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Laser cooling of CdS nanobelts: Thickness matters

Dehui Li, Jun Zhang, and Qihua Xiong

1Devision of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371, Singapore
2NOVITAS, Nanoelectronics Centre of Excellence, School of Electrical and Electronic Engineering, Nanyang Technological University, 639798, Singapore
3Equally contribute to this work

Abstract: We report on the thickness dependent laser cooling in CdS nanobelts pumped by a 532 nm green laser. The lowest achievable cooling temperature is found to strongly depend on thickness. No net cooling can be achieved in nanobelts with a thickness below 65 nm due to nearly zero absorption and larger surface nonradiative recombination. While for nanobelts thicker than ~120 nm, the reabsorption effect leads to the reduction of the cooling temperature. Based on the thickness dependent photoconductivity gain, mean emission energy and external quantum efficiency, the modeling of the normalized temperature change suggests a good agreement with the experimental results.

References and links

1. Introduction

Laser cooling of solids or optical refrigeration was first proposed by Peter Pringsheim in 1929 [1], more than 30 years before the invention of the laser. Laser cooling of solids exhibits advantages of compactness, free of vibration and cryogen and high reliability and thus has a wide range of potential applications including all solid-state cryocoolers, athermal lasers [2]. The basic principle of laser cooling is based upon an anti-Stokes luminescence process. In detail, the specifically designed high purity materials absorb photons with energy \( h\nu \) below the mean emission (fluorescence) energy, \( \nu = \nu_f h \), where \( \nu_f \) is the mean emission frequency. During the emission process the thermal energy contained in the lattice vibrations is taken away by the emitted photons resulting in the laser cooling of solids. To realize net laser cooling of solids, the material must have very high crystalline purity with proper spaced energy levels and high external quantum efficiency. Under those special constraints, the materials investigated for laser cooling are limited to rare-earth (RE) doped crystals or glasses and direct band gap semiconductors up to date [2, 3].

The breakthrough in laser cooling of solids was first accomplished in ytterbium-doped glass in 1995 [4]. Since then, a remarkable progress has been made in a variety of the RE doped crystals and glasses [5–7]. In 2011, a minimum achievable cooling temperature of 110 K from room temperature was realized in a 5% doped Yb:YLF crystal, which approaches the fundamental limit of the cooling temperature imposed by the Boltzmann statistics of electrons in RE doped systems [7].

Laser cooling of semiconductors is more interesting due to more efficient pump light absorption, much lower achievable cooling temperature and direct integrability into electronic and photonic devices [3, 8]. Although a plenty of theoretical [9–14] and experimental [15–18] studies have been carried out to investigate various aspects of laser cooling in semiconductors particularly III-V GaAs quantum wells, the net cooling was achieved only very recently by our group in CdS [19]. A net cooling of 40 K was demonstrated in a CdS nanobelt with a thickness around 110 nm starting from 290 K pumped by a 514 nm laser.

It is expected that the laser cooling of CdS nanobelts depends on their thickness since the emission peak [20], absorption band tail [21] and external quantum efficiency [22] all show thickness dependent behaviors. On the one hand, investigations on the thickness dependent laser cooling can help to clarify the mechanism of laser cooling. On the other hand, the knowledge about the thickness dependent cooling can guide us to select nanobelts with proper thickness for practical applications such as cooling of nanoelectronic devices. In this paper, the thickness dependent laser cooling in CdS nanobelts is investigated in details. The
experimental results obtained by using a noncontact pump-probe luminescence thermometry (PPLT) agree well with the theoretical calculations based on the thickness dependent photoconductivity, emission and external quantum efficiency.

2. Modeling of the cooling power and normalized temperature change

According to the Sheik-Bahae/Epstein (SBE) theory, the cooling efficiency, defined as the ratio of the cooling power to the absorbed laser power, can be expressed as [3]

$$\eta_c(h\nu, T) = \frac{\eta_{exec} \eta_{abs} \overline{\nu}(T)}{\nu} = 1 - \frac{\alpha(v, T) t P_0}{\alpha(v, T) t P_0} \left[ \eta_{exec} \eta_{abs} h\overline{\nu}(T) - h\nu \right]$$

where $\alpha(v, T)$ is the absorption coefficient at frequency $v$ and temperature $T$, $P_0$ is the power of the incident laser, $t$ is the thickness of the nanobelt, $h\nu$ is the pump laser energy, $h\overline{\nu}(T)$ is the mean emission energy; $\eta_{abs} = \frac{\alpha(v, T)}{\alpha(v, T) + \alpha_b}$ is the absorption efficiency quantifying the percentage of the absorbed photons that have engaged in laser cooling, where $\alpha_b$ is the background absorption coefficient; $\eta_{exec}$ is the external quantum efficiency, which can be further expressed as [22]

$$\eta_{exec} = \frac{\eta_e BN^2}{AN + \eta_e BN^2 + CN^3}$$

Here $\eta_e$ is the luminescence extraction efficiency; $A$, $B$ and $C$ are nonradiative recombination coefficient, radiative recombination coefficient and Auger recombination coefficient, respectively; $N$ is the $e$-$h$ population density. Therefore, the cooling power is given by [19]

$$P_{cool} = \eta_c \alpha(v, T) t P_0 = \frac{\alpha(v, T) t P_0}{h\nu} \left[ \eta_{exec} \eta_{abs} h\overline{\nu}(T) - h\nu \right]$$

In Eq. (3), the mean emission energy $h\overline{\nu}(T)$, the absorption coefficient $\alpha(v, T)$ at the band edge region and the external quantum efficiency $\eta_{exec}$ are all thickness dependent. The surface depletion induced confinement beyond the quantum confinement regime would lead to a thickness dependent absorption at a certain wavelength [21] and the shifting of the emission peak resulting in the thickness dependent mean emission energy for a fixed pumping wavelength [20]. The external quantum efficiency relies on the thickness of nanobelts, as the large surface nonradiative recombination dominates in thin nanobelts while the reabsorption effect dominates in thick ones [3]. The thickness dependent cooling power and normalized temperature change will be addressed based on the mean emission energy, photoconductivity gain and calculated external quantum efficiency.

Since the absorption coefficient of individual nanobelts cannot be directly measured, photoconductivity spectroscopy is devised to quantify the absorption [19]. The thickness dependent normalized photoconductivity gain is shown in Fig. 1(a). It can be seen 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 Fig. 1(b). As can be seen from Fig. 1(b), there is no absorption at all at 532 nm (vertical line) for those nanobelts with thicknesses below 65 nm as a consequence of the surface depletion induced confinement [20]. Therefore, we anticipate that it is impossible to achieve net laser cooling on the CdS nanobelts with thicknesses below 65 nm for a 532 nm laser pumping.

As discussed in our previous publication [19], the absorption coefficient is related to the photoconductivity gain at room temperature via $\alpha(v)t = K G(v)$, as long as the bias is

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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 nanobelts with various thicknesses we investigated the absorption coefficient is the 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 $\alpha(480\,\text{nm}) = 1.8 \times 10^5\, \text{cm}^{-1}$ [23] and then determine $K$ for each nanobelt used for calculation later.

![Fig. 1.](image)

In nanostructures, both surface recombination and reabsorption can greatly reduce the emission intensity. The surface recombination becomes more significant in nanostructures due to the large surface-to-volume ratio, while the reabsorption starts to play a role in the nanobelts with the thicknesses above half of the wavelength of the emitted light inside the belts. Therefore, the surface recombination and reabsorption together determine the luminescence intensity as well as the external quantum efficiency.

The anti-Stokes luminescence and the integrated intensity for nanobelts with different thickness excited by a 7 mW 532 nm laser are shown in Fig. 1(c) and inset, respectively. As the thickness decreases, the emission intensity increases first and reaches a maximum value around 160 nm. Smaller than 160 nm, the emission intensity decreases again with the decrease of the thickness. The integrated emission intensity is extracted from Fig. 1(c) and plotted versus the thickness shown as the inset of Fig. 1(c). 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 minimum value close to zero because the surface recombination rate becomes large and the absorption coefficient at 532 nm becomes negligible for the thinner nanobelts as seen from Fig. 1(b). The crossover thickness falls between 100 nm and 160 nm, consistent with half of the wavelength of the emitted light in CdS at room temperature, which is around 100 nm [20]. The trend of the integrated emission intensity to some extent relates to the external quantum efficiency which will be discussed in Fig. 2(a).

From Fig. 1(c), we can also see that the anti-Stokes emission peak shifts with the thickness. The mean emission energy $\hbar \nu_f$ is introduced to quantify how much energy is carried away by each emitted photon in average [19]. We extract the $\hbar \nu_f$ and plot it versus the thickness in Fig. 2(a), which suggests a non-monotonic behavior: $\hbar \nu_f$ increases as the thickness decreases and reaches a maximum value for a nanobelt around 70 nm. Below 60
nm, $h\nu_f$ decrease and reaches a stable value around 40-50 nm. This non-monotonic behavior is probably due to the surface depletion induced confinement and the surface non-radiative recombination, which may lead to heating of the sample.

Fig. 2. (a) The thickness dependent mean emission energy at room temperature for a 7 mW 532 nm laser pumping. (b) The calculated thickness dependent external quantum coefficient $\eta_{ex}$ at room temperature based on Eq. (8).

The thickness dependent external quantum coefficient $\eta_{ex}$ at room temperature cannot be directly obtained from experiments here. Nevertheless, we can deduce the external quantum efficiency with a theoretical model. Starting from the Eq. (2) 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 by [22]

$$\frac{d\eta_{ex}}{dN} = 0 \Rightarrow N_{opt} = \sqrt{\frac{A}{C}} \quad (4)$$

By inserting the $N_{opt}$ into the Eq. (2), finally we express the external quantum efficiency at the e-h population density $N_{opt}$ as

$$\eta_{ex}(N_{opt}) = 1 - 2 \sqrt{\frac{AC}{\eta_0 B}} \quad (5)$$

In this equation, the nonradiative recombination coefficient $A$ and the luminescence extraction efficiency $\eta_e$ are notably thickness-dependent. Since no defect emission peak has been observed in our CdS nanobelts [20], the surface nonradiative recombination $A_s$ dominates the coefficient $A$. The surface nonradiative combination $A_s$ relates to the thickness $t$ via surface recombination velocity $S$ by [24]

$$A_s = \frac{S}{t} \quad (6)$$

In the following calculations, the surface recombination velocity $S$ is assumed to be the same for nanobelts with different thickness since the surface recombination velocity is only dependent on the nature of the surface and independent on the carrier density and layer thickness. The luminescence extraction efficiency $\eta_e$ is formulated as [22]

$$\eta_e = \eta_0 \exp(-\alpha_{eff} t) \quad (7)$$
where $\eta_0$ is the luminescence extraction efficiency without reabsorption, $\alpha_{\text{eff}}$ is the effective absorption coefficient near the bandtail regime. Inserting the Eqs. (6) and (7) into Eq. (5), the external quantum efficiency at the optical e-h population density is rewritten as

$$\eta_{\text{ex}} = 1 - 2 \frac{\sqrt{2SC}}{\sqrt{t} B \eta_0 \exp(-\alpha_{\text{eff}} t)}$$

(8)

Since we use a 7 mW 532 nm pumping laser which has been proved as the optimum excitation power, the Eq. (5) can be applied to calculate the external quantum efficiency. By taking $B = 10^{-11} \text{cm}^3/\text{s}$, $C = 10^{-30} \text{cm}^6/\text{s}$ [25], $S = 250 \text{cm/s}$ [26], $\alpha_{\text{eff}} = 4.6 \mu\text{m}^{-1}$ and $\eta_0 = 0.996$, the thickness dependent external quantum efficiency can be obtained as displayed in Fig. 2(b). The calculated optimum e-h population density $N_{\text{opt}}$ by substituting the above parameters into Eq. (4) is around $10^{18} \text{cm}^{-3}$, which is consistent with the photogenerated e-h population density in experiment regarding the carrier lifetime is on the order of 100 ps [27]. The reason to take $\alpha_{\text{eff}} = 4.6 \mu\text{m}^{-1}$ and $\eta_0 = 0.998$ is to match the experimental results that the external quantum efficiency for the 110 nm CdS nanobelt is 0.996 and the maximum external quantum efficiency appears around 110 nm (see Fig. 4(e)). Besides, $\alpha_{\text{eff}} = 4.6 \mu\text{m}^{-1}$ corresponds to the absorption coefficient at around 520 nm, which falls into the band tail range [23].

As seen from Fig. 2(b), 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 decreases 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.

![Fig. 3. The calculated thickness dependent cooling power (a) based on Eq. (3) and normalized temperature change (b) based on Eq. (10) for a 7 mW 532 nm laser pumping at room temperature. Inset: an SEM image of a single CdS nanobelt suspended on a SiO$_2$/Si substrate. The scale bar is 1 μm.](image)

Once the thickness dependent gain, mean emission energy $\hbar\nu_f$ and external quantum efficiency are obtained, the cooling power as a function of nanobelt thickness could be calculated based on Eq. (3) and plotted as Fig. 3(a). Here the absorption efficiency is taken as unity for all nanobelts with different thickness since both the defects or surface related emission and the free carrier absorption are thickness independent [19]. As can be seen from Fig. 3(a), 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 then reaches a maximum value around 110 nm. Below 110 nm, the maximum cooling power decreases and
finally approaches nearly zero below 65 nm. Another important observation from these two plots is that for each specific thickness which is capable of providing laser cooling, the optimal pumping wavelength is thickness dependent as well.

To directly relate the experimental results, the normalized temperature change is a better quantity. Since the nanobelts used in the cooling experiments are suspended across the etched holes on a SiO₂/Si substrate to reduce the thermal loss (see the inset of Fig. 3(b)) [19], we adopt this suspended configuration to calculate the normalized temperature change. As has been demonstrated in our previous publication [19], the thermal loss is mainly due to the thermal conduction through the substrate and the loss due to blackbody radiation can be ignored. The thermal conductive loss can be expressed as [19]:

$$P_{\text{thermal}} = -2kM \frac{\Delta T}{\Delta L}$$  \hspace{1cm} (9)

where $k$ is the thermal conductivity of the CdS, $M$ is the cross-section area of the nanobelts, $\Delta T$ is the temperature difference between the cooling point and the substrate heat sink and $\Delta L$ is the distance between the cooling point to the edge of the hole. When the cooling temperature reaches its maximum value, the cooling power should be equal to the thermal conductive loss. Starting from Eqs. (3) and (9), the normalized temperature change for arbitrary external quantum efficiency and absorption efficiency can be obtained as

$$\frac{\Delta T}{P_0} = -\frac{KG(v,T)[\eta_{\text{exc}}\eta_{\text{abs}}h\nu_f(T) - h\nu] \Delta L}{2hvkM}$$  \hspace{1cm} (10)

The calculated normalized temperature change is given by Fig. 3(b) based on Eq. (10). We take $k = 5.4 \text{W} \cdot \text{m}^{-1} \text{K}^{-1}$ [28], $M = 0.2t \mu\text{m}^2$ and $\Delta L = 1 \mu\text{m}$ in the evaluation. The normalized temperature change is negative (or positive) indicating the cooling (or heating) of samples. The maximum normalized temperature change shows the same trend as the cooling power versus thickness. The net laser cooling is impossible for those nanobelts with a thickness below 65 nm pumped by a 532 nm laser. For a thinner nanobelt, the cooling is possible but the cooling power is very small as shown in Fig. 3. For a nanobelt with a thickness above 110 nm, the cooling power decreases due to the reabsorption effect. However, further studies are needed to evaluate the reabsorption effect and how the cooling power is affected by thickness for thicker samples.

3. Experiment and results

To verify the calculated results, the laser cooling of CdS nanobelts with different thickness has been carried out adopting the PPLT method, which is based on the shift of the emission peak with temperature. Due to the change of the lattice constant and the electron-phonon coupling strength, the band gap energy shows a blue (or red) shift as the temperature decreases (or increases). In this method, two beams focused at the same spot are used: the pumping beam is used to cool the nanobelts while the probe beam is to detect the local temperature change. The samples are mounted on the cold finger of a continuous-flow microscopy cryostat to maintain the surrounding temperature constant. The vacuum of the cryostat keeps $\sim 10^{-6}$ Torr to eliminate the convective coupling to the surrounding air. The CdS nanobelts are synthesized in a home-built chemical vapor deposition system. More detailed information on the PPLT method and nanobelt synthesis can be found elsewhere [19, 27].

We first measure the Stokes emission peak shift versus temperature excited by the probe beam, while the temperature of the nanobelt can be accurately controlled in the cryostat by a Lakeshore temperature controller and measured by a silicon diode temperature sensor. The temperature calibration equation, which relates the emission peak energy with the temperature, can be extracted from those Stokes emission spectra. Such calibration is done on
every individual nanobelt and the calibration curve can be used to deduce accurately the laser cooling (or heating) effect.

![Fig. 4.](image)

Fig. 4. (a) Evolution of PPLT spectra of a 95 nm CdS nanobelt pumped by a 7 mW 532 nm laser starting from 290 K. (b) and (c) Evolution of PPLT spectra of a 43 nm CdS nanobelt starting from 290 K pumped by a 6.4 mW 532 nm laser (b) and a 4.5 mW 514 nm laser (c). (d) The local temperature change versus time pumped by two different laser lines for two CdS nanobelts. The data are extracted from Fig. 4 (a)-(c). (e) 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 triangles denote the calculated results.

The Stokes photoluminescence evolution of a 95 nm CdS nanobelt upon a continuous 7 mW 532 nm pumping starting from 290 K is given in Fig. 4(a). The emission peaks gradually blue shifts with time and reaches a steady state after 30-40 minutes, indicating the maximum cooling temperature is established. After the pumping laser is blocked (indicated by the arrow in Fig. 4(a)), the emission peaks starts to red shift, suggesting the temperature rises. Figures 4(b) and 4(c) show the Stokes photoluminescence evolution of a 43 nm CdS nanobelts upon continuous 6.4 mW 532 nm laser pumping and continuous 4.5 mW 514 nm laser pumping starting from 290 K, respectively. No apparent emission peak shift is observed for both 514 nm and 532 nm pumping. Based on the temperature calibration, the local temperature change is extracted from Figs. 4(a)-4(c) and plotted in Fig. 4(d). As large as 22 K net cooling is achieved for the 95 nm nanobelt while no cooling is observed for the 43 nm belt pumped by a 532 nm laser. For the 43 nm nanobelt, the 514 nm laser leads to only a 0.7 K net cooling. Those results agree with the trend of calculation shown in Fig. 3(b).

The normalized temperature change was extracted for nanobelts with various thicknesses pumped by a 7 mW 532 nm laser as shown in Fig. 4(e) (red dots). It is found that there is no net cooling below 65 nm. As the thickness of nanobelts increases, the normalized cooling temperature change increases first and a maximum normalized cooling temperature change appears at around 110 nm. Above 110 nm, the normalized cooling temperature change decreases with further increasing the thickness. To facilitate the comparison between calculation and experiment, the calculated results extracted from Fig. 3(b) are given in Fig. 4(e) as well (blue triangles). The calculation agrees well with the experimental data. The small heating for the 43 nm nanobelt is probably due to the larger surface nonradiative...
recombination, which is consistent with the decrease of the mean emission energy below 60 nm as shown in Fig. 2(a).

4. Summary

We have investigated the thickness dependent laser cooling in CdS nanobelts pumped by a 532 nm laser. We have shown that nanobelts with a thickness around 80-120 nm present an efficient cooling. No net cooling for those belts with thicknesses below 65 nm has been observed for a 532 nm pumping, which is mainly due to the nearly zero absorption at 532 nm and the small external quantum efficiency induced by the large surface nonradiative recombination in the thinner nanobelts. Above 110 nm, both the reduction of the mean emission energy and the decrease of the external quantum efficiency due to the reabsorption contribute to the decrease of the normalized cooling temperature change. The modeling of the thickness dependent normalized temperature change has been carried out as well, which are consistent with the experimental results. If a tunable wavelength laser (500 nm – 520 nm) is available, small net cooling is possible for nanobelts below 60 nm. For thicker samples beyond ~120 nm, the cooling potentials demand further investigation since the detailed investigations on reabsorption, external quantum efficiency and mean emission energy are not available at present, because of lack of thick nanobelts. Our work suggests the significance of critical sample thickness for any practical applications on optical refrigeration using nanobelts.

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