d(T)$ and a width of $L - 2d_{eff}(T)$. It should be noted that the effective width of the depletion region $d_{eff}(T)$ differs from the real width of the depletion region d but is somewhat related to d due to the finite square potential well approximation. This assumption is reasonable at temperatures higher than around 100 K, because the donors are nearly completely ionized contributing to a high electron concentration¹⁹³, which leads to the relatively narrow depletion region with a steep

falling edge inside the structures (Figure 4-9a). For the temperatures lower than around 100 K, part of the donors start to be frozen out as predicted by expression (4-7). As a result, the electron concentration is greatly reduced, leading to the large depletion region and a gradual falling edge inside the structure (Figure 4-9b). The potential profile gradually changes approximately from a finite square potential well at high temperatures ($T > 100$ K) to a parabolic potential well at low temperatures ($T < 100$ K)¹³⁷. In a finite square potential well, no analytic solutions can be obtained. However, the graphical solutions can be obtained as shown in Figure 4-9d. The confinement eigen energy is proportional to k^2 , which is a function of both the depth ($V_d(T)$) and width ($L - 2d_{eff}(T)$) of the well. In detail, the confinement energy is linear in $\frac{\gamma^2}{[(L - 2d_{eff}(T))]^2}$, where γ is the analytical solution shown in Figure 4-9d. γ is a positive number always smaller than unity and is a function of $V_d(T)$ as give in Figure 4-9d¹⁹⁴.

At a certain temperature, $d_{eff}(T)$ and γ are approximately the same for all nanobelts. Therefore, the energy shifts of photoluminescence peaks shows $1/L^2$ dependence. Varying the temperature will change $d_{eff}(T)$ and γ , leading to the different energy shift ΔE . As the temperature is lowered, the electron concentration in conduction band decreases resulting in an increase of the depletion region width based on the charge neutrality (Figure 4-9b). However, the electrostatic potential drop V_d also decreases as the temperature decreases (Figure 4-9b). The decrease of the electrostatic potential drop would lead to a smaller γ , which further results in a smaller confinement energy as shown in Figure 4-9d. As a consequence, the confinement becomes weaker leading to the small energy shift ΔE at low temperature. Further cooling the samples down to 5 K, most donors are frozen out. The electron concentration is so low that the depletion electric field is too weak to generate any confinement. As a result, no energy shift is observed for both FXA and FXB emission peaks (Figure 4-6f and 4-7a).

At 77 K, no energy shift for those belts with a thickness less than 60 nm (Figure 4-6e) indicates that those nanobelts have been completely depleted, which further suggests that the width of the depletion region d is around 30 nm at 77 K.

Because the maximum energy shift ΔE is 8 meV, we can assume the electrostatic potential drop V_d is 8 mV. Substituting d and V_d into expression (4-6), electron concentration N_d can be estimated $\sim 8.72 \times 10^{15} \text{ cm}^{-3}$. Applying $N_d = 8.72 \times 10^{15} \text{ cm}^{-3}$ at 77 K to expression (4-7), the donor concentration $N_D = 8.36 \times 10^{16} \text{ cm}^{-3}$ is obtained. This donor concentration is much lower than the critical electron concentration for B-M effect to occur, which is around $2.1 \times 10^{18} \text{ cm}^{-3}$ for CdS according to literature¹⁹⁵. Therefore, quantitatively B-M effect cannot explain our experimental results either.

4.3.4 Surface passivation

The surface depletion induced quantum confinement effect can be further examined by the surface passivation, which can greatly reduce the surface states. The reduction of the surface states leads to the narrowing of the depletion region d and the elevation of the neutral level ϕ_0 (Figure 4-9c)¹⁹⁶. The elevated neutral level ϕ_0 would further cause the reduction of the electrostatic potential drop V_d as shown in Figure 4-8c. Both the narrowing of the depletion region and the reduction of the electrostatic potential drop would lead to the loss of the confinement strength at higher temperatures. Because the confinement energy follows the inverse square of the width of the confinement potential well, the reduction of the surface states exerts much larger influence in the thin belts than that in the thick ones. At lower temperature, the depletion electric field is so weak that no confinement can be induced. The weak depletion electric field only broadens the emission peaks. The reduction of the depletion electric field leads to the decrease of the peak broadening (electric field broadening), which would give rise to the pronounced free exciton emission peaks after surface passivation.

The photoluminescence spectra of the belts covered with a layer of PMMA are carried out as shown in Figure 4-10. The PMMA was covered on the CdS nanobelts by spin-coating followed by a hard bake at 180 °C for 5 mins. The thickness of the coated PMMA is around 200 nm by spun at 4000 RPM for 1 minute. The emission peaks show red shifts after being passivated by a layer of PMMA at room temperature (Figure 4-10a and c). Compared with the 70 nm belt (Figure 4-10c), the redshift of emission peaks is much larger in the 31 nm belt (Figure 4-10a), which demonstrates

the loss of the confinement strength after surface passivation exactly as discussed previously. At 10 K, the free exciton emission is greatly enhanced for both the 31 nm and the 70 nm belts as given in Figure 4-10b and d, suggesting the decrease of the electrical field induced peak broadening.

Figure 4-10 The photoluminescence spectra of a 31 nm and a 70 nm belts with and without a layer of polymethyl methacrylate (PMMA) at 10 K (b and d) and 294 K (a and c).

4.4 Thickness dependent emission intensity

Varying the thickness of the nanobelts, both the emission peaks and emission intensity should be influenced. How the thickness affects the peak position of FXA emission has been systematically investigated in Section 4.3. In this section, the thickness dependence of the emission intensity will be addressed, which is helpful to select proper nanobelts for laser cooling discussed in the Chapter 6.

In nanostructures, both surface recombination and reabsorption can greatly reduce the emission intensity. The reabsorption has been discussed in detail previously. The surface recombination becomes more severe in nanostructures due to the large surface-to-volume ratio, which would introduce more surface states, the origin of the surface recombination¹⁹⁷. The surface recombination rate A relates the recombination velocity S and the thickness of the nanobelts d via¹⁹⁸

$$A = \frac{S}{d} \quad (4-8).$$

In general, the surface velocity depends on the materials and surface treatment as well as material growth properties¹⁷⁹. It is reasonable to assume that surface velocity for all nanobelts maintain the same since they are synthesized by the same method. As seen from the equation (4-8), the surface recombination is inversely proportional to the thickness of the nanobelts. The thinner the nanobelt, the larger the surface recombination rate is. However, the reabsorption can be reduced or even avoided in the thinner belt. As a result, a crossover thickness appears, below which the surface recombination dominates the non-radiative recombination while above which the reabsorption gives rise to the reduction of the emission intensity.

Figure 4-11 (a) The thickness dependent photoluminescence spectra for different thickness nanobelts at room temperature. The excitation source is a 457 nm Ar ion laser with a very low power around 100 μ W. (b) The integrated emission intensity as a function of the nanobelt thickness extracted from (a).

As seen from Figure 4-11 (a), as the thickness decreases, the emission intensity increases first and reach a maximum value around 160 nm. After that, the emission intensity decreases again with the decrease of the thickness. The integrated emission intensity is extracted from Figure 4-11(a) and plotted against the thickness. The trend of the integrated emission intensity is the same as that of the emission intensity. Below 60 nm, the integrated emission intensity reaches a constant value indicating that the surface recombination rate reaches a maximum value. The

crossover thickness falls between 100 nm and 160 nm, consistent with the half wavelength of the emitted light in CdS at room temperature.

Figure 4-12 The integrated emission intensity as a function of the nanobelt thickness at 10 K and 120 K.

The integrated emission intensity as a function of the nanobelt thickness at 120 K and 10 K is shown in Figure 4-12. The trend is the same as that at room temperature. Since reabsorption is absent below the liquid nitrogen temperature, the reduction of the integrated emission intensity above 160 nm is probably due to the waveguide effect. When the emitted light is trapped inside the nanobelts, part of it will be guided to the two ends of the belts where emitted light would not be collected since the collected area in our measurement configuration is confined to a circle with a diameter of 2 μm by controlling the size of pinhole. At room temperature, the waveguide effect presents as well. However, both the long emission tail at the long wavelength side and the redshift of the emission peaks indicate that the reabsorption plays an important role at room temperature.

4.5 Summary

The thickness dependent photoluminescence measurement at various temperatures has been carried out. The rich features observed at liquid helium temperature can be attributed to the free exciton emission, bound exciton emission, recombination of donor-acceptor pairs and their phonon replicas. The emission energy of the free exciton A follows Varshni equation with temperatures. We have experimentally observed systematic blueshifts of the free exciton A emission of CdS

nanobelts scaling linearly versus the inverse square of the belt thickness, which is much larger than the bulk exciton Bohr radius. Such confinement effect beyond the quantum confinement regime is attributed to surface depletion, which modifies the actual potential wells to be much smaller than the geometric nanobelt thickness and strongly depends on carrier concentration and surface states. The width of the surface depletion is found to be ~ 30 nm at 77 K. As the temperature decreases, the decrease of the electrostatic potential leads to a weaker confinement due to the decrease of carrier concentration. Surface depletion induced quantum confinement disappears at temperatures lower than 77 K due to donor frozen-out, while the surface passivation reduces surface states leading to a loss of the confinement strength. With a layer of PMMA passivation, photoluminescence spectra exhibit pronounced red shifts due to the decrease of the surface states at room temperature. No shift is found at 10 K for both with or without PMMA passivation, suggesting much weaker depletion fields due to the frozen-out of donors. The surface induced quantum confinement may be responsible for quantum confined Stark effect⁷¹, and may find applications in electro-absorption modulators and sensors.

Chapter 5 Electron-Phonon Interaction and Phonon-Assisted Luminescence Upconversion in CdS Nanobelts

5.1 Introduction

5.1.1 Electron-phonon interaction in semiconductors

Electron-phonon interaction describes the interaction between the electrons and ionic motion¹⁹⁹. In general, the interaction Hamiltonian describing the processes of the electron-phonon interaction can be classified into three origins: deformation-potential scattering, Fröhlich interaction and piezo coupling. Electron-phonon interaction plays important roles not only in Raman scattering but also in the phonon-assisted absorption or luminescence. In the phonon-assisted upconversion luminescence, strong electron-phonon coupling is an indispensable requirement to achieve strong upconversion luminescence.

In a perfect crystal, the Hamiltonian describing the system is the sum of the kinetic energy and potential energy which can be expressed as

$$H = \sum_i \frac{p_i^2}{2m_i} + \sum_j \frac{P_j^2}{2M_j} + \sum_{j,j',j \neq j'} \frac{Z_j Z_{j'} e^2}{4\pi\epsilon_0 |\mathbf{R}_j - \mathbf{R}_{j'}|} - \sum_{i,j} \frac{Z_j e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_j|} + \sum_{i,i',i \neq i'} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_{i'}|} \quad (5-1),$$

where $\mathbf{r}_i$ and m_i are the position and mass of the i^{th} electron; $\mathbf{R}_j$ and M_j denote the position and mass of the j^{th} of the nucleus; Z_j and $\mathbf{P}_j$ are the atomic number and momentum operators of the nucleus; $\mathbf{p}_i$ is the momentum operators of the electrons; e represents the electron charge and ϵ_0 is the permittivity of the vacuum. The first term and the second term represent the kinetic energy of electrons and nucleus, respectively. The rest terms give the Coulomb potential among nucleus, between nucleus and electrons, and among electrons.

In expression (5-1), the electronic coordinate and nucleonic coordinate mix together, which makes the electron motion coupled to the nuclear motion. As a consequence, the many-body Hamiltonian (5-1) cannot be solved and two approximations are made in order to solve it. Since the valence electrons can relatively move freely inside crystal while the core electrons are tightly bound to the nuclear forming ion cores, the first approximation states that only valence electrons contributes to the part in the Hamiltonian due to the electrons. Thus, the indices i and i' only runs valence electrons while the indices j and j' label the ion cores. The second approximation is the adiabatic approximation or Born-Oppenheimer approximation, which states that the electrons can respond to the ionic motion instantaneously while the ion cores cannot follow the motion of electrons due to the much heavier ion cores compared with the electrons. In other words, the ions are stationary to the electrons and the ions can only feel a time-averaged electronic potential. Under those approximations, the Hamiltonian can be split to three terms, expressed as

$$H = H_{ion}(\mathbf{R}_j) + H_e(\mathbf{r}_i, \mathbf{R}_{j0}) + H_{e-ion}(\mathbf{r}_i, \delta\mathbf{R}_j) \quad (5-2),$$

where $H_{ion}(\mathbf{R}_j)$ is the Hamiltonian for ion cores under the influence of the ionic potential and the time-averaged electronic potential; $H_e(\mathbf{r}_i, \mathbf{R}_{j0})$ is the Hamiltonian for valence electrons assuming that the ion cores are frozen at the equilibrium positions $\mathbf{R}_{j0}$ and $H_{e-ion}(\mathbf{r}_i, \delta\mathbf{R}_j)$ represents the electron-phonon interaction describing the electronic energy change due to the vibrational displacement $\delta\mathbf{R}_j$ of ion cores from the equilibrium position $\mathbf{R}_{j0}$.

The Hamiltonian for ion cores can be further expressed as

$$H_{ion} = \sum_j \frac{P_j^2}{2M_j} + \sum_{j,j',j \neq j'} \frac{Z_j Z_{j'} e^2}{4\pi\epsilon_0 |\mathbf{R}_j - \mathbf{R}_{j'}|} - \sum_{i,j} \frac{Z_j e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_j|} \quad (5-3).$$

On the basis of expression (5-3) and under harmonic approximation, phonon dispersion curves can be obtained. The detailed information on how to solve the phonon dispersion curves can be found in many textbooks^{129,199,200}.

Similarly, the Hamiltonian for valence electrons can be written as

$$H_e = \sum_i \frac{p_i^2}{2m_i} - \sum_{i,j} \frac{Z_j e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_{j0}|} + \sum_{i,i',i \neq i'} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_{i'}|} \quad (5-4).$$

Since the valence electrons see the ion cores are stationary, we can approximate that each electron experiences a common average potential, which called mean-field approximation. Under the mean-field approximation, the electronic energy band can be obtained¹⁹⁹.

Finally, the part of Hamiltonian for the electron-phonon interaction can be expressed as

$$H_{e-ion}(\mathbf{r}_i, \delta\mathbf{R}_j) = \sum_j \left(\frac{\partial H_e}{\partial \mathbf{R}_j} \right) \bigg|_{\mathbf{R}_{j0}} \bullet \delta\mathbf{R}_j + \dots \quad (5-5).$$

The expression (5-5) is a Taylor series expansion of the electronic Hamiltonian on the basis of the Born-Oppenheimer approximation, which says that the valence electrons can respond instantaneously to the motion of the ion cores. The expression (5-5) indicates the change of the electronic band due to the displacement $\delta\mathbf{R}_j$ of the ion cores from their equilibrium position $\mathbf{R}_{j0}$. In general, the electronic Hamiltonian cannot be explicitly written down and approximations are required in order to work out the electron-phonon interaction. The origins of the electron-phonon coupling including deformation potential scattering, Fröhlich interaction and piezo coupling will be discussed briefly in the following¹.

1) Deformation potential scattering

According to the deformation potential theorem originally developed by Bardeen and Shockley²⁰¹, the atomic displacement can originate from the deformation of the crystals in the case of zone-centre acoustic phonons. The parameters known as deformation potentials are used to describe how the electronic energy changes due to the static deformations of the lattices. The atomic displacement induced strain in a crystal can be described by the strain tensor which is a symmetric second-rank tensor with six independent elements. The induced strain can result in the shift of the electronic energy. Thus, the electron-phonon interactions for the zero-centre acoustic phonons can be expressed as the expansion of the interaction Hamiltonian by using

the strain tensor. There may be many linearly independent deformation potentials which can contribute to the change of the energy for a given electronic band. By applying group theory, all linearly independent deformation potentials involved for a given electronic band can be determined.

We may take the longitudinal acoustic (LA) phonons near the zone-centre in diamond-type crystals as an example. In this case, the atomic displacement $\delta\mathbf{R}$ is parallel to the phonon wave vectors $\mathbf{q}$ and the strain tensor can be simplified to be a diagonal tensor with only three elements. For the non-degenerate bands and ignoring the shear strain, the electron-LA phonon interaction Hamiltonian can be expressed as¹⁹⁹

$$H_{e-LA} = a_{nk}(\mathbf{q} \cdot \delta\mathbf{R}) \quad (5-6),$$

where a_{nk} is the volume deformation potential of the energy level E_{nk} . In practice, the volume deformation potentials can be determined by optical measurement under hydrostatic pressure and the relative volume deformation potential can be extracted by using energy differences between two band extrema¹⁹⁹.

Another example is about the near zero-center optical phonon in nonpolar crystals, which can only lead to the microscopic distortions within the primitive unit cell rather than the macroscopic strain in the case of the long-wavelength acoustic phonons. The long-wavelength optical phonons in nonpolar crystals change the electronic band energy via altering the bond lengths and the bond angles. Since the microscopic distortions in this case are something like the deformation potential interaction of the long-wavelength acoustic phonons, the electron-optical phonon interaction is called deformation-potential electron-optical-phonon interaction¹⁹⁹. In a diamond-type semiconductor with two atoms inside a primitive unit cell, the electron-optical phonon interaction Hamiltonian can be expressed as a function of the lattice distance a_0 and the relative atomic displacement associated with the zone-center optical phonons u ¹⁹⁹

$$H_{e-OP} = D_{nk}\left(\frac{u}{a_0}\right) \quad (5-7),$$

where D_{nk} is the optical phonon deformation potential for the energy band E_{nk} . The deformation-potential electron-optical-phonon interaction is a short-range interaction due to the independence of the potential deformation D_{nk} on the phonon wave vector.

2) Fröhlich interaction

Unlike the deformation-potential electron-optical-phonon interaction in nonpolar crystals, the long-wavelength longitudinal-optical (LO) phonons in polar crystals can lead to the separation of the oppositely charged atoms, which can generate a macroscopic electric field inside the crystals. The change of the energy in the electronic band is realized through the interaction between the electric field and carries¹. The interaction between the electrons and LO phonons in this case is called Fröhlich interaction. The Fröhlich interaction Hamilton interaction can be written as

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$$H_{Fr} = \sum_q (iC_F / q)(c_q^+ \exp(i(q \cdot r - \omega_{LO}t)) - c.c.) \quad (5-8).$$

where $C_F = \frac{e}{\sqrt{4\pi\epsilon_0}} [\frac{2\pi\hbar\omega_{LO}}{NV} (\epsilon_\infty^{-1} - \epsilon_0^{-1})]^{1/2}$; c_q^+ is the phonon creation operators; i is

the imaginary unit; ω_{LO} is the frequency of the LO phonons; ϵ_∞ and ϵ_0 are the high- and low-frequency dielectric constants, respectively; r and t are the electronic coordinate and time, respectively; N is the number of the unit cells per unit volume and V is the volume of the crystal; $c.c.$ denotes the complex conjugate. In the II-IV group semiconductor compounds, the Fröhlich interaction is very strong and further enhanced in nanostructures resulting in the strong upconversion luminescence which will discussed in the following⁴¹.

3) Piezo coupling

In a non-centrosymmetric crystal, the piezo-electric effect occurs, which says the strain, *i.e.*, the lattice distortion, in the crystals can result in the electric field. The phonons in the crystal can be viewed as a periodic modulation of the lattice parameters. As a consequence, through the piezo-electric effect a varying electric field would be produced, which interacts with carries. This interaction is called piezo coupling. The Hamiltonian of the piezo coupling can be written as¹⁹⁹

$$H_{pe} = \frac{|\varepsilon|}{\varepsilon_{\infty}\varepsilon_0 q^2} \mathbf{q} \bullet \mathbf{e}_m \bullet (\mathbf{q} \delta \mathbf{R}) \quad (5-9),$$

where ε is the strain tensor and $\mathbf{e}_m$ is a third-rank electromechanical tensor which can be estimated by using empirical models such as the tight-binding model.

5.1.2 Anti-Stokes luminescence

The term ‘luminescence’ was first introduced by Eilhard Wiedemann in 1888²⁰², which was used to describe the emission of light by materials not due to heat. The origins for luminescence include chemical reactions (chemiluminescence), passing an electric current through a p-n junction (electroluminescence), and absorption of photons (photoluminescence). The well-known application of luminescence is light emission diodes (LED), which belongs to the electroluminescence. In this thesis, when we say luminescence, it means photoluminescence.

For photoluminescence, the emission of light is a result of the absorption of the photons. Stokes shift and anti-Stokes shift are used to describe the energy difference between the emitted photons and absorbed photons. If the energy of the emitted photons is smaller (larger) than the absorbed photons, the energy difference is called Stokes (anti-Stokes) shift while the corresponding emission is called Stokes (anti-Stokes) luminescence. Anti-Stokes luminescence is also called luminescence upconversion since the emitted photons have a higher energy compared with the absorbed photon energy¹⁷⁹. The anti-Stokes luminescence has been observed in rare-earth metal doped glasses or crystals^{52,55,203-205}, semiconductors^{9,45,206,207} and dyes²⁰⁸.

Both two-photon absorption and phonon assisted transition can lead to the upconversion luminescence in semiconductors. During the two-photon absorption induced luminescence upconversion, an electron in the valence band is excited to the conduction band by absorption two photons simultaneously. Afterward the excited electron decay to the bottom of the conduction band by emitting phonons. Finally, a photon emitted via the radiative recombination of the electron and hole as shown in Figure 5-1a. Therefore, the two-photon absorption induced luminescence upconversion contributes heat to the samples. Since the two-photon absorption is a

nonlinear process, a pulse laser light is usually required to excite the samples. The two-photon absorption induced upconversion has been used to investigate the reabsorption effect in the CdS film¹⁸².

Figure 5-1 Schematic image of two-photon absorption induced upconversion luminescence process (a), the phonon-assisted upconversion luminescence for the incident photon energy around band gap (b) and smaller than the band gap (c) in semiconductors.

In contrast to the two-photon absorption induced luminescence upconversion when phonons are created, the phonon-assisted upconversion is able to annihilate phonons. The phonon-assisted upconversion can be classified into two categories as shown in Figure 5-1b and c respectively. For the incident photon energy exactly matching the band gap of the semiconductor, the electrons are excited from the top of the valence band to the bottom of the conduction band forming cold carriers. The cold carriers then undergo the thermalization processes and reach the thermal equilibrium when the carriers obey Fermi-Dirac statistics as shown in Figure 5-1b^{47,48}. The recombination of the electrons and holes after thermalization gives the luminescence upconversion. In this kind of luminescence, the energy difference between the incident photons and the mean energy of the emitted photons is around the thermal energy $k_B T$. For the incident photon energy smaller than the band gap energy, extra phonons are required in order to excite the electrons from the top of valence band to the bottom of the conduction band. The luminescence upconversion is achieved after thermalization as shown in Figure 5-1c⁶⁰. During this process, energy carried away for per photon emission is around several $k_B T$, which is preferred for the laser cooling of semiconductors as will be discussed in the Chapter 6.

The phonon assisted luminescence upconversion is the basis of the laser cooling of semiconductors. Besides, by applying the luminescence upconversion, the

efficiency of the solar cells can be greatly improved²⁰⁹⁻²¹³. The surface plasma enhanced upconversion has been proposed to further increase the efficiency of the solar cells²¹⁴. In addition, it is fundamental important to investigate the upconversion processes in semiconductors in view of that the mechanism behind it remain elusive.

5.2 Resonant Raman scattering and upconversion luminescence in CdS nanobelts

5.2.1 Resonant Raman scattering

Raman scattering is a powerful technique to investigate phonons in nanomaterials and nanostructures. In polar semiconductors, the resonant Raman scattering involves multiple longitudinal optical (LO) phonons, which is important for understanding the multiple LO-phonon assisted anti-Stokes luminescence in the polar semiconductor CdS nanobelts to be discussed in the next section.

The resonant Raman scattering theory in a vibronic system was first developed by A.C. Albrecht, in which he described as “A-term” and “B-term” activities²¹⁵. In polar semiconductors, resonant Raman scattering, particularly involving multiple LO phonons, has been discussed by a series of seminal papers. For instance, D.C. Hamilton²¹⁶ discussed on the perturbation theory of Fröhlich interactions using parabolic bands without considering the excitonic effect; R. Merlin *et al.*²¹⁷ discussed it by considering the Fröhlich interactions between the LO phonons and excitons; and more recently A. Garcia-Cristobal *et al.*²¹⁸ gave an exact account for second order resonant Raman scattering by considering both exciton and electron-hole continuum. In Merlin’s work, their conclusion of the Raman matrix elements for an n-th order phonon process is formally identical to the Albrecht A-term. Merlin explained the experimental data observed in YbS crystals, in which up to 5th order LO scattering (Stokes process) was observed and the coupling strength was extracted. A.P. Alivisatos, L.E. Brus and co-authors used the Albrecht A-term derived for molecules, combined with Merlin’s method to extract the coupling strength, to explain the resonant Raman scattering in CdSe quantum dots, in which up to 3rd-order LO multi-phonon scattering was observed²¹⁹.

For Stokes Raman scattering of multiple LO phonon, there are two ways to generate multiple LO phonons. The first way is that they can be generated in a single step whereas in cascade process that carriers make real transitions to high energy in conduction band, when the carriers relax to the bottom of conduction band, they excite multiple LO phonons in a cascade mode²²⁰. A more general way is to involve a variety of virtual intermediate states, in which cascade model is not applicable. The final transition probability has to sum over all the possible intermediate states. For instance, Leite, Scott and Damen²²¹ reported up to 9th LO resonant scattering at room temperature immediately followed by another report in the same issue by Klein and Porto²²² who also reported the emission-resonant enhancement in CdS. While Leite and Porto first reported resonant enhancement of Raman scattering 2LO due to absorption-resonance²²³, they proposed possible processes involved in the resonance which later were re-visited by J.F. Scott along with Leite and Damen to explain the resonant effect in a few semiconductors including both III-V and II-VI materials²²⁴. It should be noted that those earlier reports all discussed higher order Stokes process (n-LO creation), while we observed multiple LO anti-Stokes Raman scattering (n-LO annihilation) in the CdS nanobelts in the following.

Figure 5-2 The upconversion luminescence of a CdS nanobelt with thickness of 100 nm excited by a 2.7 mW 532 nm laser at room temperature. The phonon peaks are labeled as well.

Figure 5-3 Raman peak assignments and peaks fittings of a single CdS nanobelt excited by a 2.7 mW 532 nm laser at room temperature. The photoluminescence background has been subtracted. Experimental integral intensity ratios of anti-Stokes and Stokes 1LO and 2LO are shown in the plot.

Figure 5-2 shows a Raman spectrum including both Stokes and anti-Stokes components of a CdS nanobelt. In order to examine the Raman intensity, the photoluminescence background was subtracted as shown in Figure 5-3. All the features can be clearly identified from scattering by optical phonons⁹³, such as 2LO, LO, LO₂, TO₂ and TO₁. In addition, a broad band due to surface optical (SO) modes is also observed, which are usually activated due to symmetry breaking in the nanoscale regime such as diameter modulation^{157,225,226}. The intensity of Stokes Raman scattering reflects the creation of phonon population, while the intensity of anti-Stokes Raman reflects the phonon annihilation. Therefore, the ratio between Stokes and anti-Stokes intensities carries the information regarding the sample temperature and the competition between phonon creation and annihilation processes. Under the *non-resonant* Raman scattering situation, because the phonon population follows Bose-Einstein statistics, the intensity of anti-Stokes Raman should be always smaller than that of Stokes Raman. The integrated intensity ratio of Stokes to anti-Stokes components can be written as²²⁷

$$\frac{A_S^{LO}}{A_{AS}^{LO}} = \gamma \cdot \exp(h\nu_{LO}/k_B T) \quad (5-10a),$$

$$\frac{A_S^{2LO}}{A_{AS}^{2LO}} = \gamma \cdot \frac{2\exp(2h\nu_{LO}/k_B T) - \exp(h\nu_{LO}/k_B T)}{\exp(h\nu_{LO}/k_B T) - 2} \quad (5-10b),$$

Where γ is a parameter reflecting the instrument response which can be determined experimentally, k_B is the Boltzmann constant, T is the absolute temperature of sample, $h\nu_{LO}$ is energy of LO phonon. In our system, γ is about 0.82 in the visible region evaluated by a standard sample of [111] silicon wafer. Following equation 5-10a and 5-10b, we can calculate that $A_{AS}^{LO}/A_S^{LO} = 0.29$ and $A_{AS}^{2LO}/A_S^{2LO} = 0.09$ using the LO phonon energy of 38 meV for bulk at 294 K. However, under *resonant* Raman scattering, equation 5-10 no longer apply. The ratio between anti-Stokes and Stokes Raman intensity in resonant situation has the following dependence²²⁸:

$$\left(\frac{A_S^{LO}}{A_{AS}^{LO}} \right)_{res} = \left(\frac{A_S^{LO}}{A_{AS}^{LO}} \right)_{nonres} \times \frac{(E_{ex} + nh\nu_{LO} - h\nu)^2 + \Gamma^2}{(E_{ex} - nh\nu_{LO} - h\nu)^2 + \Gamma^2}, \quad (5-11).$$

When the anti-Stokes is in resonance, *i.e.* $E_{ex} = h\nu + nh\nu_{LO}$, and $2nh\nu_{LO} \gg \Gamma$, the $\left(\frac{A_{AS}^{LO}}{A_S^{LO}} \right)_{res} > 1$ is readily satisfied. In high-order LO phonon-assisted anti-Stokes resonant Raman scattering in a CdS nanobelt, we experimentally obtained that $A_{AS}^{LO}/A_S^{LO} = 1.43$ and $A_{AS}^{2LO}/A_S^{2LO} = 1.03$ for a 100 nm thick CdS nanobelt (as shown in Figure 5-3 and table 5-1). Both the first order and the second order ratios suggest that the anti-Stokes scattering cross-section is significantly enhanced by a factor of 4.9 and 11.4 for the LO and 2LO phonon, respectively. Therefore high order LO phonon-annihilation dominates in CdS nanobelts due to strong electron-phonon coupling (see Huang-Rhys factors in section 5.2.2), which leads to a resonant high order LO annihilation.

Table 5-1 The fitting results of LO and 2LO in spectrum in Figure 5-3.

	Peak (cm ⁻¹)	Intensity	FWHM (cm ⁻¹)	Area
Stokes LO	300	255	9	3623
anti-Stokes LO	-301	328	10	5166
Stokes 2LO	600	391	16	9973
anti-Stokes 2LO	-602	360	18	10236

5.2.2 Huang-Rhys factor

Huang-Rhys factor is an important parameter to evaluate the exciton-phonon coupling strength. Generally speaking, higher order phonon scattering will be activated when the resonant Raman scattering is satisfied or strong electron-phonon coupling occurs²²¹. The coupling strength of the electron-phonon interaction can be evaluated by comparing the relative intensities of the overtones to the fundamental Raman bands. According to the Albrecht A term, the Raman scattering cross section for an n -th optical phonon process is given by²¹⁷

$$|R^n(\omega)|^2 = \mu^4 \left| \sum_{m=0}^{\infty} \frac{\langle n|m \rangle \langle m|i \rangle}{E_{\text{ex}} \pm nh\nu_{LO} - h\nu + i\Gamma} \right|^2, \quad (5-12).$$

where $+nh\nu_{LO}$ means Stokes resonance and $-nh\nu_{LO}$ means anti-Stokes resonance, μ is the electronic transition dipole moment, $|m\rangle$ denotes the intermediate vibrational level in the excited state, $|i\rangle$ denotes the initial state, E_{ex} is the electronic transition energy, and Γ is the homogeneous linewidth of the electronic state²²⁹. The Franck-Condon overlap integral $\langle n|m \rangle$ between the ground and excited states can be expressed as²¹⁹:

$$\langle n|m \rangle = \left(\frac{n!}{m!} \right)^{1/2} \exp\left(-\frac{1}{2}\Delta^2\right) \Delta^{n-m} L_m^{n-m}(\Delta^2), \quad (5-13)$$

where L is the associated Laguerre polynomial, and Δ is the dimensionless displacement for the Fröhlich interaction. The Huang-Rhys factor S is defined^{219,230} as $S = \Delta^2/2$. From equations (5-12 and 5-13), one can see that S can be determined by measuring the ratio of the integrated intensities of different overtones.

Figure 5-4 Huang-Rhys Factor depends on the nanobelt thickness. The gray line is measured from bulk CdS crystal.

The corresponding Huang-Rhys factors as a function of the nanobelt thickness of CdS are shown in Figure 5-4. It can be seen that the electron-LO phonon coupling is significantly enhanced in the nanoscale regime with a factor of four enhancement compared to bulk with a peak value at around 55 nm thickness. It is well known that the electron-LO coupling is strong in CdS. For instance, as high as the 9th-order LO-phonon Stokes component has been reported in a bulk CdS crystal under Stokes resonant excitation at cryogenic temperatures²²¹.

As the thickness decreases, the Huang-Rhys factors first increases and then decreases. The mechanism for this trend is still not clear. Actually, the size dependence of the Huang-Rhys factor is still a controversial topic⁴⁰. The experimental results exhibit different trends for different materials or different measurement methods. Further investigations are required to clarify this issue.

5.2.3 Photoluminescence Upconversion

Figure 5-5a shows the anti-Stokes photoluminescence spectra of a CdS nanobelt excited by a 532 and 514 nm laser at 294 K at three different pumping powers. Strong anti-Stokes photoluminescence with a peak position ~ 506 nm is identified, facilitated by resonant annihilation of multiple LO phonons (one for 514 nm and three for 532 nm, $h\nu_{LO} \sim 37$ meV or 300 cm^{-1}). It is important to note that 514 nm pumping led to much stronger upconversion due to stronger bandtail absorption.

Figure 5-5 (a) Room temperature anti-Stokes photoluminescence spectra of a single CdS nanobelt (100 nm) excited by a 532 nm laser at three power levels. (a) Power dependence of anti-Stokes photoluminescence pumped by 532 and 514 nm at 294 K. Below ~ 12 mW, the intensity scales linearly with power. Two-photon absorption induced photoluminescence starts to play a role only at high power.

As discussed in section 5.1.2, the luminescence upconversion may originate from two-photon absorption or from phonon-assisted transition. This can be identified through excitation power dependent anti-Stokes photoluminescence intensity. For the linear absorption, according to the Beer-Lambert law and assuming that the incident light propagates along z direction, the energy loss can be expressed as

$$\frac{dI}{dz} = -\alpha I \quad (5-14),$$

where I is the light intensity and α is the linear absorption coefficient. For the two-photon absorption, the energy loss can be written as²³¹

$$\frac{dI}{dz} = -\alpha I - \beta I^2 \quad (5-15),$$

where β is two-photon absorption coefficient. As seen from express (5-15), the two-photon absorption becomes significant only if the incident light intensity is high. Two-photon absorption dominated optical density should be quadratic dependent on the incident light intensity. As a result, one can differentiate the two processes by the pump-power dependence of the anti-Stokes luminescence. .

Systematic study on anti-Stokes photoluminescence intensity versus laser power (Figure 5-5b) indicates that two-photon absorption can be excluded under a low-moderate power ($\sim$ below 12 mW), at which our laser cooling experiments (to be discussed in Chapter 6) are conducted. Analysis of the Stokes and anti-Stokes Raman spectra reveals that both the 1LO and 2LO anti-Stokes components are stronger than their Stokes counterparts, suggesting that multiple LO phonon annihilation rate dominates over creation process, which can be readily achieved in CdS under resonant conditions, *i.e.*, when $E_{laser} + nh\nu_{LO} \sim E_{exciton}$ is satisfied (Figure 5-3). Besides, we find that S is significantly enhanced in CdS at nanoscale (Figure 5-4). Therefore, we speculate that the resonant annihilation of one or more LO phonons facilitates the upconversion in CdS nanobelts due to a strong exciton-LO phonon coupling. The microscopic mechanism of how multiple LO phonons are actually involved in the upconversion still remains to be addressed within the framework of higher order LO phonon-exciton coupling.

5.3 Thickness dependent luminescence upconversion

5.3.1 Thickness dependent upconversion emission intensity

The thickness dependent integrated photoluminescence intensity has been discussed in Chapter 4. The integrated photoluminescence intensity increases first and then decreases as the thickness of the nanobelts decreases. The possible reason is probably related to the thickness dependent surface recombination rate and the reabsorption effect. The luminescence upconversion and the integrated intensity for nanobelts with different thickness excited by a 7 mW 532 nm laser are shown in Figure 5-6a and b, respectively. The integrated upconversion luminescence intensity

shows the same trend as integrated photoluminescence intensity with thickness (see Chapter 4). Thus, we can draw the conclusion that it is also the surface recombination rate and reabsorption leading to this kind of trend and the recombination processes of the luminescence upconversion is the same as that of photoluminescence after the carriers are excited.

Figure 5-6 (a) The thickness dependent luminescence upconversion excited by a 7 mW 532 nm laser at room temperature for different thickness CdS nanobelts. (b) The integrated emission intensity extracted from (a) against the thickness of the nanobelts.

5.3.2 Mean emission wavelength

Mean emission wavelength is an important parameter of the laser cooling of semiconductors as will be discussed in the next Chapter. To evaluate whether the overall emission is blue or red shifted compared to the laser excitation, it is important to evaluate the “*averaged*” emission frequency or wavelength weighted by the intensity as the luminescence varies over a relatively large range. The mean emission frequency is defined as⁴⁵

$$\bar{\nu}_f = \frac{\int \nu N(\nu) d\nu}{\int N(\nu) d\nu} \quad (5-16),$$

where $N(\nu)$ is the count of the luminescence photons at a certain frequency ν . The mean emission frequency corresponds to a mean energy $h\bar{\nu}_f$, where h is the Planck constant. The mean emission wavelength $\bar{\lambda}$ is defined as $\bar{\lambda} = c/\bar{\nu}_f$, where c is the speed of light. If the $h\bar{\nu}_f$ is blue shifted compared to laser energy $h\nu$, then the energy

difference $\Delta E = h\bar{\nu}_f - h\nu$ is defined as how much energy each emitted photon takes away from the sample in each cooling cycle. ΔE has to be positive in order to achieve net cooling. Therefore, the energy difference ΔE is one key parameter that evaluates the laser cooling potential. It is important to note that the Raman scattering features due to silicon substrate have to be excluded in the accurate determination of mean emission wavelength of CdS nanobelts.

Figure 5-7 (a) The thickness dependence of the anti-Stokes photoluminescence excited by a 532 nm laser at room temperature. (b) The thickness dependence of the mean emission wavelength calculated from (a), indicating the largest energy difference parameter ΔE around 70 nm.

Figure 5-7a and b summarizes the thickness dependence of the anti-Stokes photoluminescence spectra and the mean emission wavelength of CdS nanobelts deposited on SiO_2/Si substrates excited by a 7 mW 532 nm laser at room temperature. The mean emission wavelength $\bar{\lambda}_f$ gradually blue shifts with thickness and reaches a minimum ($\Delta E_{\text{max}} = h\bar{\nu}_f^{\text{max}} - h\nu \approx 130 \text{ meV}$) for a belt around ~70 nm in thickness. Below 70 nm, the blue-shifts decrease and they reach a constant value ~ 110 meV at 40-50 nm. Two factors may contribute to this non-monotonic behaviour of the thickness dependence of the anti-Stokes photoluminescence mean emission wavelength. The first effect is the monotonic blue-shift of the photoluminescence spectra as the thickness decreases, originating from a surface depletion induced confinement of the carriers³³. The detailed explanation can be found in Chapter 4. The second possible reason is the surface non-radiative recombination, which may lead to heating to the sample, considering that surface recombination becomes significant when the thickness is small as discussed in Chapter 4.

5.4 Temperature and power dependence luminescence upconversion

As discussed previously, the luminescence upconversion is the essential ingredient towards the laser cooling of semiconductors. Therefore, it is critical to work out the temperature range and power range at which the luminescence upconversion can occur excited by a certain wavelength. On the other hand, the luminescence upconversion spectra are very broad and the emitted photons have a large energy distribution as a consequence of the thermal broadening. Thus, the mean emission wavelength is used to evaluate how much energy in average is taken away for each emitted photon, which is defined as $\Delta E = h\bar{\nu}_f(T) - h\nu$. If the energy is taken away from the belts by the emitted photons, the energy difference ΔE should be positive and vice versa.

Figure 5-8 Surface plot of ΔE as a dependence on temperature and pump power. (a) anti-Stokes photoluminescence spectra taken from 4.7 K to 340 K with an excitation of 8.0 mW 532 nm laser. (b) Anti-Stokes photoluminescence spectra of the same nanobelt excited by a 4.0 mW 514 nm laser. Below 200 K, DAP emission peaks appear and dominate the spectra. The spectra are offset vertically for clarity with vertical dash lines indicating the position of the pump lasers, dashed boxes indicating the 1st order anti-Stokes, Stokes and 2nd order Raman features, respectively, from

silicon substrate in (a) and (b). (c) ΔE surface plot versus temperature and power for a 532 nm laser pumping. The maximum energy difference ~ 173 meV is obtained around 180 K. Below 180 K, DAP emission peaks (see (a)) appear and lead to significant red shifts of the mean wavelength of luminescence. (d) ΔE surface for a 514 nm laser pumping. The maximum $\Delta E \sim 52.5$ meV is achieved around 200 K. Below 200 K, the DAP peaks (see (b)) appear and dominate the emission, leading to the red shift of the mean wavelength of luminescence. Because the DAP energy levels resonate with the pump laser approximately, the DAP emission is much stronger than that of the exciton emission, which leads to the negative ΔE below 180 K, suggesting no net cooling is achievable by the 514 nm laser pumping. For both (c) and (d), Si Raman features have been excluded before the mean emission wavelength is evaluated.

We have evaluated the ΔE systematically as a dependence on pump power and temperature (between 5-340 K) pumped by 514 and 532 nm. Measurements were conducted by using six different laser powers, for every temperature between 5 and 340 K with an interval of ~ 20 K. Cooling is possible only if ΔE is positive, therefore the sign and magnitude of ΔE at a defined temperature carries important implications to the cooling potential. Figure 5-8a and 5-8b display the temperature evolution of anti-Stokes photoluminescence spectra at 532 nm (8.0 mW) and 514 nm (4.0 mW) laser excitation, respectively. As the temperature is decreased from 340 K to 180 K, the photoluminescence peak gradually blue shifts. Below ~ 180 K, DAP emission becomes pronounced. Both DAP and exciton emissions blue shift marginally. For 514 nm laser pumping, DAP emission peaks appear and dominate the spectra below 200 K.

By extracting the mean emission frequency, $\Delta E = h\bar{\nu}_f(T) - h\nu$ surface plots can be obtained and displayed in Figure 5-8c and 5-8d. For the 532 nm pumping, a maximum $\Delta E \sim 173$ meV is reached around 180 K. With a further decrease of the temperature, the DAP emission appears and leads to a reduction of ΔE . In the whole temperature range we investigated (4.7-340 K), ΔE remains positive indicating that net cooling is possible. While for the 514 nm pumping, a maximum ΔE of ~ 53 meV is reached around 200 K, below which the DAP emission appears and leads to a transition from a positive to a negative ΔE around 180 K. Therefore, it is impossible to achieve net cooling below 180 K pumped by 514 nm. In the power range we

investigated, no strong dependence of ΔE on power is observed, as manifested by the vertically striped bands in the surface plot. However, the net laser cooling is possible only below 12 mW because the two-photon process will dominate the luminescence upconversion when a higher power is used.

The strong luminescence upconversion luminescence, even the FXA emission located at 488 nm at 4.7 K still can be observed. No multiple phonon assisted absorption or emission at liquid helium temperature has been reported so far. It should be noted that the peak at 488 nm is more than 500 times of the thermal energy above the pumping laser. Under such condition, it seems that the phonon assisted upconversion cannot occur and two-photon absorption induced upconversion may play an important role. Nevertheless, the power dependence analysed shows only some minor contribution from the two-photon absorption induced upconversion. At 4.7 K as shown in Figure 5-9a, the integrated anti-Stokes DAP emission shows linear dependence on power pumped by 532 nm, while the integrated anti-Stokes band-edge exciton is still dominated by linear dependence with some minor contributions from two-photon pumping (see the quadratic coefficient). For 502 nm and 514 nm pumping, both integrated DAP emission show linear dependence on power, excluding any two-photon pumping process (Figure 5-9b).

Figure 5-9 (a) Power dependence of anti-Stokes photoluminescence pumped by 532 at 4.7 K. The DAP integrated intensity (504-530 nm) shows a linear dependence on the laser power, but the integrated band-edge exciton intensity (476-498 nm) shows a minor contribution from two-phonon absorption induced photoluminescence (refer to

the coefficients of linear and quadratic components). (b) Power dependence of anti-Stokes photoluminescence pumped by 514 and 502 nm at 4.7 K. For these two wavelengths, only the exciton emission is the anti-Stokes process. The exciton integrated intensity (476-498 nm) shows a linear dependence on the laser power for both of 514 and 502 nm.

Furthermore, two-photon absorption induced photoluminescence is usually pumped by high power ultrafast lasers (ns-fs) with a high power density, e.g. ~ 60 MW/cm² for CdS crystals. It was a surprise that we have observed anti-Stokes photoluminescence with minor contribution from two-photon excitation by a continuous wave 532 nm laser with a much lower power density (~ 0.5 MW/cm²), which deserves further investigations.

5.5 Electron-phonon coupling in photoconductivity spectra

5.5.1 Urbach tail

The exponential tails of a 230 nm belt at various temperatures was given in Figure 4.18 (a). The exponential tail was observed in the absorption spectrum of various materials, which was called Urbach tail^{127,132,145,183}. Urbach tail has various origins, which including impurities and imperfections¹⁴⁵, electric field^{71,123}, structure disorder¹⁴⁴ and electron-phonon interactions¹³². The Urbach tail can be fitted by the expression^{127,232}

$$\alpha = \alpha_0 \exp\left(-\frac{\sigma(h\nu - E_0)}{kT}\right) \quad (5-17),$$

where α is the absorption coefficient, α_0 and E_0 are fitting parameters and σ is the steepness related to the structure disorder, electron-phonon interaction.

Figure 5-10 (a) The exponential tail of a 230 nm belt at various temperatures. (b) The temperature dependence of the steepness for a 230 nm belt.

The steepness is a very important parameter to characterize a material. The temperature dependence of the steepness can be fitted by²³³

$$\sigma = \sigma_0 \left(\frac{2kT}{\hbar\omega} \right) \tanh\left(\frac{\hbar\omega}{2kT} \right) \quad (5-18),$$

where $\hbar\omega$ is the average energy of phonons which contribute to the exponential tail through electron-phonon interaction. The steepness can be obtained by fitting the exponential tail in Figure 5-10a using the expression (5-17). The plot of the steepness as a function of the temperature can be further fitted by expression (5-18) as shown in Figure 5-10b. The fitting gives $\hbar\omega = 64.3$ meV, much larger than the energy of the longitudinal optical phonon of CdS, which is 38 meV¹²⁷. This large average phonon energy indicates that more than one phonon participates the electron-phonon interaction, which demonstrates the strong electron phonon interaction in our samples.

5.5.2 Exciton ionization

The photoconductivity and photoluminescence spectra of a 46 nm nanobelts at 10 K are shown in Figure 5-11. The emission peaks and absorption peaks are assigned by comparison of the photoconductivity and photoluminescence spectra. It should be noted that the electrons and holes in excitons are bounded together through the Coulomb interaction. Thus, excitons will not contribute to the photocurrent unless they are ionized. The presence of the exciton peaks in photoconductivity spectrum indicates the exciton ionization. The presence of the exciton peaks in

photoconductivity spectra has been reported but no explanation was given²³⁴. The thermal ionization is impossible at such a low temperature. Both the applied electric field and the surface electric field (see Chapter 4) are too small to ionize the excitons as well. Therefore, the exciton ionization at 10 K can be probably ascribed to the electron-LO phonon coupling and requires further investigation.

Figure 5-11 The photoconductivity (PC) and photoluminescence (PL) spectra of a 46 nm nanobelt at 10 K. The applied source-drain voltage is 1 V. The photoluminescence spectrum was taken excited by a 400 μ W 457 nm laser.

5.6 Summary

The resonant Raman scattering in CdS nanobelts has been observed at room temperature. It is found that the anti-Stokes scattering cross-section is greatly enhanced for both the first order and second order LO phonons indicated by the large intensity ratio of anti-Stokes to Stokes signals. The strong luminescence upconversion has been observed in CdS nanobelts, which can be ascribed to the multiple LO phonon assisted upconversion rather than the multiple photon absorption induced emission supported by the excitation power dependent integrated anti-Stokes luminescence intensity. The Huang-Rhys factor, which is a parameter to quantify the exciton-LO phonon coupling strength, has been greatly enhanced at nanoscale with a maximum value at round 55 nm. Enhanced exciton-LO phonon coupling facilitates the strong multiple LO-phonon assisted upconversion in CdS nanobelts.

Since both the Huang-Rhys factor and bandtail absorption depend on thickness and temperature, the mean emission wavelength and the energy difference or energy blue shifting parameter have been evaluated as a function of temperature and thickness, which is essential for selecting the nanobelt with an optimal thickness and temperature range to achieve the net laser cooling of semiconductors. As the thickness decreases, the mean emission wavelength decreases first and then reaches a minimum value around 70 nm in thickness. Below 70 nm, the mean emission wavelength increases again and finally reaches a stable value around 40~50 nm due to the competition between the surface depletion induced confinement and the surface nonradiative recombination induced heating effect. The temperature ranges for potential net cooling are above 200 K for 514 nm laser pumping, and 5 K to 340 K for 532 nm laser pumping, while the pumping power should be kept within the linear regime, below ~ 12 mW for both 514 nm and 532 nm pumping.

Finally, the strong electron-LO phonon coupling has been demonstrated in photoconductivity measurement. The temperature dependent Urbach tail indicates that the average phonon energy contributing to the tail is larger than the LO phonon energy, suggesting that more than one LO phonons participate the phonon assisted band tail absorption, which is an evidence of the strong electron-LO phonon coupling. Besides, the presence of the exciton peaks in photoconductivity spectra even at 10 K shows that the excitons are ionized probably due to the strong exciton-LO phonon interaction.

Chapter 6 Laser Cooling of CdS Nanobelts

6.1 Introduction to laser cooling of semiconductors

Laser cooling of solids exhibits the advantages of compactness, vibration- and cryogen-free, and high reliability⁴⁸ with potential applications in all-solid-state cryocooler²³⁵, and athermal or self-cooling laser⁴⁸. Since 1995 when the laser cooling of solids was first demonstrated, remarkable progress has been made in a variety of RE doped glasses and crystals^{47,48,52,55,235}. However, no net laser cooling of direct bandgap semiconductors, *e.g.*, GaAs, has been achieved till this year although a plenty of experimental and theoretical work have been carried out^{9,50,63,64}. Nevertheless, the laser cooling of semiconductors is more appealing because semiconductors exhibit more efficient pump light absorption, much lower achievable cooling temperature and direct integrability into electronic and photonic devices^{9,62-64}. Further investigations are demanded to search new materials or design novel structures to accomplish the net laser cooling in semiconductors.

According to the theory developed by Sheik Bahae-Epstein(SB-E)^{46,50}, the cooling efficiency $\eta_c(\hbar\nu, T)$ of optical refrigeration in semiconductors follows:

$$\eta_c(\hbar\nu, T) = \eta_{exe} \eta_{abs} \frac{\bar{\nu}_f(T)}{\nu} - 1, \quad (6-1)$$

where ν is the pump laser frequency, T is the temperature of the sample, and $\bar{\nu}_f(T)$ is the escaped mean emission frequency. η_{exe} is the external quantum efficiency being written as $\eta_{exe} = \eta_e W_{rad} / (\eta_e W_{rad} + W_{nr})$, where η_e is the luminescence extraction efficiency which described how many percentages of the emitted photons escaped from the sample, W_{rad} and W_{nr} are the radiative and non-radiative recombination rates, respectively. $\eta_{abs} = [1 + \alpha_b / \alpha(\nu, T)]^{-1}$ is the absorption efficiency, quantifying the percentage of photons absorbed that are engaged in cooling, where α_b is the background absorption coefficient due to the free carriers absorption or defect

absorption below the fundamental band gap, and $\alpha(\nu, T)$ is the semiconductor absorption coefficient.

As seen from expression (6-1), net laser cooling requires $\eta_c(\hbar\nu, T) > 0$. To achieve net laser cooling, three interconnected pathways can be pursued. The first pathway is to achieve a large energy difference $\Delta E = \hbar\bar{\nu}_f(T) - \hbar\nu$. The energy difference depends on microscopic mechanism by which phonons are involved in the luminescence upconversion, specific materials and the temperature. In rare-earth doped systems and GaAs heterostructures, each cooling cycle removes $\sim k_B T$ during the thermalization of cold electrons and holes due to absorption of various phonons. In GaAs, single LO phonon assisted transition in Urbach tail has been proposed to facilitate anti-Stokes luminescence, further laser cooling^{60,236}. To obtain a larger ΔE , it is also proposed that the band structure can be engineered, *e.g.*, by introducing donor-acceptor pairs, which modifies the density of states. However, experimentally it is difficult to realize because the doping density and binding energies of both donors and acceptors have to be simultaneously optimized. We have found strong multiple LO phonon assisted upconversion in CdS nanobelts as discussed in last Chapter due to the strong exciton-LO phonon coupling in CdS. In this case, the annihilation of one or more LO phonons leads to removal of heat by several $k_B T$ in each cooling cycle. Therefore, CdS nanobelts are good candidate for laser cooling in the aspect of the energy difference.

The second pathway to achieve net laser cooling is to have η_{ex} approach unity. The external quantum efficiency closely relates to materials and geometry of the structures. For a material with high external quantum efficiency, it should have a large radiative recombination rate but a smaller nonradiative recombination rate. Besides, the geometry of the structure should be intentionally designed in order to obtain high luminescence extraction efficiency. For example, ZnS or ZnSe domes are used to improve luminescence extraction efficiency⁴⁷.

The third one is to approach unity of η_{abs} by minimizing the background absorption α_b . The background absorption mainly originates from the free carrier absorption and surface or defect absorption. As will be discussed below, the best way

to achieve the high absorption efficiency is to grow the high crystalline quality samples.

In the following section, the absorption and the electron-hole pair recombination in intrinsic direct bandgap semiconductors are discussed, which are indispensable factors for laser cooling of semiconductors.

At the steady state for a certain temperature when an intrinsic direct bandgap semiconductor uniformly irradiate with light, the carrier generation rate due to the optical absorption balances the recombination rate. The recombination includes both the radiative and nonradiative recombination. Under such condition, the electron-hole (e-h) population density N maintains as a constant with time. For a given temperature the rate equation is given by

$$\frac{dN}{dt} = G - W_{nr} - W_r = 0 \quad (6-2),$$

where G is the carrier generation rate; W_r and W_{nr} are the radiative and nonradiative recombination rates, respectively. The carrier generation rate G relates the incident light intensity I , frequency ν and the absorption coefficient $\alpha(\nu)$ via,

$$G = \frac{\alpha(\nu)I}{h\nu} \quad (6-3).$$

In practice, due to the large refractive index mismatch between the semiconductors ($n \sim 3$) and the vacuum ($n \sim 1$), the reabsorption occurs. We have discussed this in Chapter 4. Basically, the reabsorption represents a substantial amount of the emitted photons, which would suffer a total internal reflection if the size of the sample is larger than the half wavelength of the emitted light inside the sample³³. Hence, only a fraction η_e of the total luminescence light can be extracted from the sample while the remaining part $(1 - \eta_e)$ will be trapped and recycled inside the sample, thus contributing to the carrier generation again. As a consequence, the radiative recombination rate escaping from the sample is $\eta_e W_r$ while the trapped part is $(1 - \eta_e) W_r$. As discussed in Chapter 4, the reabsorption leads to a red-shift of the mean emission wavelength, which is thus detrimental to the laser cooling efficiency. Taking the reabsorption effect into account, the expression (6-2) can be rewritten as

$$\frac{dN}{dt} = \frac{\alpha(\nu)I}{h\nu} + (1 - \eta_e)W_r - W_{nr} - W_r = \frac{\alpha(\nu)I}{h\nu} - \eta_e W_r - W_{nr} = 0 \quad (6-4).$$

6.1.1 Absorption in direct bandgap semiconductors

(1) Fundamental absorption

The most important process in absorption is called fundamental absorption, in which an electron from the valence band transits to the conduction band by absorbing one photon with energy greater than the bandgap energy¹⁰. As a consequence, an electron-hole pair is generated. The fundamental absorption leads to a sharp rise in the absorption coefficient in the ideal case when the band tail absorption is ignored. In practices, a long absorption tail always presents due to various origins which will be discussed below.

The absorption coefficient for the interband absorption relates to the transition matrix and the joint density of the states for the conduction and valence bands. By applying the $k \cdot p$ theory in a direct bandgap semiconductor with a parabolic band structure, the absorption coefficient can be simply written as

$$\alpha(h\nu) \propto \sqrt{(h\nu - E_g)} \quad (6-5),$$

where E_g is the band gap energy. As seen from expression (6-5), the absorption coefficient suddenly diminishes when the incident photons with energy smaller than the bandgap energy, suggesting the existence of a sharp threshold.

It should be noted that expression (6-5) can only be applied to the low density excitation or low e-h population density N . For the high density excitation or high e-h population density N , the electronic states at the bottom of conduction band and the top of the valence band are occupied. Thus, the band filling effect occurs, leading to the absorption saturation and the blue-shift of the optical bandgap^{10,237}.

(2) Absorption band tail or Urbach tail

Although the absorption drops dramatically below the bandgap energy, a long absorption tail is always present. The long absorption band tail is important for laser cooling of semiconductors. The absorption tail usually exponentially decay below the fundamental bandgap, which was first observed by Urbach in 1953 thus named as

Urbach tail¹⁸³. Later, it is proved that the Urbach tail is a quite universal phenomenon and has been observed in a number of semiconductors¹⁴⁵. There are various origins of the absorption tail including Franz-Keldysh effect^{10,123,238}, excitonic effect¹⁰, phonon assisted absorption¹³² and unintentionally doped impurities.

The Franz-Keldysh effect describes the presence of an exponential decay absorption tail as a result of the electric field as discussed in detail in Chapter 3. The electric field can be either external applied field or internal field due to the surface charge or unintentionally doped ionic impurities. In the nanostructures, the large surface-to-volume ratio would introduce a substantial amount of surface charge, thus leading to a strong surface electric field, which would give rise to a pronounced Franz-Keldysh effect.

As previously mentioned, an exciton is a quasi-particle consisting of one electron and one hole bound together due to the Coulomb interaction. The energy levels of the excitons are discrete and a little below the conduction band. There are free excitons and bound excitons, both of which can contribute to the absorption below the fundamental absorption edge thus leading to the Urbach tail. Since the excitonic energy levels are much like the hydrogenic energy levels, ideally the excitonic absorption spectra should contain a series of discrete lines. Nevertheless, the experimental data shows a different result: a broad peak just below the fundamental absorption. An absorption band tail is present due to the broadening of the excitonic absorption peaks as a result of the scattering of excitons with phonons or lattice imperfections. The broadening of the excitonic peaks is temperature dependent and the linewidth of the excitonic absorption $\Gamma(T)$ can be approximately expressed as¹⁷⁷

$$\Gamma(T) = \Gamma_{inh} + \gamma_{ph}T + \frac{\gamma_{LO}}{\exp(\hbar\omega_{LO}/k_B T) - 1} \quad (6-6),$$

where Γ_{inh} is the inhomogeneous linewidth, γ_{ph} is the coupling strength of the electron acoustic phonon, γ_{LO} is the coupling strength of the electron LO phonon and $\hbar\omega_{LO}$ is the energy of the LO phonon. The first term represents the broadening due to the imperfections or surface electric field in nanostructures while the second and third terms are due to the scattering of excitons with LA and LO phonons, respectively.

Figure 6-1 Schematic diagram of 1st order (left) and 2nd order (right) exciton-LO phonon interactions. $n=1, 2, 3$ represents the lowest three exciton parabolic levels, while the horizontal line represents the ground states. Hatched area represents the continuum states. The small arrows between the bands present the “scattering” of intermediate state excitons by LO phonons, which changes both the momentum and energy²³⁹.

Furthermore, phonon assisted absorption can contribute to the Urbach tail as well. The exciton-LO phonon interactions within the context of optical absorption have been extensively discussed in early theoretical literature, which are also related to how the Urbach tail are developed^{132,240-242}. The creation of excitons with a simultaneous absorption (annihilation) of one or two LO phonons has been addressed which are manifested as additional features in absorption edge in spectroscopy. Figure 6-1 displays the first-order (1LO) and second-order (2LO) LO phonon assisted absorption and emission discussed by Segall and Mahan²³⁹. In CdS crystal, up to third-order (3LO) LO phonon assisted absorption at room temperature and first-order (1LO) phonon assisted absorption at 77 K have been observed, which introduces a long absorption tail as shown in Figure 6-2²⁴³.

Figure 6-2 The absorption coefficient in dependence on photon energy in CdS crystals. The arrows indicate the energy difference of one or several LO phonons from the resonant line position²⁴³.

Besides, the unintentionally doped impurities during crystal growth can introduce shallow or deep energy levels inside the forbidden band gap, which can lead to an absorption tail since the absorption can occur either from the valence band or acceptors to donors or the conduction band. For example, due to the different vapour pressures for Cd and S at a certain temperature, the stoichiometric defects including sulphur and cadmium vacancies, sulphur and cadmium interstitials and sulphur and cadmium anti-sites can be unintentionally introduced during the synthesis of CdS nanobelts, which would result in a long absorption tail below the fundamental absorption edge. This has been proved by the photoconductivity spectra of individual CdS nanobelt devices⁹² as discussed in Chapter 3.

(3) Free carrier absorption

Free carrier absorption is a kind of wavelength-dependent intraband absorption, which becomes important below the fundamental absorption edge. The spectrum of free carrier absorption is monotonic and structureless⁹². After absorbing a photon, the electron undergoes a transition to a higher energy states within the same conduction band and the momentum conservation during the transition is satisfied by interacting with the phonons or by scattering from ionized impurities.

In general, three processes contribute to the free carrier absorption coefficient: acoustic phonons, optical phonons and ionized impurities. The free carrier absorption coefficient would be a weighted sum of the three modes of scattering^{244,245}

$$\alpha_f = A\lambda^{1.5} + B\lambda^{2.5} + C\lambda^{3.5} \quad (6-7),$$

where A , B and C are constants and λ is the wavelength. The first and second terms represent the scattering by acoustic phonons and optical phonons while the third term originates from scattering with ionized impurities. The impurities concentration determines which term dominates the free carrier absorption.

In practice, the free carrier absorption coefficient can be evaluated by a classical formula⁹²

$$\alpha_f = \frac{Ne^2\lambda^2}{8\pi^2m_e n c^3 \tau} \quad (6-8),$$

where N is the carrier concentration, e is the electron charge, n is the refractive index, τ is the relaxation time reflecting the influence of the scattering, c is the light speed in vacuum and m_e is the effective mass of electron. As seen from expression (6-8), the free carrier absorption coefficient is proportional to the carrier concentration and quadratic dependent on the wavelength, indicating that the free carrier absorption plays an important role in the longer wavelength and in samples with high impurities concentration. In the laser cooling of semiconductors, the free carrier absorption contributes to the background absorption, thus detrimental to the cooling efficiency.

In summary, the fundamental absorption, absorption tail and free carrier absorption are discussed in this section. In practice, the absorption coefficient can be evaluated by either absorption spectroscopy or obtaining from photoluminescence spectrum by van Roosbroeck-Shockley relation¹⁰.

6.1.2 Recombination processes in direct bandgap semiconductors

The carriers excited by incident photons will undergo the recombination processes including both radiative and nonradiative recombination. The competition between them determines the external quantum efficiency, one of the most important factors for laser cooling of semiconductors⁴⁵. In this section, the radiative and nonradiative recombination processes are discussed in detail.

(1) Radiative recombination

For laser cooling of semiconductors, strong radiative recombination is required so that the thermal energy can be taken away by the emitted photons during

the luminescence upconversion. In the steady states, the radiative recombination rate W_r can be expressed as the product of the electron density n in the conduction band and hole density p in the valence band times the radiative recombination coefficient B :²³⁷

$$W_r = Bnp \quad (6-9).$$

For the intrinsic wide bandgap semiconductors, the thermal excited carriers can be ignored so that the optical excitation induced electron density equals to the hole density $n=p=N$, where N is the e-h population density. The expression (6-9) can be rewritten as²³⁷

$$W_r = BN^2 \quad (6-10).$$

The radiative recombination time relates the radiative recombination rate via

$$\tau_r = \frac{N}{W_r} = \frac{1}{BN} \quad (6-11).$$

The radiative recombination coefficient B can be obtained by integrating over the emission spectrum¹⁰:

$$BN^2 = \int R(\nu) d\nu \quad (6-12),$$

where $R(\nu)$ is the luminescence spectral density at frequency ν . The radiative recombination coefficient B is temperature dependent due to the temperature dependent luminescence spectral density. In bulk materials, the temperature dependent radiative recombination coefficient B for temperature above 100 K can be written as

$$B(T) = B(300) \left(\frac{300}{T} \right)^{3/2} \quad (6-13a).$$

In 2D structures, the expression (6-13a) changes to²⁴⁶

$$B(T) = B(300) \left(\frac{300}{T} \right) \quad (6-13b).$$

As seen from expression (6-13), the radiative recombination coefficient B increases as the temperature decreases for both 3D and 2D structures.

(2) Nonradiative recombination

The nonradiative recombination is another channel for the photogenerated carriers to decay. The released energy during nonradiative recombination process converts to the heat, which is detrimental to the laser cooling of semiconductors. There are three pathways for nonradiative recombination: defects related nonradiative recombination²⁴⁷⁻²⁵⁰, surface related nonradiative recombination and Auger process¹⁰.

The defects would introduce the deep level within the forbidden gap, which serves as a nonradiative centre. An electron in the conduction band is first captured by the nonradiative center and then the bound electron combines with a hole in the valence band. The amount of released energy equals to the band gap energy dissipated through multi-phonon emission²⁴⁷⁻²⁴⁹, which can heat up the samples. The nonradiative recombination coefficient for the defect related nonradiative recombination can be expressed as²⁴⁹

$$A(T) = A(300K) \exp\left(-\frac{E_a}{k_B T}\right) \quad (6-14),$$

where E_a is the activation energy. The activation energy is the energy required for the deep level states to cross into the conduction or valence band. The nonradiative recombination coefficient decreases as the temperature decreases.

For semiconductors with high crystalline quality, the deep level defects can be neglected. The large surface-to-volume ratio results in the large surface recombination rate, which becomes the dominated component of nonradiative recombination process especially for nanostructures. The surface recombination rate A_s relates the surface recombination velocity S and the thickness of the active layer of a planar structure t via^{198,251}

$$A_s = \frac{2S}{t} \quad (6-15).$$

Here we assume that both surfaces are in the same environment, thus having the same surface recombination velocity. The surface recombination velocity only depends on the nature of the surface and is independent of the carrier density and layer thickness. For example, the surface velocity is around $250 \text{ cm} \cdot \text{s}^{-1}$ in bare CdS crystal²⁵² and of the order of $10^7 \text{ cm} \cdot \text{s}^{-1}$ in GaAs^{179,253}. The temperature dependent surface recombination coefficient can be expressed as¹⁹⁸

$$A(T) = \frac{S_0 \exp(-\frac{E_a}{k_B T})}{2t} \quad (6-16),$$

where S_0 is the surface recombination velocity at room temperature. Expression (6-16) indicates that the surface recombination rate increases as the thickness of structures is reduced and decreases as the temperature decreases. It should be noted that the surface recombination rate is greatly enhanced in nanostructures due to their large surface-to-volume ratio.

Nonradioactive Auger process involves a band-to-band, three-body scattering, in which the energy released by the recombination of an electron with a hole is immediately transferred to another electron in the conduction band or hole in the valence band, which then dissipates the energy by the phonon emission¹⁰. The Auger process depends on the nature of the possible transitions, the carrier density and the band gap energy of the semiconductors. The Auger nonradiative recombination rate can be expressed as a function of the carrier density as¹⁰

$$R_A = CN^3 \quad (6-17),$$

where C is the Auger nonradiative recombination coefficient, which is related to the temperature through²⁵⁴

$$C(T) = C_0 \exp(-\frac{E_a}{k_B T}) \quad (6-18).$$

Here C_0 is the Auger nonradiative recombination coefficient at room temperature. $E_a = \alpha E_g$ is an activation energy usually greater than the bandgap energy, where α is a constant usually greater than one. One can see from expression (6-17) that the Auger process becomes significant for a higher carrier density or higher $e-h$ population density. Besides, the Auger process becomes smaller for the larger bandgap semiconductors, or at lower temperature as clearly seen from expression (6-18).

In summary, the nonradiative recombination rate for defect related and surface related nonradiative recombination can be expressed as,

$$W_{nr} = \frac{N}{\tau_{nr}(T)} = A(T)N \quad (6-19),$$

while the Auger nonradiative recombination rate can be written as the expression (6-17). As a result, the expression (6-4) can be rewritten as,

$$\frac{dN}{dt} = \frac{\alpha(\nu)I}{h\nu} - AN - \eta_e BN^2 - CN^3 = 0 \quad (6-20)$$

and the external quantum efficiency can be re-expressed as,

$$\eta_{exe} = \frac{\eta_e BN^2}{AN + \eta_e BN^2 + CN^3} = \frac{\eta_e h\nu BN^2}{\alpha(\nu)I} \quad (6-21).$$

One can increase the external quantum efficiency by increasing the emission extraction efficiency and the radiative recombination rate while decreasing the nonradiative recombination rate.

6.2 Pump-probe luminescence thermometry (PPLT)

To precisely determine the local temperature at the sample upon laser cooling, we devise a pump-probe luminescence thermometry (PPLT) technology, which is based on the sensitivity of the luminescence peak blue (red) shifts when the temperature is decreased (increased) in semiconductors. This technique is believed to have a much better sensitivity compared to other non-contact temperature probes, such as infrared camera. As explained, the bandgap values of semiconductor as a function of temperature follows a Varshni equation¹⁰. Above 77K, the emission wavelength is very sensitive to temperature, which can be used as a local probe of the sample temperature. As a result, the intensity variation method based on differential luminescence thermometry is no longer necessary^{55,235}, since in our laser cooling experiments the temperature change is sufficient that our high resolution spectrometer can detect the cooling from the blue-shifting of the luminescence.

Figure 6-3 Laser cooling pump-probe luminescence thermometry (PPLT). (a) SEM image of a single CdS nanobelt suspended on a SiO₂/Si substrate. Laser cooling demonstration was conducted on the suspended segment as shown in the inset. (b) The measurement set-up with two laser beams (pump and probe) aligned at the same spot. (c) The time sequence of the PPLT. For every 5 min pumping (*e.g.*, by 532 nm laser), the pump laser was blocked and the probe Stokes photoluminescence spectrum was acquired immediately, excited by a 20 μ W 473 nm laser.

The sample image, setup and time sequence are schematically shown in Figure 6-3. The CdS nanobelt was suspended across inverted pyramid-shaped holes ($\sim 3 \mu\text{m}$ width) on a SiO₂/Si substrate to decrease the thermal conductive loss through substrates and to improve the luminescence escape efficiency. The holes are etched by a potassium hydroxide solution. To maintain the surrounding temperature constant and to vary the temperature of sample during the calibration, the sample was mounted on the cold finger of a continuous flow microscopy cryostat. A solid state 532 nm laser and Ar ion laser (514 nm, 502 nm and 488 nm) are used as a pump laser. A 473

nm solid state laser with a power of 20 μ W is used as a probe beam to measure the cooling or heating effect. Such low power for probe beam used is to eliminate the laser heating effects due to the probe beam. Both pump (Ar ion laser 488 nm, 502 nm and 514 nm, and Nd:YAG solid state 532 nm laser) and probe beams are collimated and focused thorough a 50 $\times$ objective onto a single CdS nanobelt that crossed the etched hole. All the spectra are collected by a confocal triple grating spectrometer (Horiba-JY T64000) in a backscattering configuration. Equipped with a 640 mm focal length and 1,800/mm grating, the spectrometer has very high the spectral resolution of $\sim 0.5 \text{ cm}^{-1}$, corresponding to $\sim 0.01 \text{ nm}$ around 500 nm. During the cooling experiments to extract the local temperature change, each Stokes photoluminescence spectrum was recorded after an interval of ~ 5 -min pumping, when the pump laser was blocked momentarily.

6.3 Laser cooling of CdS nanobelts

6.3.1 Calibration

Firstly, the temperature calibration curves have been measured and evaluated by monitoring the peak shift of the photoluminescence of the CdS nanobelt excited by the probe beam around each starting temperatures. Then, these calibration curves are used to deduce the laser cooling temperature, by comparing the peak shift versus temperature.

To calibrate the peak shift versus temperature change, the peak position of the Stokes photoluminescence spectra as a function of an accurate sample temperature is demanded. This was achieved by accurately measuring the temperature of a copper cold finger of a continuous flow microscopy cryostat. The silicon substrate was glued onto the cold finger by GE varnish to ensure good thermal contact. The cold finger temperature can be precisely controlled by a Lakeshore temperature controller and accurately measured by a silicon diode temperature sensor, which is enclosed inside a radiation shielding box. This is important, since we do not want the sensor to be affected by the stray light of the laser beam. Adequate waiting time was ensured to allow the system to reach a thermal equilibrium.

Several Stokes photoluminescence spectra have been taken to monitor the emission and to make sure that there was no visible peak shift occurred between sequential measurements. This confirms that the system reaches thermal equilibrium and the heating effect due to the excitation laser is negligible. Two calibration spectra and calibration curves for a 100 nm thick CdS nanobelt are given in Figure 6-4, starting from 320 K (Figure 6-4a and b) and 120 K (Figure 6-4c and d), respectively. The spectra are shifted vertically for clarity. For a starting temperature of 120 K, we choose the exciton peak located at ~ 492 nm to serve for the calibration purpose (Figure 6-4 c and d), because the exciton peak exhibits a higher sensitivity to temperature variation than DAP peaks located around 518 nm. Calibration curves shown in Figure 6-4b and d are extracted from Figure 6-4a and c correspondingly, plotted as temperature changes (referenced to their starting temperature 320 K and 120 K, respectively) versus the photoluminescence peak shift in energy (meV). Both calibration curves can be fitted linearly. This is a good approximation of the Varshni equation when the temperature range is small.

Figure 6-4 PPLT calibration spectra and curves of laser cooling for a 100 nm thick CdS nanobelt at starting temperature of 320 K and 120 K. (a) the temperature dependence of the Stokes photoluminescence spectra excited by a 473 nm laser from

320 K to 268 K. (b) the temperature differences versus peak shifts in energy, both referenced to 320 K. (c) the temperature dependence of Stokes photoluminescence spectra from 120 K to 78 K. (d) the temperature difference as a function of peak shift in energy, both referenced to 120 K. The peak position of free-exciton A (located at ~492 nm in (c)) was chosen for temperature calibration function because it is more sensitive to temperature than the DAP (located at ~518 nm). All the spectra are offset vertically for clarity in (a) and (c). The temperature difference versus peak shift (in meV) extracted and plotted in (b) and (d) can be well fitted by a linear function in the measured temperature range, yielding the relation between the temperature difference and photoluminescence peak shift. This was used as an intrinsic temperature calibration of the laser cooling.

Figure 6-5 DLT calibration spectra and curves of laser cooling for a 100 nm thick CdS nanobelt at starting temperature of 320 K and 120 K. (a) photoluminescence differences (PLD) spectra from Figure 6-4a, all referenced to 320 K spectrum. (b) the calibrated differential luminescence thermometry (DLT) signal was obtained by plotting the temperature difference ΔT versus the peak-to-valley value of the PLD spectra in (a). (c) the PLD spectra corresponding to Figure 6-4c, and (d) DLT calibration curve from 120 K to 78 K.

Differential luminescence thermometry (DLT) was devised to evaluate small ΔT ($< 5\text{K}$) of laser cooling in GaAs-based semiconductor heterostructures, when such small cooling or heating leads to only a negligible peak shift which is usually difficult to be detected¹⁷⁹. The essential idea is to normalize and subtract the luminescence spectra at two different temperatures. If the resultant spectrum shows as a peak followed by a valley, it suggests cooling; while if the spectrum shows as a valley followed by a peak, it indicates heating. Then the difference between the peak and valley can be used as a calibration to measure the temperature change. In our laser cooling experiment, much larger cooling (15-40 K) is achieved. The peak shift can be readily detected in our high resolution spectrometer with a sensitivity of $\sim 0.01\text{ nm}$. Therefore, DLT is no longer necessary. Nevertheless, to confirm that DLT and PPLT give the consistent results, we also conducted DLT processing to our calibration spectra as shown in Figure 6-5a-d for starting temperature of 320 K and 120 K, respectively. As shown in Figure 6-5a and c, all the differential luminescence curves show a peak followed by a valley. The peak-to-valley difference has been extracted to calibrate the change of temperatures as shown in Figure 6-5b and d. Similar magnitude of temperature change can be obtained using PPLT (calibration curves Figure 6-4b and d) or DLT (Figure 6-4b and d).

6.3.2 Experimental results

The detailed data plotted as the probe Stokes photoluminescence spectra of a 100 nm thick CdS nanobelt evolution for four different wavelengths (532, 514, 502 and 488 nm) are shown in Figure 6-6a-d (290 K) and Figure 6-7a-d (100 K). Each spectrum was taken with a 5 minute interval during pumping, when the pump laser was blocked momentarily. As can be seen from whether the photoluminescence is blue-shifted or red-shifted upon laser pumping, we can unambiguously identify that at 290 K, both 532 and 514 nm pumping leads to cooling, while 502 and 488 nm pumping cannot cool the nanobelt. This is because the mean emission wavelengths for both pumping wavelengths are red-shifted. While for both 532 and 514 nm pumping the mean emission wavelengths are blue-shifted. At 100 K, only 532 nm leads to laser cooling, all other three wavelength pumping leads to net heating to the nanobelt.

Figure 6-6 PPLT spectra of a 100 nm thick CdS nanobelt taken in every 5 minute interval for four different laser pumping at 290 K. (a), (b), (c), (d) corresponds to 532, 514, 502 and 488 nm laser pumping at 290 K. At 290 K, both 532 and 514 nm lead to net laser cooling. The spectra have been shifted vertically for clarity.

Figure 6-7 PPLT spectra taken of a 100 nm thick CdS nanobelt in every 5 minute interval for four different laser pumping at 100 K. (a), (b), (c), (d) corresponds to 532, 514, 502 and 488 nm laser pumping at 100 K. At 290 K, only 532 nm laser pumping leads to net laser cooling. The spectra have been shifted vertically for clarity.

Figure 6-8 Net laser cooling of CdS nanobelts. (a) The evolution of PPLT spectra starting from 290 K, pumped by 514 nm with a power of ~ 6.3 mW. Solid curves represent the cooling cycle, while the dashed curves represent the warming up after the pump laser is switched off. Dashed curves are shifted vertically for clarity. (b) The temperature change ΔT versus time pumped by four laser lines (532, 514, 502 and 488 nm), with data extracted from the PPLT spectra shown in Figure 6-6 and the corresponding calibration curve around 290 K shown in Figure 6-4b. (c) The evolution of PPLT spectra for another nanobelt pumped by 532 nm laser with 6.5 mW starting from 100 K. Similar cooling and warming up cycles are observed as shown in (a). (d), The Temperature change ΔT versus time pumped by four laser lines (532, 514, 502 and 488 nm), with data extracted from the PPLT spectra shown in Figure 6-7 and the corresponding calibration curve around 100 K shown in Figure 6-4d.

For clarity, Figure 6-8a and 6-8c display only the Stokes photoluminescence peak evolution upon a continuous 6.3 mW 514 nm and 6.5 mW 532 nm laser

pumping again, starting from 290 K and 100 K, respectively. Solid curves represent the cooling cycle, while the dashed curves represent the warming up after the pump laser is switched off. Dashed curves are shifted vertically for clarity. We can observe a pronounced systematic blue shift upon laser pumping until a steady state is reached in ~30-40 minutes, suggesting that a maximum net cooling is established. After the cooling is stopped (switching off pump laser), the Stokes photoluminescence red shifts, indicating a temperature rise. Based on the calibration curves shown in Figure 6-4, the temperature change ΔT extracted from Figure 6-6 and 6-7 is plotted in Figure 6-8b and 6-8d, which show a net laser cooling of ~40 K and 20 K for 514 nm and 532 nm pumping at 290 K, respectively. At 100 K, only 532 nm can lead to a net laser cooling of 15 K while 514 nm laser cannot due to red shifting of the mean emission wavelength at 100 K consistent with the conclusion obtained in last Chapter. 488 and 502 nm laser pumping leads to heating of the sample at all the temperatures.

6.3.3 Discussions

Luminescence extraction or escape efficiency η_e

Figure 6-9 The side view (left) and front view (right) of the CdS nanobelt. The width and the thickness are 2 μm and 100 nm, respectively. The length is about 10 μm . Through adjusting the confocal hole, the volume over which we collected the emitted light is a cylinder with a diameter of 400 nm and a height of 100 nm. The dimensions are not drawn to scale in the schematic diagram above.

The luminescence extraction or escape efficiency η_e is an important parameter, which describes the percentage of emitted photons being effectively “removed” from the medium. The remaining photons will be trapped and recycled

leading to re-absorption and heating. Re-absorption usually results in a red shifting of the emission and therefore should be avoided in laser cooling. Low luminescence extraction efficiency is one of the underlying processes which make the net cooling impractical in GaAs-based semiconductors although a ZnS or ZnSe dome has been used to improve the extraction efficiency⁴⁷.

The luminescence extraction efficiency for the CdS nanobelt used in laser cooling experiments is obtained via geometrical optical analysis. The thickness of the nanobelts used here are around 100 nm. No Fabry-Pérot cavity can be formed in the perpendicular direction at this thickness. Therefore, there is no total internal reflection perpendicular to the nanobelts. Along the length direction of the nanobelt, the reflected light will be deflected to the unsuspended part of the nanobelt due to the total internal reflection rather than to the suspended part where the photoluminescence spectra are collected (shown in Figure 6-9). The size of the beam spot on the sample is $\sim 2 \times 2 \mu\text{m}^2$, which corresponds to a confocal pinhole of $\sim 200 \times 200 \mu\text{m}^2$ for the total signal throughout. In cooling experiments, in order to accurately detect the local temperature of sample, only the fluorescence emitted from a $\sim 0.4 \times 0.4 \mu\text{m}^2$ area at the center of the laser spot was measured by adjusting the confocal pinhole to $\sim 40 \times 40 \mu\text{m}^2$. Through controlling the confocal pinhole, the area of the emission being collected is controlled to be within a cylinder with a diameter of ~ 400 nm and a height of ~ 100 nm. The unsuspended part of the nanobelt is closely in contact with the substrate and can quickly transfer heat to the substrate. The width of the nanobelt is around $2 \mu\text{m}$ so that the maximum angle θ is 2.9° , which is much smaller than the critical angle 23.6° of the total reflection in the width direction of nanobelt (The refractive index of CdS at around 500 nm is 2.5 corresponding to a critical angle of 23.6°). The photons emitted in plane can either propagate along the nanobelt length direction via multiple internal reflections to the substrate or can escape via near-normal incidence along the width direction. From the above discussions, we can safely draw the conclusion that the luminescence extraction efficiency η_e approximately approaches to unity.

External quantum efficiency

As previously discussed, the external quantum efficiency can be expressed as²³⁵

$$\eta_{\text{exe}} = \eta_e W_{\text{rad}} / (\eta_e W_{\text{rad}} + W_{\text{nr}}) = \eta_e \tau_{\text{nr}} / (\eta_e \tau_{\text{nr}} + \tau_{\text{rad}}) \quad (6-22),$$

where the W_{rad} (W_{nr}) and τ_{rad} (τ_{nr}) are the radiative (nonradiative) recombination rate and life-time, respectively. In order to evaluate the radiative and nonradiative life-time, we analyzed our time-resolved photoluminescence spectroscopy data taken from an ensemble of CdS nanobelts, which were mounted into a continuous flow cryostat with variable temperatures from 300 K to 77 K. More details of time-resolved dynamics of CdS nanobelts can be found in previous publication²⁵⁵. Figure 6-10a shows the time integrated photoluminescence spectra from a streak camera from 300 K to 77 K. The spectra have a much lower resolution than all the steady-state photoluminescence or anti-Stoke photoluminescence spectra because the spectrometer in time-resolved photoluminescence spectroscopy is equipped with a 150 g/mm grating with a focal length of 250 mm (in comparison, all steady state photoluminescence spectra were collected in a Horiba-JY T64000 spectrometer equipped with a 1800 g/mm grating with a focal length of 640 mm). Figure 6-10b displays the time-resolved decay dynamics (red circle) extracted from a streak camera for the band indicated with stars in Figure 6-10a. Above 77 K the emission is composed of contributions from both FXA and FXB up to room temperature¹⁸⁰. To evaluate the recombination lifetimes, time-resolved spectra were fitted by a bi-exponential decay function as follows:

$$A(t) = A_1 \exp(-t_1/\tau_1) + A_2 \exp(-t_2/\tau_2) \quad (6-23),$$

where the τ_1 and τ_2 represent the two different decay channels probably accounting for FXB and FXA, respectively. The blue solid curves are fitting results by equation (6-23), with the time constants (τ_1 and τ_2) summarized in Figure 6-10c. The slower decay channel τ_2 is ~150 ps at 150 K, and ~300 ps at 300 K, while the faster decay channel τ_1 is ~40 ps at 200 K, and ~100 ps at 300 K, respectively. Both channels (thus corresponding to different free excitons) exhibit a minimum around 150-200 K, suggesting a competition between radiative and nonradiative processes and their different dependence on temperature.

The decay process of photoluminescence includes both radiative recombination and nonradiative recombination. Therefore, the measured decay time includes both radiative and nonradiative contributions, which can be expressed as²⁴⁶:

$$\frac{1}{\tau(T)} = \frac{1}{\tau_{rad}(T)} + \frac{1}{\tau_{nr}(T)} \quad (6-24a).$$

Above 100 K the temperature dependence for $\tau_{rad}(T)$ is nominally $\sim T^{3/2}$, while in 2D quantum wells $\tau_{rad}(T)$ follows a linear T dependence²⁴⁶. For CdS nanobelts we take the linear temperature dependence of the radiative recombination time as expressed by

$$\frac{1}{\tau_{rad}(T)} = \frac{1}{\tau_{rad}(300 \text{ K})} (T / 300)^{-1} (T \geq 100 \text{ K}) \quad (6-24b).$$

The nonradiative recombination time has a well-known thermal activation dependence as expressed by²⁵⁶

$$\frac{1}{\tau_{nr}(T)} = \frac{1}{\tau_{nr}(0 \text{ K})} \exp\left(-\frac{E_a}{k_B T}\right) \quad (6-24c),$$

where the E_a represents the thermal-activation energy for the nonradiative process. Equations (6-24a, b, c) are combined to fit the temperature dependence of the decay time τ_2 above 100 K as plotted separately in Figure 6-10d. The grey solid curve is the least-square fit with the fitting parameters of $\tau_{rad}(300 \text{ K}) = 305 \pm 2 \text{ ps}$, $\tau_{nr}(0 \text{ K}) = 7 \text{ ns}$, and $E_a = 70 \text{ meV}$. The fitting result of the thermal-activation energy is close to that found in CdS quantum dots²⁵⁶. Following the equations (6-22b, 11c), we obtained $\tau_{nr}(294 \text{ K}) \simeq 110 \text{ ns}$, $\tau_{nr}(100 \text{ K}) \simeq 23 \text{ } \mu\text{s}$, $\tau_{rad}(294 \text{ K}) \simeq 299 \text{ ps}$ and $\tau_{rad}(100 \text{ K}) \simeq 102 \text{ ps}$. Substituting those values into equation (6-22), nearly unity external quantum efficiency is obtained with $\eta_{exe} \approx 99.5\%$ for $\eta_e = 50\%$ and $\eta_{exe} \approx 99.7\%$ for $\eta_e = 100\%$ at 294 K, slightly higher than the values reported for bulk CdS crystals, in which $>92\%$ external quantum efficiency was reported²⁵⁷. These results indicate that extraction efficiency is not that critical any more when the non-radiative recombination lifetime is much larger than the radiative recombination lifetime. At low temperatures, the external quantum efficiency is even higher than that at 294 K. Those values (99.5% or 99.7%) are adequate to achieve net cooling for all upconversion energy differences ΔE from 53 meV (requires $\eta_{exe}^{\min} = 98\%$ for $\eta_c > 0$)

to 173 meV at 180 K (requires $\eta_{xe}^{\min} = 93\%$, for $\eta_c > 0$) as we discussed in last Chapter. It is important to note that the existence of surface states and the resultant surface depletion does not affect the external quantum efficiency significantly for the nanobelts around 100 nm we examined here, presumably because the electrons see the surface depletion potential and therefore are repelled from the surface²⁵⁸. In addition, the surface recombination speed in CdS is 3-4 orders of magnitude smaller than in GaAs, all without surface passivation^{253,259}. As such, the surface recombination may be suppressed considerably. The unpassivated CdS nanobelt surfaces do not lead to dissociation of excitons (thus won't affect the high quantum efficiency) is also to probably the low indexing terminating planes (note the rectangular cross section) and large exciton binding energy of 28-30 meV²⁶⁰. In Chapter 4, we have discussed the surface effect in CdS nanobelt in more detail.

Figure 6-10 Temperature dependent time-resolved photoluminescence spectra of an ensemble of CdS nanobelts. (a) Time-integrated photoluminescence spectra (normalized and shifted upward for clarity) of CdS nanobelts from 300 K to 77 K using 470 nm excitation (150 fs, 1 kHz, 10 μ W). The blue stars indicate the positions where the time-resolved photoluminescence dynamics shown in (b) were extracted. (b) Normalized transient photoluminescence decay dynamics from 300 K to 77 K. The solid curves correspond to the bi-exponential decay function fittings. (c) The temperature dependence of the decay lifetimes τ_1 , τ_2 extracted from (b). (d) The

lifetime analysis as a function of temperature. The grey solid curve is the fitting result based on equation (6-21) above 150 K.

Fundamental absorption

The absorption at the band tail is crucial to evaluate the upconversion and laser cooling of semiconductors. At the single nanobelt level, the direct measurement of optical absorption remains elusive. We therefore devised a photoconductivity measurement to provide a direct quantification of the absorption⁷¹. The photocurrent and gain spectra of a typical CdS with a thickness of 96 nm nanobelt device at room temperature are shown in Figure 6-11a. In our photoconductivity gain measurements, we obtained $G(532 \text{ nm}) = 0.04 \times G(480 \text{ nm}) = 2.0$ based on the gain spectra as shown in Figure 6-11a. Considering the gain $G(\nu)$ is proportional to the optical density (*i.e.*, the optical absorption coefficient times the optical path $\alpha(\nu)t$, where t is the thickness of the nanobelt). If we consider $\alpha(480 \text{ nm}) = 8 \times 10^5 \text{ cm}^{-1}$ ⁹³, we obtained $\alpha(532 \text{ nm}) = 3 \times 10^4 \text{ cm}^{-1}$. This value is in good agreement with the reported value^{26,93,261}. Therefore, we obtain $\alpha(\nu)t = 0.15 \times G(\nu)$, where $t = 100 \text{ nm}$ and $G(\nu)$ is a dimensionless variable. It demonstrates the photoconductivity gain is an accurate method to measure absorption of the single nanostructure around room temperature.

Figure 6-11 Quantifying the optical absorption at the individual nanobelt level. (a) The AC photocurrent (red, right axis) and gain (blue, left axis) spectra of a typical single CdS nanobelt with a thickness of 96 nm taken at room temperature. The applied source-drain voltage is 2 V. (b) The photoconductivity gain (green) and calculated

absorption spectra from the photoluminescence spectrum (blue) by van Roosbroeck-Shockley relation (red) at room temperature.

Another indirect approach is to calculate the absorption rate from the spontaneous emission rate based on van Roosbroeck-Shockley relationship¹⁰, which is derived from the principle of detailed balance, *i.e.*, the spontaneous emission rate is equal to the absorption rate under the thermal equilibrium. The van Roosbroeck-Shockley relationship can be expressed by¹⁰,

$$R(\omega) = \frac{\alpha(\hbar\omega)(\kappa\hbar\omega)^2}{(\pi c)^2 \hbar^3 \left[\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1 \right]} \quad (6-25),$$

where $R(\omega)$ is the spontaneous emission rate, $\alpha(\hbar\omega)$ is the absorption coefficient, κ is the refractive index, $\hbar\omega$ is the photon energy and $k_B T$ is the thermal energy. Figure 6-11b displays the photoconductivity gain (blue), which is a direct evaluation of absorption under low excitation power and low transverse electric field, and the absorption rate evaluated by the van Roosbroeck-Shockley relationship based on equation (6-25) (red). The photoluminescence spectrum is given as a reference. Both methods (*i.e.*, direct photoconductivity measurement and indirect transformation from equation (6-25) gave similar optical absorption edge, indicating the validity of using photoconductivity gain to assess the optical absorption of the individual nanobelts.

Background absorption

Background absorption generates heat through converting the incident photon energy, thus it is detrimental to the laser cooling. In our cooling experiments, the background absorption has two contributions: defects or surface recombination and free carrier absorption.

In the large upconversion energy ($\Delta E = \hbar\bar{\nu}_f - \hbar\nu$) case (for instance, 532 nm pumping for a CdS nanobelt), the excitation moves into the Urbach tail region. Therefore the free-carrier absorption can no longer be ignored.²³⁵ In this situation, we require that $C \geq \sigma_{fca} \eta_e B / \alpha(\nu)$ to ensure that the free carrier losses are negligible²³⁵.

For CdS, $\sigma_{fca} \approx 10^{-23} \text{ m}^2$, $B \approx 10^{-17} \text{ m}^3 / \text{s}$, $C \approx 10^{-42} \text{ m}^6 / \text{s}$ and

$\alpha(532 \text{ nm}) \approx 10^4 \text{ cm}^{-1}$ ^{26,93,261}, and we can then obtain $\frac{C}{\sigma_{fca} \eta_e B / \alpha(v)} \geq 10^2$ for $\eta_e \leq 1$.

Therefore, the free-carrier absorption is negligible for 532 nm excitation. Besides, the nearly zero dark current in a DC I-V sweep (Figure 6-12) suggests that the nanobelts have very high crystalline quality with a low carrier concentration without photon irradiation, which also shows that the free carrier absorption should be quite small since free carrier absorption is proportional to the carrier concentration (expression (6-8)).

Figure 6-12 The I-V characteristics of a CdS nanobelt device in the dark and with light illumination of 475 nm at room temperature. The current resolution is ~ pA. The dark current is approximately zero. With 475 nm illumination, the nanobelt exhibits a conductance of ~ 20 nS. Inset: SEM image of a typical CdS nanobelt device. The channel width is 1 μm .

The other major background absorption stems from the surface recombination and defects emission located below pumping laser energy. Those surface recombination and low energy defects emission will significantly lead to the laser heating effects. In our cooling sample, we did not observe any emission on the lower energy side of 532 nm, suggesting no contribution to background absorption due to defects or surface recombination.

Based on the above discussion, we can safely draw the conclusion that the background absorption of the CdS nanobelt used here with a thickness of 100 nm can be neglected and thus the absorption coefficient can be approximately taken to be unity.

Estimation of the Cooling Efficiency

Following the equation (6-1), the external quantum efficiency must meet the condition $\eta_{exe} > \frac{\nu}{\bar{\nu}_f} \left[1 + \frac{\alpha_b}{\alpha(\nu)} \right]$ to achieve laser cooling ($\eta_c > 0$), where α_b is the background absorption. As we discussed above, α_b is negligible in our experiments because the nanobelt is suspended, is optical thin, and has high crystalline quality with negligible free carrier, surface and low energy defects absorption. Based on the upconversion energy difference ΔE as plotted in Figure 6-6 in the Chapter 5, we can evaluate the minimum external quantum efficiency required for net cooling which is $\eta_{exe} = 98\%$ for $\Delta E = 53$ meV (corresponding to pumping by a 514 nm laser at 200 K) and $\eta_{exe} = 93\%$ for $\Delta E = 173$ meV (corresponding to pumping by a 532 nm laser at 180 K), suggesting a relaxation of the external quantum efficiency requirement if a large ΔE is achievable.

Next we evaluate the cooling efficiency at 290 K and 100 K using the cooling data shown in Figure 6-8. The mean wavelength of the anti-Stokes photoluminescence is 506 nm and 520 nm for 290 K and 100 K, respectively. Following equation (6-1) and taking $\eta_{exe} \approx 99.5\%$ (for $\eta_e = 50\%$), $\eta_{abs} = 100\%$ (no background absorption in suspended sample), we obtain $\eta_c = 4.6\%$ for 290 K and $\eta_c = 1.8\%$ for 100 K, respectively. If we suppose the cooling region of the optically thin nanobelt cannot trap the emitted photons, i.e. $\eta_{exe} \approx 99.7\%$ (for $\eta_e = 100\%$), we obtain $\eta_c = 4.8\%$ for 290 K and $\eta_c = 2.0\%$ for 100 K, respectively. While for 514 nm pumping at 290 K, we obtain a cooling efficiency $\eta_c = 1.3\%$.

Analysis of the Cooling Power and Thermal Load

Starting from expression (6-1), the cooling efficiency can be further written as

$$\eta_c(h\nu, T) = \frac{\alpha(\nu, T)tP_0 \left[\eta_{exe}\eta_{abs}h\bar{\nu}_f(T) - h\nu \right]}{\alpha(\nu, T)tP_0h\nu} \quad (6-26),$$

where P_0 is the power of the incident laser and t is the thickness of the nanobelt. The cooling power can be defined as:

$$P_{cool} = \eta_c \alpha(\nu, T) t P_0 = \frac{\alpha(\nu, T) t P_0 [\eta_{exe} \eta_{abs} h \bar{\nu}_f(T) - h\nu]}{h\nu} \quad (6-27).$$

Considering the nanobelt used with a thickness of 100 nm, we have obtained a high external quantum efficiency ($\eta_{exe} \approx 99.5\%$) for the optically thin nanobelts, and zero background absorption ($\alpha_b = 0$, thus $\eta_{abs}(\nu, T) = \alpha(\nu, T) / [\alpha(\nu, T) + \alpha_b] = 1$) for the suspended sample configuration. Therefore, by taking $\eta_{exe} = 100\%$ and $\eta_{abs}(\nu, T) = 1$, the equation (6-24) can be re-written as:

$$\eta_c(h\nu, T) = \frac{\alpha(\nu, T) t P_0 [h \bar{\nu}_f(T) - h\nu]}{\alpha(\nu, T) t P_0 h\nu} = \frac{\alpha(\nu, T) t P_0 \Delta E}{\alpha(\nu, T) t P_0 h\nu} \quad (6-28).$$

This expression is the same as the expression of cooling efficiency in an ideal situation^{52,235}. The cooling power can be further simplified as

$$P_{cool} = \alpha(\nu, T) t P_0 \Delta E / h\nu \quad (6-29).$$

Based on $\alpha(532 \text{ nm}) = 3 \times 10^4 \text{ cm}^{-1}$, and 100 nm thickness of nanobelt, we obtained the cooling power $P_{cool} \approx 97 \text{ } \mu\text{W}$ for -20 K cooling pumped by 6.3 mW 532 nm laser starting from 290 K. For 514 nm pumping, the $\alpha(514 \text{ nm}) = 1.8 \times 10^5 \text{ cm}^{-1}$, the corresponding cooling power is $\sim 197 \text{ } \mu\text{W}$. From the above analysis, it is important to note that high cooling efficiency does not necessarily lead to high cooling power, as the final cooling power depends on both energy blue shifting parameter and bandtail absorption.

For our experimental setup, the thermal dissipation consists of two contributions: one is the radiative load, and the other one is the thermal conductive contribution from the substrate heat sink. For the radiative load, If the sample radiates as a black body, the radiative power obeys the following relationship⁵²:

$$P_{rad} = \sigma A (T_C^4 - T_S^4) \quad (6-30),$$

where $\sigma = 5.7 \times 10^{-8} \text{ W} \cdot \text{m}^{-2} \text{ K}^{-1}$ is the Stefan-Boltzmann constant, A is the surface area of the cooling zone (equal to the area of laser spot, $4 \text{ } \mu\text{m}^2$), T_C is the chamber

temperature and T_s is the sample temperature of the cooling location. Therefore, we estimated $P_{rad} = 0.4$ nW for -20 K cooling pumped by 6.3 mW 532 nm laser starting from 290 K. It is much smaller than the cooling power $P_{cool} \approx 97$ μ W. Therefore, the radiative load is negligible in our cooling setup.

For the thermal conductive load, the conducted power has the relation as follows:

$$P_{cond} = k(T_c - T_s) \cdot S / \Delta L \quad (6-31),$$

where k is the thermal conductivity of CdS ($k = 20$ W $\cdot$ m $^{-1}$ K $^{-1}$)⁹³, ΔT is the temperature difference between local cooling point and heat sink of substrate, S (~ 0.2 μ m 2) is the cross-section area of CdS nanobelt and ΔL (~ 1 μ m) is the length between laser spot to the edge of SiO $_2$ hole. Therefore, we estimated $P_{cond} = 80$ μ W for -20 K cooling pumped by 6.3 mW 532 nm laser starting from 290 K. This value is very close to the calculated cooling power $P_{cool} \approx 97$ μ W. Conclusively, we believe the thermal conductive load dominates the in our experimental setup.

At room temperature and under small applied source-drain voltage, the gain of the photoconductivity $G(v)$ is proportional to the absorption coefficient, $\alpha(v)t = KG(v)$, where $K = 0.15$ for $t = 100$ nm nanobelt. In the low temperature region, *i.e.*, $k_B T < \min\{E_{DAP}^{bound}, E_{exciton}^{bound}\}$, where E_{DAP}^{bound} , $E_{exciton}^{bound}$ corresponds to the binding energy of DAP and the exciton, the equation $\alpha(v) = KG(v)$ is no longer valid because the bound excitons cannot be completely ionized, therefore we can no longer evaluate the absorption coefficient from the photoconductivity gain. Hence, absorption of a photon may lead to the formation of an exciton. However, the photon will not necessarily contribute to the photocurrent unless this exciton is ionized. Nevertheless, in CdS nanobelts, the excitons are usually completely ionized at room temperature⁹³. By using photoconductivity spectroscopy, we obtain the $G(v)$ for an individual nanobelt at 290 K. Therefore, the *normalized temperature change* $\Delta T/P_0$ can be written as:

$$\frac{\Delta T}{P_0} \equiv \frac{T_s - T_c}{P_0} = -\frac{\zeta K \Delta L}{k S h \nu} G(v, T_c) \Delta E \equiv \frac{-\chi \cdot G(v, T_c) \Delta E}{h \nu} \quad (6-32),$$

where $\chi = \frac{\varsigma K \Delta L}{kS}$ and ς is the correction parameter. For the different pump energies and low excitation powers, the mean emission wavelength of the luminescence is approximately equal to a constant. For ~100 nm CdS nanobelts, the mean wavelength of the luminescence is ~506 nm at 290 K. For a 532 nm laser with a power of 6.3 mW, $\Delta T = -20$ K which gives $\varsigma = 0.82$ and $\chi = 30.8 \text{ K} \cdot \text{mW}^{-1}$. Applying the obtained χ to equation (6-32), the calculated *normalized temperature change* can be obtained.

Figure 6-13a displays the Stokes photoluminescence (black curve) and the corresponding photoconductivity gain spectra (blue curve, and red curve in logarithmic scale) of a 100 nm thick belt at 290 K. We find that at 532 nm, there is about 6% absorption compared to the maximum absorption around 480 nm, while at 514 nm, this value is ~ 36%. Based on expression (6-32), Figure 6-13b shows the normalized temperature change as a dependence on pumping laser wavelength at 290 K (blue curve). The pink squares are the measured cooling temperature change normalized to pump laser power under different excitation wavelengths. Here, $\Delta T/P_0 < 0$ corresponds to the cooling zone and $\Delta T/P_0 > 0$ indicates the heating zone. When the pump laser energy is equal to the mean energy of luminescence, the heating and cooling cancel each other and result in with a vanishing $\Delta T/P_0$. The experimental temperature change ΔT in K/mW pumped by four different laser lines is in good agreement with theoretical analysis except for 488 nm. The final cooling power depends on both ΔE and bandtail absorption. In CdS nanobelts at 290 K, 514 nm appears as the optimal cooling wavelength with the highest cooling power. The red region corresponds to the laser cooling tail.

Figure 6-13 (a) Photoconductivity gain spectra (blue curve), log(Gain) (red curve) and Stokes photoluminescence spectra (black curve) of a single CdS nanobelt device at

290 K. (b) Summary of measured maximum ΔT (pink square) and theoretically calculated temperature change curve (solid blue) normalized to pump power in K/mW for different pump wavelengths at 290 K. The red region corresponds to the cooling zone.

The large deviation between the experimental data and the theoretic result for 488 nm pumping probably originates from the current measurement method, which underestimates the actual heating. It should be noted that our temperature change measurement is not a real-time measurement. In our PPLT measurement, a probe beam is turned on immediately after the pump beam is turned off, nonetheless it takes $\sim$ one minute to collect the Stokes photoluminescence spectrum. Larger temperature difference (ΔT), *e.g.*, at 488 nm pumping, means larger thermal conduction power (equation (6-31)). As a result the measured temperature will be lower than the actual temperature during pumping, which is the solid curve (Figure 6-13 b) according to our model discussion in this section.

6.3.4 Summary

We have demonstrated for the first time a substantial net laser cooling of a semiconductor CdS nanobelt by ~ 40 K from room temperature pumped by 514 nm, while ~ 15 K from 100 K pumped by 532 nm. A cooling efficiency of $\sim 4.8\%$ at 290 K and $\sim 2.0\%$ at 100 K is estimated for 532 nm pumping, while a cooling efficiency of 1.3% for 514 nm pumping at 290 K. The cooling power is estimated to be ~ 97 and $180 \mu\text{W}$ for 532 nm and 514 nm pumping at 290 K, respectively, with the corresponding thermal conductive load to be about 80 and $160 \mu\text{W}$, in good agreement with the cooling power. The radiative load is negligible based on a black body model for both wavelengths, suggesting that the thermal conductive load dominates the heat dissipation.

The achievement of the net laser cooling in CdS nanobelts can be attributed to the strong electron-phonon interaction, high external quantum efficiency and negligible background absorption. In GaAs-based semiconductors, both high parasitic background absorption and low luminescence extraction efficiency lead to heating and prevent the observation of net laser cooling^{46,48,235}. In CdS nanobelts, benefiting from the extremely strong exciton-LO phonon coupling (the Fröhlich coupling

constant in bulk is 0.51 for CdS and 0.07 for GaAs²⁶², this coupling is even stronger in nanoscale as shown in the last Chapter), each cooling cycle can remove more heat than in GaAs due to the larger obtained energy difference ΔE under resonant conduction. High crystalline quality of the CdS nanobelts grants the negligible free carrier absorption and no background absorption contribution due to the defects or surface recombination, which is further proved by the absence of emission on the lower energy side of 532 nm. The luminescence extraction efficiency approaches unity because of sub-wavelength thickness based on the geometrical analysis. Compared to GaAs, CdS has a much smaller surface recombination speed²⁵⁹ and a much lower Auger non-radiative recombination coefficient due to a larger bandgap¹⁷⁹. Our previous data²⁵⁵ and more in-depth analysis above justify the nearly unity external quantum efficiency of >99% in CdS nanobelts.

6.4 Pumping power dependence of laser cooling

Figure 6-14 Power dependence of laser cooling/heating temperature starting from 290 K and 100 K, respectively, for 532 nm pumping. (a) Laser cooling effect at an optimal pumping of 7 mW by 532 nm laser at 290 K. (b) When the pump laser power is increased to 17 mW, pronounced heating effect is observed manifested by the red-shifting of the peak. This belt was damaged after 10 minutes at this power, therefore

only two traces were collected. (c) and (d) The corresponding results at 100 K. At 7 mW, cooling was observed, while at 17 mW, heating is introduced. (e) Summary of laser induced temperature change as a power dependence at two different temperatures (290 and 100 K) pumped by 532 nm. Optimal pumping power to achieve the largest cooling is around 7 mW.

The laser cooling of CdS nanobelts is highly dependent on laser power. The anti-Stokes photoluminescence intensity scale linearly versus laser power for both 532 and 514 nm excitation up to approximately 12 mW as previously discussed. This suggests that in *moderate and low* laser power, the upconversion is not due to a two-photon absorption process. However, when the laser power increases further, two-photon absorption starts to play a role, manifesting as a quadratic increasing of photoluminescence intensity versus laser power. Therefore, all the laser cooling experiments are achieved under moderate power laser pumping ~7 mW. To illustrate how the laser cooling depends on pump power, we have conducted a series power dependence experiments at 290 K and 100 K, at which our laser cooling was demonstrated. As shown in Figure 6-14a, when the 532 nm laser power is 7 mW, laser cooling is achieved as seen from the anti-Stokes photoluminescence peak evolution. While when the laser power is 17 mW (Figure 6-14b), laser induced heating (red shift of photoluminescence) is observed. In fact, at such a high laser power, the nanobelt was structurally damaged. At 100 K, similar trend was also observed, *i.e.*, laser cooling was achieved at 7 mW (Figure 6-14c), while at 17 mW only laser heating was observed (Figure 6-14d). At 100 K, the nanobelt can sustain higher laser power compared to 290 K, so after the laser is turned off, we can observe that the photoluminescence recovers (Figure 6-14d). The laser cooling effect as a dependence on laser power for 532 nm pumping was summarized in Figure 6-14e. Below ~12mW, laser cooling is likely to be achieved. Similar trend is also applied to 514 nm pumping. Therefore for our laser cooling demonstration, the pump laser power was kept at optimum around 7 mW. Therefore, we can safely conclude that under the laser cooling parameters we used, the power is optimized to exclude laser induced heating and two-photon pumping processes.

6.5 Thickness dependence of laser cooling

It is expected that the laser cooling of CdS nanobelts depends on the thickness of nanobelts since energy difference ΔE , external quantum efficiency η_{ex} and absorption coefficient $\alpha(\nu, T)$ or photoconductivity gain $G(\nu, T)$ are thickness dependent. As discussed in Chapter 4, the surface depletion induced confinement beyond the quantum confinement regime would lead to the shifting of the band edge resulting in the thickness dependent energy difference for a fixed pumping wavelength and the thickness dependent photoconductivity gain at a certain wavelength. The external quantum efficiency relies on the thickness of nanobelts mainly due to the larger surface nonradiative recombination for nanobelts with smaller thickness and the reabsorption for thick nanobelts. In this section, the thickness dependent cooling power and normalized temperature change will be discussed.

The thickness dependent normalized photoconductivity gain is shown in Figure 6-15a. One can see that the band edge gradually shifts to the higher energy side and the band tail becomes shorter and shorter as the thickness of the nanobelts decreases. To clearly see the band tail region, we re-plot the band tail region in the logarithm scale as shown in Figure 6-15b, which indicates that there is no absorption at all at 2.33 eV (corresponding to a wavelength of 532 nm) for those nanobelts with thicknesses below 65 nm as a consequence of the surface depletion induced confinement. Therefore, we can foresee that it is impossible to achieve net laser cooling on the CdS nanobelts with thicknesses below 65 nm.

As previously discussed, the absorption coefficient relates to the photoconductivity gain at room temperature via $\alpha(\nu)t = KG(\nu)$. It is expected that K should be different from belt to belt due to the variation of the channel length and the belt width. Here we determine K for each belt investigated from the absorption coefficient at a certain wavelength, *e.g.* 480 nm, far above the band edge region. We assume that for all thickness nanobelts we investigated the absorption coefficient is same far above the band edge, which is reasonable since the surface depletion only poses influence on the band edge region. Therefore, we take the absorption coefficient

at 480 nm as $\alpha(480 \text{ nm}) = 8 \times 10^4 \text{ cm}^{-1}$ and then obtain K for each nanobelt used for calculation later.

Figure 6-15 (a) The thickness dependent photoconductivity gain at room temperature. To compare them, all spectra are normalized by their corresponding maximum value. (b) To clearly see the band tail region, the band tail region of (a) is plotted again in the logarithm scale.

Figure 6-16 (a) The thickness dependent energy different ΔE at room temperature for a 7 mW 532 nm laser pumping. (b) The calculated thickness dependent external quantum coefficient η_{exe} at room temperature based on equation (6-36).

The thickness dependent energy different ΔE at room temperature for a 7 mW 532 nm laser pumping is shown in Figure 6-15a, which is extracted from the thickness dependent mean emission wavelength as given in Chapter 5. The trend of the energy difference ΔE with the thickness in Figure 6-15a can be attributed to the surface

depletion induced confinement and the surface nonradiative recombination induced heating effect.

The thickness dependent external quantum coefficient η_{exe} at room temperature cannot be directly obtained from experiments here. Nevertheless, we can obtain the external quantum efficiency by applying the theoretical model. Starting from the expression (6-21) by taking the first derivative of the external quantum efficiency with respect to the e-h population density N , the optimum e-h population density N_{opt} for the maximum external quantum efficiency can be determined

$$\frac{d\eta_{exe}}{dN} = 0 \Rightarrow N_{opt} = \sqrt{\frac{A}{C}} \quad (6-33).$$

By inserting the N_{opt} into the expression (6-21), finally we get the external quantum efficiency at the e-h population density N_{opt}

$$\eta_{exe}(N_{opt}) = 1 - 2 \frac{\sqrt{AC}}{\eta_e B} \quad (6-34).$$

In this expression, only the nonradiative recombination coefficient A and the luminescence extraction efficiency η_e depends on the thickness. As previously discussed, the surface nonradiative recombination A_s dominates the coefficient A . While the luminescence extraction efficiency η_e can be formulated as

$$\eta_e = \eta_0 \exp(-\alpha_{eff} t) \quad (6-35).$$

Inserting the expression (6-15) and (6-35) into (6-34), the external quantum efficiency at the e-h population density N_{opt} can be rewritten as

$$\eta_{exe} = 1 - 2 \frac{\sqrt{2SC}}{\sqrt{d} B \eta_0 \exp(-\alpha_{eff} t)} \quad (6-36).$$

Since we used a 7 mW 532 nm pumping laser which has been proved as the optimum excitation power in the section 6.4, the expression (6-36) can be applied to calculate the external quantum efficiency. By taking $B=10^{-11} \text{ cm}^3/\text{s}$, $C=10^{-30} \text{ cm}^6/\text{s}$, $S=250 \text{ cm/s}$, $\alpha_{eff}=4.6 \mu\text{m}^{-1}$ and $\eta_0=0.996$, the thickness dependent external quantum efficiency can be obtained as given in Figure 6-16b. The reason taking $\alpha_{eff}=4.6 \mu\text{m}^{-1}$ and $\eta_0=0.998$ is to match the experimental result that the external quantum efficiency for the 110 nm

CdS nanobelt is 0.996. Besides, $\alpha_{eff}=4.6 \mu m^{-1}$ corresponds to the absorption coefficient at around 520 nm, which falls into the band tail range⁹³.

As seen from Figure 6-16b, the external quantum efficiency increases first and reaches a maximum value of around 99.6% around 110 nm. Below 110 nm, the external quantum efficiency decrease again due to the large surface nonradiative recombination in the thinner nanobelt. The decrease of the external quantum efficiency in the thick nanobelt is due to the reabsorption effect which starts to play a role for those belts with thicknesses larger than 100 nm. It should be noted that the external quantum efficiency only changes around one percentage when the thickness decreases from 110 nm to 30 nm due to the small surface recombination velocity $S=250 \text{ cm/s}$ in CdS.

Figure 6-17 The calculated thickness dependent cooling power (a) based on equation (6-27) and normalized temperature change (b) based on equation (6-37) for a 7 mW 532 nm laser pumping at room temperature.

Once the thickness dependent gain, energy difference and external quantum efficiency are obtained, the cooling power as a function of nanobelt thickness can be calculated based on the equation (6-27) as shown in Figure 6-17a. Here the absorption efficiency is still taken as unity for all thickness nanobelts as well since both the defects or surface related emission and the free carrier absorption are thickness independent. One can see that the cooling power is strongly thickness dependent. As the thickness decreases, the wavelength for the maximum cooling power shows a blueshift for those belts with thicknesses larger than 65 nm. The maximum cooling power increases first and reaches a maximum value around 110 nm. Below 110 nm,

the maximum cooling power decreases again and finally approaches zero below 65 nm.

To directly relate the experimental results, the normalized temperature change is a better quantity. For the normalized temperature change calculation here, the expression (6-27) cannot be applied due to the non-unity external quantum efficiency. Starting from expression (6-27) and (6-31), the normalized temperature change for arbitrary external quantum efficiency and absorption efficiency can be obtained as

$$\frac{\Delta T}{P_0} = \frac{KG(\nu, T)P_0 [\eta_{exe}\eta_{abs}h\nu_f(T) - h\nu]}{h\nu kS} \quad (6-37).$$

The calculated normalized temperature change is given in Figure 6-17b based on the expression (6-37). The maximum normalized temperature change shows the same trend as the cooling power with thickness. The net laser cooling is impossible on those nanobelts with thickness below 65 nm.

Figure 6-18 The thickness dependent normalized temperature change for a 7 mW 532 nm laser pumping starting at room temperature. The red dots represent the experimental data and the blue circles and green squares denote the calculated results with two different thermal conductivity k .

To verify the calculated results, the laser cooling of CdS nanobelts with different thickness was carried out by adopting PPLT method as discussed in section 6.2. The pumping laser used here is a 7 mW 532 nm green laser. The normalized temperature change was extracted for various thickness belts as shown in Figure 6-18 (red dots). It is found that there is no net cooling below 65 nm. As the thickness of

nanobelts increases, the normalized temperature change increases first and a maximum normalized temperature change appears at around 110 nm. Above 110 nm, the normalized temperature change decreases again with further increasing the thickness. To sum up, we found that nanobelts with a thickness around 80-120 nm showed efficient cooling. In thicker nanobelts, re-absorption effect starts to play a role leading to a red-shift of the mean emission wavelength.

We have extracted the calculated results from Figure 6-17b by taking two different thermal conductivities: $k = 20 \text{ W} \cdot \text{m}^{-1} \text{K}^{-1}$ (green squares in Figure 6-18) and $k = 5.4 \text{ W} \cdot \text{m}^{-1} \text{K}^{-1}$ (blue circles in Figure 6-18). The blue circles agree better with the experimental data since the thermal conductivity reduces at nanoscale. The thermal conductivity $k = 5.4 \text{ W} \cdot \text{m}^{-1} \text{K}^{-1}$ falls into the range previously reported²⁶³.

Based on the previous analysis of gain and external quantum efficiency, no net cooling for those belts with thicknesses below 65 nm is mainly due to the nearly zero absorption at 532 nm rather than the small external quantum efficiency induced by the large surface nonradiative recombination in the thinner nanobelts during 532 nm laser pumping. Above 110 nm, both the reduction of the energy difference and the decrease of the external quantum efficiency due to the reabsorption contribute to the decrease of the normalized cooling temperature.

6.6 Summary

A PPLT technique based on the temperature dependent bandgap shift was developed to measure the local temperature change during the laser cooling of the CdS nanobelts. The net cooling was observed for both 532 nm and 514 nm pumping at room temperature while only 532 nm pumping starting from 100 K can lead to the net cooling. For 502 nm and 488 nm pumping, heating effect was observed at all temperatures investigated. The estimated cooling efficiency and cooling power for 514 nm pumping at room temperature are 1.3 per cent and 180 μW , respectively. At 100 K, the 532 nm laser pumping leads to a cooling efficiency of around 2 per cent. The thermal analysis reveals that the thermal conduction via substrate dominates the heat dissipation and the block body radiation can be neglected.

The pumping power dependence of the laser cooling has been investigated. For both 532 nm and 514 nm pumping, the optimum pumping power seems to be around 7 mW. No net laser cooling can be achieved above 12 mW because the two photon absorption starts to play an important role which will result in the heating effect.

The thickness dependence of laser cooling is important since it can provide information for selecting proper thickness nanobelts to achieve the largest cooling temperature. The laser cooling of different thickness CdS nanobelts was carried out pumping by a 532 nm laser with an optimum power of 7 mW. It is found that the optimum thickness for the laser cooling is around 110 nm. Above 110 nm, the decrease of the energy difference and the external quantum efficiency give rise to a reduction of the cooling temperature as the thickness increases. The increase of the surface nonradiative recombination and the decrease of absorption coefficient at band tail leads to the decreases of the cooling temperature below 110 nm. Due to the zero band tail absorption below 65 nm, no net cooling can be achieved on those belts with thicknesses smaller than 65 nm.

The accomplishment of the net laser cooling in CdS nanobelts can be attributed to the strong coupling between electron and longitudinal optical phonons, high external quantum efficiency and negligible background absorption. In principle, the thermal conductive load can be further minimized by device engineering to facilitate the laser cooling of CdS nanobelts from ambient to liquid nitrogen temperature. Our work opens up the new territory of designing materials for the laser cooling of semiconductors with strong electron-LO phonon coupling. Our work also makes one step closer to the optical refrigeration based on semiconductors. It would be an immediate advance to search other II-VI materials in the single crystal, thin film or nanomaterial morphologies for laser cooling.

Chapter 7 All Solid-State Semiconductor Cryocoolers

In this Chapter, we demonstrate the concept of all-solid-state optical refrigerator based upon a CdS nanobelt, which is in good thermal contact with a patterned silicon-on-insulator (SOI) substrate. The top crystalline Si layer in a SOI substrate provides the thermal load, and simultaneously the ratio of Si Stokes and anti-Stokes Raman signal of the crystalline Si layer can be used as a local thermometry to detect the temperature variation upon laser cooling.

7.1 Introduction

In Chapter 6, the laser cooling of semiconductor CdS nanobelts themselves has been successfully demonstrated for the first time starting from both 290 K and 100 K⁴¹. However, from the application perspective, the laser cooling of another thermal load by coupling with CdS nanobelts is more appealing, which is exactly the concept of all-solid-state optical refrigerator⁴⁵. The laser cooling of a thermal load GaAs to 165 K by using Yb: YLF has been realized⁵⁶ and later to 110 K has reported from ambient temperature⁴⁹. However, the all-solid-state cryocoolers based on semiconductors remains elusive due to the difficulty of achieving the net laser cooling of semiconductors. Immediately after our demonstration of the laser cooling of CdS nanobelts, we started to think the design and implementation of a semiconductor all-solid-state cryocoolers. In fact, our laser cooling data on CdS nanobelt already suggested heat exchange between the CdS nanobelt and the surrounding substrate from the large time constant ~ 30 minutes. Here, we demonstrate that the temperature of the Si layer beneath the CdS nanobelt decreases by 20 K and 30 K starting from 290 K under a 3.8 mW 514 nm and a 4.4 mW 532 nm pumping, respectively. In contrast, heating effect has been observed pumped by 502 nm and 488 nm lasers. During the probing time, the pumping laser is off. As a result, heat dissipation via substrate leads to a smaller cooling temperature for the cooling of SOI substrate compared with the results from the laser cooling of CdS itself carried out on the suspended segment as discussed in Chapter 6.

Figure 7-1 Photoconductivity gain spectra (blue curve), $\log(\text{Gain})$ (red curve) and Stokes photoluminescence spectra (gray curve) of a single CdS nanobelt with a thickness of around 100 nm at 290 K.

As we discussed in Chapter 6, the cooling power depends on the mean emission wavelength, the absorption coefficient at the pump wavelength and the external quantum efficiency, all of which are thickness dependent. As a consequence, the range of the pumping wavelength probably enabling to achieve the net laser cooling varies with the thickness of the nanobelts. It is necessary to estimate the range based on the anti-Stokes photoluminescence and photoconductivity spectra before performing the laser cooling experiments. Figure 7-1 displays the photoluminescence (gray curve) and the corresponding photoconductivity spectra (blue and red in logarithmic scale) of a CdS nanobelt with a thickness around 100 nm at 290 K. The band tail of the photoconductivity spectrum extends to 540 nm, which is much longer than the mean emission wavelength around 507 nm. This indicates that the net cooling is possible when the pump laser wavelength ranges from 508 nm to 540 nm as indicated by the black arrow.

7.2 Temperature calibration

The local temperature change of the Si layer beneath the CdS nanobelt is deduced from the intensity ratio of the Stokes and anti-Stokes Raman signals. The phonon population follows the Bose-Einstein statistics. The intensity ratio of the Stokes to anti-Stokes Raman signals depends on the phonon population and is thus temperature dependent following the expression^{264,265}

$$\frac{I_{Stokes}}{I_{anti-Stokes}} = A \exp\left(\frac{h\omega_0}{k_B T}\right) \quad (7-1),$$

where I_{Stokes} and $I_{anti-Stokes}$ are Stokes and anti-Stokes Raman intensities, $h\omega_0$ is the phonon energy, A is a parameter depending on the materials and wavelength, and $k_B T$ is the thermal energy at the temperature of interest. This exponential dependence can be used as a very sensitive local thermometry, given that the anti-Stokes Raman signal is still measurable. For Si in this experiment, we find that anti-Stokes Raman signal becomes very weak below 140 K. Therefore, our method is no longer applicable to determine the temperature below ~ 140 K.

The calibration curve should be first obtained in order to deduce the temperature variation during the laser cooling experiments. The Stokes and anti-Stokes evolution with temperature from the Si layer upon a 4.4 mW 532 nm laser irradiation is given in Figure 7-2a. As the temperature decreases, the ratio of the Stokes and anti-Stokes Raman signal continually decreases, as plotted in Figure 7-2b. By applying equation (7-1), the fitting curve and parameters are given in Figure 7-2b as well, giving a phenomenological calibration equation as:

$$\frac{I_{Stokes}}{I_{anti-Stokes}} = 0.517 \exp\left(\frac{739}{T}\right) \quad (7-2a).$$

Figure 7-2 (a) The temperature-dependent intensities of the Stokes and anti-Stokes Raman from Si top layer in the SOI substrate excited by a 532 nm laser with a power of 4.4 mW. The spectra are vertically offset for clarity. (b) The intensity ratio of the

Stokes and anti-Stokes Raman signal extracted from (a) (blue dots). The red curve is a fitting according to equation (7-2a) with the fitting parameters denoted in the Figure.

Figure 7-3 The ratio of the intensity of Stokes and anti-Stokes from Si layer on the top of SOI substrate at 290 K. The excitation power is kept as low as 100 μ W in order to diminish the laser heating effect.

Alternatively, we have determined the parameter A in equation (7-1) by repeatedly measured the ratio of the intensities of the Stokes and anti-Stokes of Si layer excited by a 532 nm laser with a power of 100 μ W at 290 K as shown in Figure 7-3. By using the ratio of the intensities and taking the Si first-order transverse optical (TO) phonon energy $\hbar\omega_0 = 65 \text{ meV}$, the calibration equation can be obtained, which can be expressed as

$$\frac{I_{Stokes}}{I_{anti-Stokes}} = 0.489 \exp\left(\frac{754}{T}\right) \quad (7-2b).$$

Therefore, the local temperature can be deduced from the equation (7-2a) or (7-2b). Although the parameter A is determined at room temperature, this calibration equation (7-2b) should still hold at a lower temperature due to the temperature independence of parameter A and the weak temperature dependent phonon energy $\hbar\omega_0$. To eliminate the probe beam heating effect, the equation (7-2b) is used to deduce the temperature

change of the Si during the laser cooling experiments. Nevertheless, the calibration equation (7-2a) and (7-2b) give nearly identical temperature change for the 4.4 mW 532 nm pumping within the experimental uncertainty.

7.3 Laser cooling of silicon on insulator (SOI)

7.3.1 Experimental details

The CdS nanobelts were grown in a home-built vapor transport chemical vapor deposition (CVD) system. The detailed growth conditions, morphology and crystalline characterizations can be found in Chapter 2. The cartoon presentation of the concept and the actual device image are shown in Figure 7-4a and 7-4b. The SOI substrate was patterned into grids by e-beam lithography and etched by reactive ion etching. This is to decrease the thermal conductive loss and to provide a reference without a thermal load (suspended segment). The cryocooler demonstration is conducted from the frame part, where CdS nanobelt is in good thermal contact with the crystalline Si top layer. The chip was mounted on the cold finger of a continuous flow microscopy cryostat to control the starting temperature and to keep the surrounding temperature constant. The ratio of the Stokes to anti-Stokes Raman signal from the Si top layer is used to determine the local temperature variation of the Si beneath the CdS nanobelt.

Figure 7-4 Semiconductor all-solid-state cryocoolers. (a) Cartoon presentation of the cryocoolers. (b) An false-color SEM image of an actual device consisting of a single CdS nanobelt supported on a patterned SOI substrate.

The probe beam of 532 nm is kept as low as 0.8 mW in order to minimize the cooling or heating effect from probe beam except for 532 nm pumping, when the power of the probe beam is the same as the pumping beam. The 532 nm laser is far away from the emission peak of CdS, therefore, we select it as the probe beam to eliminate the influence of emission from CdS on the Si Raman peaks. Both pump (Ar ion laser 488 nm, 502 nm and 514 nm, and Nd:YAG solid state 532 nm laser) and probe beams (532 nm laser) are collimated and focused through a 50 $\times$ objective onto a single CdS nanobelt adhered on top of the SOI substrate. All spectra are collected by a confocal triple grating spectrometer (Horiba-JY T64000) in a backscattering configuration. During the laser cooling experiments, each spectrum is taken within 5 minute interval when the pumping laser is blocked temporally except for the 532 nm laser pumping. A pump-probe luminescence thermometry (PPLT) technique is used to cool and measure the local temperature variation of CdS nanobelts suspended on the holes as well⁴¹. The details can be found in the previous chapter.

7.3.2 Results and discussions

Figure 7-5a displays the Stokes and anti-Stokes Raman spectra evolution of a Si layer beneath the CdS nanobelt upon a continuous 4 mW 532 nm laser radiation starting at 290 K. Each spectrum was taken within a 5 min interval. The local temperature change ΔT of the Si beneath the CdS nanobelt extracted from the Raman spectra (Figure7-5a) is shown in Figure7-5b versus pumping time. One can observe that the local temperature gradually decreases from 290 K and reaches an equilibrium temperature $\sim$ 270 K after $\sim$ 30 minutes. The maximum cooling effect is $\sim$ 20 K. The local temperature change ΔT against time for different pump wavelengths (532 nm, 514 nm, 502 nm and 488 nm) is plotted in Figure 7-5c. The temperature of the sample reaches a stable value after pumping $\sim$ 20-30 minutes. A net laser cooling of 20 K and 30 K is achieved for 532 nm and 514 nm pumping, while a heating effect is observed for 502 nm and 488 nm pumping, which is consistent with our previous report⁴¹. After the pump laser is stopped as indicated by red arrows in Figure 7-5c, the local temperature of Si gradually returns to the starting temperature of 290 K.

Figure 7-5 (a) The time evolution of the Stokes and anti-Stokes from Si layer on the SOI substrate with a 4.4 mW 532 nm pumping starting from 290 K. All the spectra are normalized and offset vertically for clarity. (b) The time evolution of the temperature change of Si extracted from (a). (c) The time evolution of the temperature change of Si for various pumping wavelengths (532 nm, 514 nm, 502 nm and 488 nm) starting from 290 K. The red arrows indicate the pumping lasers are switched off. (d) The theoretical calculated (solid curve) and the experimental (discrete points) results of normalized temperature change for different pumping wavelength starting from 290 K.

According to the Sheik Bahae-Epstein(SB-E) model and taking both the external quantum efficiency and absorption efficiency as unity^{45,47}, the cooling power can be expressed as

$$P_{cool} = KG(\nu, T)tP_0\Delta E / h\nu \quad (7-3),$$

where P_0 is the power of the pumping laser, t is the thickness of the nanobelt, ΔE is the energy difference between the energy of the pumping laser and the mean luminescence energy, $h\nu$ is the energy of the pumping laser and $G(\nu, T)$ is the

photoconductivity gain relating the absorption coefficient $\alpha(\nu, T)$ via $\alpha(\nu, T)t = KG(\nu, T)$, where K is a constant related to the thickness of the nanobelt and the applied source-drain voltage. The photoconductivity measurement provides an indirect way to evaluate the absorption at the temperature above 180 K, when the strong electron-longitudinal optical phonon interaction leads to the complete ionization of excitons and bound excitons^{33,41}.

In our experiments, the thermal dissipation is contributed from both the black body radiation and thermal conduction via the substrate heat sink. As discussed in our previous publication⁴¹, the thermal dissipation in our experiments dominates by the thermal conduction through the substrate heat sink while the dissipation through black body radiation can be neglected. Provided that the conducted thermal power is proportional to the temperature difference between the CdS nanobelt T_s and the substrate heat sink T_c , it can be expressed as

$$P_{cond} = -C(T_s - T_c) \quad (7-4),$$

where C is constant related to the thermal conductivity k of Si layer and the heat distribution of the substrate. After reaching thermal equilibrium, the cooling power should be equal the conducted power in idea case. Therefore, combining equation (7-3) and (7-4), the *normalized temperature change* $\Delta T/P_0$ can be expressed as

$$\frac{\Delta T}{P_0} \equiv \frac{T_s - T_c}{P_0} \equiv \frac{-Kt \cdot G(\nu, T_c) \Delta E}{Ch\nu} \quad (7-5).$$

The theoretical analysis based on the equation (7-5) is given as the red solid line in Figure 7-5d taking $\frac{Kt}{C} = 0.81$. The discrete data points in Figure 7-5d represent the experimental results of the normalized temperature change $\Delta T/P_0$ for the nanobelt used with a mean emission wavelength of 507 nm. The experimental data points agree well with the theoretical analysis except for 488 nm, when the theoretical value is too large for the thermal equilibrium between the substrate and CdS nanobelt to be established during the probe time, same as the previous report⁴¹. The region enclosed by the horizontal gray line and the red line indicates the cooling zone with 513 nm being the optimum cooling wavelength at 290 K.

Figure 7-6 (a) The time evolution of the local temperature change of Si layer and (b) the corresponding upconversion luminescence spectra from CdS nanobelt pumped by a 7.8 mW 532 nm laser starting at 290 K.

Due to the small size of the CdS nanobelts and unstable nature of the sample stage, the laser spot cannot always irradiate at the same position for a long time during the measurement. The intensity of the upconversion luminescence collected during the pumping is used to monitor whether the laser beam is irradiating on the CdS nanobelts or not and to interpret the local temperature variation of the Si layer. The time evolution of the local temperature change of Si layer and the corresponding upconversion luminescence spectra from CdS nanobelt pumped by a 7.8 mW 532 nm laser starting at 290 K are given in Figure 7-6. At the first 15 minutes, the intensity of the upconversion luminescence remains constant while the local temperature of the Si layer gradually decreases. After 15 minutes, the local temperature starts to increase. Meanwhile, the intensity of the upconversion luminescence begins to decrease indicating the laser spot shifts away from the starting position. After manually shifting the laser spot to the starting position at 35 minutes, the intensity of the upconversion luminescence returns to the starting value and the local temperature of the Si layer decreases further again. The correlation between those two plots verifies the laser cooling of the Si layer by using the CdS nanobelt.

The theoretic calculation on the laser cooling of SOI substrate by using CdS nanobelts has been performed by using the general static heat conduction module in Ansys program package. Assuming the isotropic property regarding the heat transfer in the materials during simulation, symmetry treatment can be adopted in the geometric modeling, meaning that the simulated area can be efficiently reduced to 1/4

of the original size. As shown in Figure 7-7, the laser beam hits the CdS nanobelt on a circle spot with a diameter of 2 μm . The belt is placed perpendicular to and at the center of the Si ridge, which is 4 μm wide and 2.5 μm thick. The thickness of middle layer SiO_2 is 1.5 μm . The Si ridge repeats each other with a gap of 10 μm in two directions on the middle layer SiO_2 surface and form a set of square grid. The extension of Si ridge grid and SiO_2 can be assumed infinite compared to the size of the nanobelt. For simplicity, only 4×4 squares are adopted due to symmetry treatment during simulation. In practice, there is a Si substrate on which a SiO_2 layer is deposited. Regarding the much smaller thermal conductivity of SiO_2 , the substrate can be assumed to be at the same temperature and thus be removed from the model.

Figure 7-7 Temperature distribution along the z axis line through the spot center from the up CdS surface to Si- SiO_2 interface with contact thermal conductance of $5 \times 10^6 \text{ W/m}^2 \text{ K}$ for a 4mW 532 nm laser pumping.

During the simulation, the thermal conductivity for Si and SiO_2 are taken to be $70 \text{ WK}^{-1} \text{ m}^{-1}$ ²⁶⁶ and $1.5 \text{ WK}^{-1} \text{ m}^{-1}$, respectively while $8 \text{ WK}^{-1} \text{ m}^{-1}$ for CdS nanobelts, which is half of its bulk value²⁶⁷. It is found that the thermal contact resistance plays a very important role in the heat distribution process; however, such information is not available at present. Therefore, we have tried many values and finally we have found that the contact thermal conductance of $5 \times 10^6 \text{ W/m}^2 \text{ K}$ can give an acceptable value

compared with experimental results. The calculated result is given in Figure 7-7. A sharp temperature rises appears at the interface due to the contact thermal resistance.

Figure 7-8 (a) The time evolution of the Stokes and anti-Stokes from Si layer on the SOI substrate with a 4 mW 532 nm pumping starting from 270 K. All the spectra are normalized and offset vertically for clarity. (b) The time evolution of the temperature change of Si starting at 270 K (extracted from (a)) and at 180 K. (c) The theoretical calculation of the normalized temperature change at various starting temperature above 180 K. (d) The experimental (blue discrete points) and theoretical calculated (red discrete points) temperature change at different starting temperature under a 4mW 532 nm laser pumping.

The starting temperature dependence of the laser cooling of SOI substrate is investigated for temperatures above 150 K, below which the anti-Stokes Raman signal from Si is too weak to be used as the temperature probe. According to equation (7-5), the cooling power is proportional to the absorption coefficient and the energy difference ΔE if we take the external quantum efficiency as unity. In view of the high external quantum efficiency of 99.6% at room temperature, we can take the external quantum efficiency as unity for all temperatures below room temperature based on the fact that the external quantum efficiency usually increases at lower temperatures.

Furthermore, as the temperature decreases, the emission peak blue shifts leading to a large ΔE for a fixed pumping wavelength while the absorption band tail moves far away from the fixed pumping wavelength, giving rise to a smaller absorption coefficient at the pumping wavelength. The energy difference ΔE can be experimentally obtained from the temperature dependent anti-Stokes photoluminescence spectrum while the absorption coefficient can be obtained from the temperature dependent photoconductivity gain as aforementioned. Based upon the equation (7-5) together with temperature dependent mean emission wavelength, photoconductivity gain and thermal conductivity of Si²⁶⁸, the temperature change dependence of the pumping wavelength at various starting temperature is calculated under a 532 nm pumping with a power of 4 mW as shown in Figure 7-8c assuming the Kt in equation (7-5) maintains constant for all starting temperatures.

As seen from Figure 7-8c, the optimal cooling wavelength blue shifts whereas the cooling temperature ΔT firstly increases and then decrease with a maximum value appearing at 270 K as the temperature decreases. Below 180 K, the cooling temperature rises again. The energy difference ΔE increases with the lowering of the temperature which would give a larger cooling temperature ΔT . On the other hand, the absorption coefficient decreases at a fixed pumping wavelength on the band tail as the temperature decreases because the band edge shifts far away from the pumping laser as aforementioned. The competition between those two factors gives rise to the largest cooling temperature at 270 K and the smallest cooling temperature appearing at 180 K. Below 180 K, the presence of the DAP emission gives rise to the redshift of the mean emission energy, which leads to the increase of the absorption again. Therefore, the cooling temperature gradually increases again as shown in Figure 7-8c.

The time evolution of the Si Raman intensity normalized by the Stokes intensity starting at 270 K are shown in Figure 7-8a. After turning on the pumping laser, the anti-Stokes Si Raman intensity gradually decreases and finally reaches a minimum value. The extracted temperature variation of the Si layer based on equation (7-2b) for the starting temperature of 270 K and 180 K is displayed in Figure 7-8b. The starting temperature dependence of the cooling temperature is shown in Figure 7-8d as the blue dots for a 4 mW 532 nm laser pumping. The theoretical values for a

532 nm laser pumping are picked out from Figure 7-8c as shown in Figure 7-8d as well (blue dots), which agrees well with the experimental data except for 240 K.

Figure 7-9 (a) The evolution of PPLT spectra starting from 290 K, pumped by a 532 nm laser with a power of ~ 7 mW. The red asterisk indicates the pumping laser is stopped. All spectra are normalized and offset vertically for clarity. (b) The time evolution of the temperature change for both laser cooling of CdS nanobelt itself on the suspended segment (filled triangles) and laser cooling of SOI substrate on the contacted segment (filled circles) starting from 290 K under different pumping wavelengths (532 nm: black, 514 nm: red, 502 nm: green, 488 nm: blue). The red arrows indicate the time the pumping lasers are switched off. (c) The experimental and theoretical calculation of the normalized temperature change for both cooling of CdS nanobelt itself (black squares) and SOI (red circles) starting from 290 K for different pumping wavelength.

To compare the results of the laser cooling of SOI substrate with the previous reported results of the laser cooling of CdS itself measured by PPLT method, we conducted both the cooling of SOI substrate using the ratio of the intensities of Stokes and anti-Stokes and the cooling of suspended CdS nanobelt itself on the same belt. Figure 7-9a displays the evolution of PPLT spectra starting from 290 K, pumped by a 532 nm laser with a power of ~ 7 mW. Each spectrum is taken with a 5 minutes interval, when the probe beam of a 20 μ W 473 nm laser is blocked temporarily. A pronounced systematic blueshift is observed upon the laser pumping. The blueshift ceases after ~ 25 minute pumping suggesting the maximum cooling temperature is achieved. After the pumping laser is switched off (indicated by the red asteroid in Figure 7-8a), the emission peak gradually red shifts, indicating the temperature rises again.

Based on the calibration curve, the temperature variation of the CdS nanobelt can be extracted from the Figure 7-9a and shown in Figure 7-9b (only data for the 532 nm laser pumping was shown here). The detailed information on how to deduce the temperature from the calibration curve can be found in Chapter 6⁴¹. The results for the laser cooling of SOI substrate are given in Figure 7-9b as well. For both the laser cooling of the SOI substrate and the laser cooling of CdS nanobelt itself, a net cooling is observed for 532 nm and 514 nm pumping while 502 nm and 488 nm pumping leads to a heating of the sample. We have achieved a 34 K and 43 K net laser cooling of SOI substrate starting from 290 K under a 4.5 mW 514 nm and a 7 mW 532 nm pumping, respectively. A net laser cooling of 49 K and 51 K for the suspended segment has been demonstrated starting from 290 K pumped by a 514 nm and 532 nm laser, respectively. The *normalized temperature change* for both the laser cooling of SOI substrate and the laser cooling of CdS nanobelt itself are extracted from Figure 7-9b and plotted versus wavelengths as shown in Figure 7-9c. The theoretical calculation based on equation (7-5) with taking $\frac{Kt}{C}=0.92$ is also displayed, in good agreement with the experimental data except for 488 nm. Compared with the cooling of the CdS nanobelt itself, the heating of substrate and the heat dissipation via substrate during the probe time lead to a smaller *normalized temperature change* for 514 nm and 532 nm laser pumping and a larger *normalized temperature change* for 502 nm and 488 nm laser pumping for the laser cooling of SOI substrate.

7.4 Summary

We demonstrate an all-solid-state semiconductor cryocooler concept using a CdS nanobelt as the cooling element while a silicon-on-insulator substrate as the thermal load. The local temperature variation of the SOI substrate beneath the CdS nanobelt is measured by using the ratio of the intensities of Stokes and anti-Stokes from Si layer on the top of the substrate. A 20 K and 30 K net laser cooling of SOI substrate has been achieved starting from 290 K under a 3.8 mW 514 nm and a 4.4 mW 532 nm pumping, respectively. The starting temperature dependence of the cooling temperature is systematically investigated. Based on the temperature dependent anti-Stokes photoluminescence, photoconductivity gain and the thermal conductivity of Si, the relation between the cooling temperature and the pumping

wavelength at various temperatures above 180 K is obtained, which is in agreement with the experimental results of the laser cooling of SOI substrate. Finally, laser cooling of SOI substrate and laser cooling of suspended CdS nanobelt itself by using the PPLT method are conducted on the same belt. The results show that the heating of SOI substrate and a larger heat dissipation during the probe time lead to a smaller cooling temperature compared with the results from the suspended segment. Our finding suggests that II-VI semiconductors may find promising applications in cryogenics with the advantages of compactness, vibration- and cryogen-free, high reliability and direct integrability into nanoscale electronic and photonic devices.

Chapter 8 Conclusions and Future Work

8.1 Conclusions

In this dissertation, the optical and optoelectronic properties of one-dimensional CdS nanostructures, in particular nanobelts, are investigated. The excellent luminescent properties and the exceptional strong exciton-phonon coupling lead to the surprising discovery of laser cooling of CdS nanobelts. Therefore, this dissertation is primarily focused on the laser cooling of semiconductors and its related topics, which are crucial towards the profound understanding of the laser cooling mechanism and the characterizations. This dissertation can be divided into four parts including the size and dimensionality dependent electroabsorption, the confinement beyond the quantum confinement regime, the electron phonon coupling and the demonstration of laser cooling.

The photoconductivity measurement of individual CdS nanowire and nanobelt devices has been systematically investigated. The gain and response speed of the individual CdS nanobelts are of the order of ~ 1000 and ~ 100 ms respectively, which agrees with previously reported results. As the temperature decreases, the gain gradually decreases probably due to the decrease of the surface depletion electric field. The interference patterns due to the silicon oxide layer on the substrate and the nanobelts have been observed in the photoconductivity spectra, which can be used to properly tune the maximum gain at a desired wavelength by selecting the substrate or the thickness of the CdS nanobelts. By applying a source-drain voltage, the Franz-Keldysh effect, Stark effect and field induced exciton ionization have been observed from the photoconductivity spectra. The Franz-Keldysh effect is identified by the quasiperiodic oscillations just above the band edge region for all nanobelts and nanowires investigated. The Stark effect is observed in the thinner nanobelts and nanowires while the field induced exciton ionization is identified in the thick nanobelts. The Franz-Keldysh effect, Stark effect and field induced exciton ionization all show size and dimensionality dependence. The investigations on the electroabsorption near the band edge region provide valuable information for the cooling efficiency analysis of the laser cooling in CdS nanobelts.

The anomalous blue-shift of the free exciton emission peaks in CdS nanobelts above 77 K has been observed beyond the quantum confinement regime. Below 77 K, such anomalous blue-shift is absent. A surface depletion induced confinement model has been proposed to explain this phenomenon. In the presence of the surface depletion, the surface electric field will modify the confinement potential to be much smaller than actual geometrical thickness, thus leading to confinement beyond the quantum confinement regime. As the temperature decreases, most of the donors will be frozen-out, leading to the smaller surface electric field. As a result, the change of the confinement potential due to the surface electric field can be negligible resulting in the absence of the anomalous blue-shift below 77 K. The surface depletion induced confinement is supported by comparing the emission spectra before and after the surface passivation. After covering a layer of PMMA, the surface depletion greatly reduces as a consequence of the reduction of the surface states. As a consequence, the free exciton emission peaks show a red-shift after surface passivation. In addition to the surface depletion induced confinement, the reabsorption effect has been observed for those nanobelts with thicknesses larger than 100 nm. The information on thickness dependent emission is particularly helpful to select nanobelts with proper thickness for the laser cooling experiments and to explain the laser cooling results.

Strong electron phonon coupling is essential for the phonon-assisted anti-Stokes luminescence to occur. We find that the electron-longitudinal optical phonon coupling is greatly enhanced in CdS nanobelts. The electron-phonon coupling strength can be quantified by the Huang-Rhys factor, which is dependent on nanobelt thickness. Under a resonant condition, the strong anti-Stokes luminescence has been observed in CdS nanobelts by simultaneously absorbing or annihilating multiple longitudinal optical phonons, which is verified by the power dependent anti-Stokes luminescence intensity. The power, thickness and temperature dependent anti-Stokes luminescence has been systematically investigated since that information is crucial for the laser cooling of the semiconductors.

For the first time, we demonstrate the laser cooling of the semiconductors in CdS nanobelts. A pump-probe luminescence thermometry technique is devised to detect and measure the local temperature change. As large as 40 K cooling temperature is achieved starting from room temperature pumping by a 514 nm laser. Starting from room temperature, both 532 nm and 514 nm laser pumping can lead to a

net cooling while 502 nm and 488 nm laser pumping give a heating effect. At 100 K, only 532 nm laser pumping can lead to the net cooling. Through the thermal analysis, we find that the heat conducted through substrate dominates the heat dissipation while the heat loss due to the black body radiation is negligible.

In the aspect of applications, all-solid-state cryocoolers based on semiconductors are the ultimately goal for laser cooling of semiconductors. We have successfully demonstrated the concept by cooling silicon on insulator (SOI) substrate using a CdS nanobelt sitting on top, which is laser cooled. The local temperature change is detected by using the intensity ratio of the anti-Stokes Raman to the Stokes Raman signals from the crystalline silicon. The temperature of the SOI substrate decreases by 20 K and 30 K for 532 nm and 514 nm laser pumping, respectively. Compared with the laser cooling of CdS nanobelts themselves, the cooling temperature for cooling silicon layer is smaller due to the large thermal load.

8.2 Future work

(1) Photoconductivity at low temperature

As mentioned in Chapter 2, the gain decreases as the temperature decreases. Besides, the photocurrent versus the applied source-drain voltage gradually changes from the linear to nonlinear curves with the lowering of the temperature as shown in Figure 8-1. As previously discussed, one possible reason for the decrease of the gain with temperature is the reduction of the surface electric field. However, the nonlinear photocurrent versus the applied source-drain voltage cannot be explained. The possible explanation for this nonlinear behaviour is the space charge limited current due to the surface depletion^{269,270}. On one hand, as the temperature decreases, the strength of the surface electric field decreases. On the other hand, the width of the surface depletion region increases leading to the space charge limited current. To confirm the space charge limited current, we can perform the incident light power dependent the photocurrent versus applied voltage. If the turning point from linear to nonlinear moves to the high voltage side with the increase of the incident light power, this behaviour is indeed the space charge limited current²⁷⁰.

Figure 8-1 The photocurrent versus the applied source-drain voltage at various temperature from 77 K to room temperature in linear scale (a) and in logarithm scale (b).

Further, the presence of the exciton in photocurrent spectra even at 10 K indicates that excitons are ionized as discussed in Chapter 5. The possible reasons for the exciton ionization in such low temperature include longitudinal optical phonon assisted dissociation and exciton-exciton scattering. Considering the very low density of longitudinal optical phonon at 10 K, it is more likely that the exciton-exciton scattering leads to the exciton dissociation. However, more evidences are required to clarify this hypothesis. One feasible way is to monitor the magnitude of photocurrent by tuning the excited wavelength near the band edge at low temperature. Since exciton-exciton scattering cross-section depends on the temperature, another possible way is to monitor how the magnitude of the photocurrent changes with the temperature during excited at a fixed wavelength near the excitonic energy. Clarifying the mechanism of the exciton ionization at 10 K may shed light on the understanding of the strong anti-Stokes luminescence at 10 K.

(2) Laser cooling of semiconductors

We have already achieved the net laser cooling of CdS nanobelts and demonstrated a proof-of-concept of all-solid-state cryocoolers by using the CdS nanobelts. A number of experiments can be immediately followed up to further advance the field of laser cooling in semiconductors.

The net laser cooling has been achieved in CdS nanobelts. So the question is whether it is possible to achieve net laser cooling in other semiconductors with strong

electron photon coupling? We have found strong anti-Stokes luminescence in CdSe nanobelts excited by a 785 nm laser. The next step is to check whether net laser cooling can be realized in CdSe nanobelts. Besides, we have successfully synthesized the ternary $\text{CdS}_x\text{Se}_{1-x}$ nanobelts with good morphologies. If net laser cooling can be achieved by using those ternary nanobelts, we would have more choice to select the pumping laser.

Up to now, we only demonstrated the net laser cooling effect close to 77 K. Are we able to cool down to much lower temperature even liquid helium temperature as the theory predicted? It is more significant to cool the semiconductors down to below liquid nitrogen temperature since the lowest achievable temperature for rare-earth doped systems is only around 110 K. The main problem is to find out the proper method to detect the temperature change at such low temperatures. The PPLT technique cannot be applied below 77 K since the shift of the emission peak with temperature is too small and the rich features in the emission spectra further makes this technique even more disadvantageous at low temperatures.

Furthermore, it is essential to understand the detailed processes how the phonon assisted anti-Stokes luminescence occurs involving multiple LO phonons. Thoroughly understanding of the underlying mechanism of the anti-Stokes luminescence is important not only for the fundamental research but also for the potential applications. During the synthesis of the CdS nanobelt, various defects are introduced due to the different vapour pressure of Cd and S. How those defects involve the anti-Stokes luminescence deserves to be further investigated. Once we get the information on the roles of those defects during the anti-Stokes emission, we can intentionally engineer those defects so that we can obtain the maximum cooling efficiency.

In the laser cooling of semiconductors, the strong electron longitudinal optical phonon coupling under resonant condition leads to the strong anti-Stokes luminescence resulting in the net laser cooling. If the dominated process is the anti-Stokes Raman scattering rather than the anti-Stokes luminescence, one question arises: is it possible to realize laser cooling of a certain phonon mode by anti-Stokes Raman scattering under resonant condition? The laser cooling of a certain phonon mode has been investigated extensively in ions, optomechanical systems and diamonds for the

potential applications in the quantum computing. In semiconductors, it is speculated that we can even prepare entangled states even at room temperature due to the large phonon energy.

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