Near-field Raman microscopy using a dielectric microsphere

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NEAR-FIELD RAMAN MICROSCOPY USING A DIELECTRIC MICROSPHERE

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School of Physical and Mathematical Sciences

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

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Summary

The aim of this work is to investigate methods to improve the spatial resolution of Raman microscopy and to enhance Raman signal. There are three main parts that will be studied.

The first part elaborates the setup of a new approach near-field Raman microscopy using dielectric microsphere. During imaging, the sample is put inside a water-filled sample cell with polystyrene microspheres. The incoming laser is used to trap an individual microsphere using optical tweezers mechanism. This new approach will offer the flexibility over the conventional scanning near-field Raman microscopy techniques. The sub-diffraction limit spatial resolution achieved is ~ 80 nm ($\sim \lambda/7$) with the decay length of ~ 140 nm by using 532 nm excitation laser. To show the capability of our approach, near-field Raman imaging on various samples, i.e. PMOS transistors with SiGe source drain stressors, gold nanopatterns and carbon nanotubes on silicon substrate, are shown. The advantages of this technique are non-destructive, high reproducibility (almost 100%), easy to use, and fast, making this technique can serve as an alternative technique to other conventional near-field Raman techniques in achieving sub-diffraction limit spatial resolution.

The second part discusses about the use of different sizes of individual polystyrene microsphere to enhance the Raman signal. It will be shown that different sizes of polystyrene microsphere will give different enhancement factor, which depends on the diameter of the incoming beam. Maximum enhancement can be

achieved when diameter of microsphere is approximate to the incoming beam diameter. Simulation studies using COMSOL Multiphysics® modeling software are also shown, and the simulation results agree well with the experimental results. Besides intensity enhancement, simulation results also show that sub-diffraction focus spot can be obtained as well. Enhanced Raman scattering of 4-MBA molecules by individual polystyrene microsphere shows normalized enhancement factor of about 500 times. With the capability to increase the Raman signal and to focus light into sub-diffraction limit spot size, individual polystyrene microsphere can be used for high-resolution Raman imaging.

The last part will be on plasmon-enhanced Raman spectroscopy for sensitive surface characterization. Different thicknesses of silver film were deposited on 20 nm strained silicon layer using DC magnetron sputtering. Local-mode plasmons, excited by the roughness of metal film, and localized surface plasmons, from the interference of surface plasmons on surface of metal film, can selectively enhance the Raman signal from the sample surface. The maximum enhancement from the coated sample can reach 12.89 times as compared to the Raman signal of the uncoated sample. To further increase the surface sensitivity, we used the fact that the polarization of the near-field signal is different from that of the far-field signal. An analyzer is used to block the far-field signal and dramatic surface enhancement as high as 25.4 times as compared to that without metal coating can be achieved. This technique will be very useful for Raman study on samples that suffer from overlapping background signal, e.g. 20 nm strained silicon layer grown on 1 μm relaxed $\text{Si}_{0.75}\text{Ge}_{0.25}$ /2 μm graded $\text{Si}_{1-x}\text{Ge}_x$ ($x = 0$ to 0.25)/bulk silicon.

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Chapter 1

Introduction

1.1 Background

For recent 45 nm complementary metal oxide semiconductor (CMOS) technology and beyond, strain engineering has become the dominant approach in further scaling of CMOS device for high speed and low power applications [1,2]. Straining the silicon can suppress the inter-valley scattering and reduce the effective carrier mass. Hence, it results in an improvement of the effective carrier mobility in silicon. Appropriate strain applied to the channel region can significantly improve transistor performance. However, excessive strain applied will also degrade the performance. Beside those, NMOS and PMOS transistors need to be strained differently. The compressive strain is known to be beneficial for PMOS and the tensile strain is known to improve the NMOS performance [3,4]. All these suggest that techniques to characterize strain reliably are important and high in demand.

Raman spectroscopy has mostly been applied in chemical studies, giving information on the chemical composition, structure and crystallinity of a sample. It also has been a popular tool for strain measurement because it is non-destructive and quantitative [5-7]. Compressive strain shifts the Raman peak to higher frequency, while the tensile strain result in a red shift [8]. However, Raman intensity is weak due

to its small scattering cross section. So only a very small fraction of photons (approximately 1 in 10^7 photons) is inelastically scattered. In order to obtain accurate information of the sample, having good signal to noise ratio of Raman signal is very important.

As the dimension of devices gets smaller, strain characterization by micro-Raman spectroscopy is also facing an uphill challenge. The features of interest may be beyond the resolution of micro-Raman microscopy. The spatial resolution, which is limited by diffraction of light, is indeed too big to resolve the tiny size of transistors, which at the moment has reached 45 nm technology node. To improve the spatial resolution to sub-diffraction limit, near-field optical technique can be used. Dated back to 1928, scanning near-field optical microscopy (SNOM) was proposed by E. H. Synge [9], and SNOM in visible region was only realized in 1984 by Pohl *et al.* [10] after the invention of scanning probe microscopy. The combination of this technique with micro-Raman spectroscopy has realized a Raman microscopy with spatial resolution beyond the diffraction limit, which is also known as scanning near-field Raman microscopy (SNRM). This technique has a great potential to be one of the routine characterization techniques used to study strain in silicon-based devices.

As mentioned above, SNRM is based on the principle of SNOM, which consists of aperture and apertureless techniques. In aperture approach, an optical fiber with a small aperture (50-100 nm) is used to deliver the laser light and the fiber is kept at a

close distance (~tens of nanometer) above the sample surface. In apertureless approach, laser is focused on a sharp metallic tip to create a strongly confined optical field. The first approach has poor signal to noise ratio for the near-field Raman signal, due to the facts that the laser emerging from the aperture is extremely weak (typically in the order of μW) and the small Raman scattering cross section (typically 1 in 10^7 photons). The second approach depends on the reproducibility in fabricating a “hot” tip, where strongly enhanced electromagnetic field can be excited on the apex of the tip. The reproducibility of this “hot” tip is still poor, due to the mismatch between the frequency of the excitation laser and the resonance frequency of the tip. Due to the diffraction limit, the laser spot focused on the tip apex also causes an intense background (far-field signal) that should be eliminated to achieve better signal to noise ratio. The metallic tip also faces wear-tear and oxidation problems. These challenges must be overcome for the apertureless technique to be used as a routine characterization technique in nano-science and nano-technology.

In order to avoid the challenges in the conventional SNRM, we have developed a near-field Raman microscopy based on the trapping of a dielectric microsphere, wherein the laser is focused to a spot smaller than diffraction limit by a dielectric microsphere. Besides being used as the excitation source for Raman spectroscopy, the incident laser beam is also used to hold the microsphere just above the sample surface, through the optical tweezers mechanism. Hence, sample can be scanned, or vice versa.

Besides using laser to tweeze the microsphere, it also can be attached to an atomic force microscopy (AFM) tip. This approach is particularly advantageous when the sample of interest cannot be immersed in liquid. The microsphere itself will focus the incoming laser and collect the Raman lights in the near field. Hence, good signal to noise ratio can be obtained.

To improve the Raman signal, one can also resolve to surface-enhanced Raman spectroscopy (SERS). SERS is an area of intense interest because this technique can allow probing of small collections of, and in certain cases, individual molecules using relatively straightforward spectroscopic techniques and nanostructured substrates. This technique is based on the surface plasmon resonance on the metal nanostructures. A surface plasmon is a quantum of a plasma oscillation, which is the collective oscillation of conduction electrons that is confined to the surface. With the appropriate configurations, surface plasmons can be excited to enhance the Raman signal. On a crystalline sample like silicon, polarized SERS can even be used to further enhance the Raman signal from the thin strained layer by suppressing the background signal from the substrate. Hence, accurate strain information can be obtained readily.

1.2 Objectives and scopes

The main objectives of this project were to improve the spatial resolution and signal to noise ratio of Raman microscopy. There were several approaches taken in order to achieve them.

Near-field Raman system with a trapped dielectric microsphere was realized. The trapping was done with the optical tweezers mechanism. With this approach, a good quality Raman spectrum of a silicon device could be collected in 1s integration time or less with modest laser power. We succeeded in mapping near-field Raman images on transistors with SiGe stressors. Another similar approach was also developed. Instead of using the incoming laser to trap the microsphere, an AFM tip was used to hold the microsphere. This is a giant step towards general application of SNRM and makes it an extremely powerful analytical technique for both fundamental research and applications.

Recently, sub-diffraction limit focus spot of visible light achieved by a dielectric microsphere has been studied extensively. In addition to the improvement of the focus spot, the implementation of this effect to Raman spectroscopy also gives rise to an enhanced Raman signal of about 10 times depending on the objective lens and the size of microsphere used. Simulation studies were carried out to understand this effect. With smaller focus spot and stronger Raman signal, dielectric microsphere showed to

be critical for Raman microspectroscopy, where smaller focus spot and stronger Raman signal translate to higher spatial resolution and shorter imaging time, respectively.

The ability of SERS to selectively enhance the surface signal of silicon-based sample makes it attractive for the strain study on thin strained layer. With the combination of polarizer and analyzer, the Raman signal from the background substrate can be further suppressed. Hence, the signal from the surface region will be clearer. This approach will be beneficial for accurate strain determination from a thin strained silicon layer on a crystalline substrate.

So, in achieving the main objectives, the project will be carried out with a number of more specific objectives with their own scope of study. Next section will elaborate on the organization of the thesis.

1.3 Organization of thesis

Chapter 1 gives a brief introduction on how Raman microscopy is useful for strain study on CMOS device, the development of near field Raman with spatial resolution beyond diffraction limit, and SERS to improve signal to noise ratio of Raman signal. Near-field Raman microscopy using microsphere was also introduced. Objectives and scopes of the projects were also discussed.

Chapter 2 summarizes the previous works that lead to the development of near-field Raman microscopy using dielectric microsphere and works on Raman signal enhancement by surface-enhanced Raman spectroscopy.

Instrumentation of ultra high-resolution near-field Raman microscopy with optically trapped microsphere is discussed in Chapter 3. In this Chapter, the details of near-field Raman microscopy with microsphere on AFM tip will also be discussed. The details of the sample fabrications will be elaborated, with many types of samples for different experiments. In Chapter 4, the fabrication of different types of sample cells is presented. Some of the samples used in the experiments, i.e. transistor samples and graphene sample were obtained from collaboration works with colleagues from Nanyang Technological University, Chartered Semiconductor Manufacturing, and North Carolina State University. The mechanism of laser trapping and Brownian motion are also discussed. An attempt to attach a single microsphere on an AFM probe is shown in this chapter as well.

In Chapter 5, the lines profiles of embedded SiGe (eSiGe)/Si periodic lines from different sizes of microsphere are shown. The spatial resolution and the decay length of the microsphere near-field Raman imaging are calculated based on experimental results. Follow by Chapter 6, in which the Raman imaging of the PMOS silicon devices, gold nanopatterns, and carbon nanotubes is used to show the capability of the microsphere near-field Raman microscopy. An attempt to reduce and eliminate

Brownian motion using sugar solution and microsphere attached to an AFM probe are presented. Besides near-field Raman imaging, we also present a near-field white light microscopy, which has a potential in metallic nanostructures and biological studies.

Chapter 7 deals with our attempt to enhance the Raman signal using individual polystyrene microsphere. Simulation results from COMSOL Multiphysics® modeling software will be used to understand further the experimental results. Chapter 8 shows the plasmon-enhanced polarized near-field Raman study on strained silicon sample. Polarized Raman is used to obtain better surface enhancement. Finally, Chapter 9 concludes the report and gives insights for future works.

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Chapter 2

Literature review

2.1 Optical microscopy

Optical lenses have been one of the important tools for scientists for centuries. It has been used in microscopy for studies of materials and biological samples. Optical microscopy can be used to image and study various kinds of samples in many types of environments, which may include considerable extremes of temperature, or pressure. A great advantage of optical microscopy is the non-perturbing and non-destructive nature of the light used in imaging to a certain extent.

Through the years, as technology and research require smaller and smaller resolution, the boundary imposed by far-field diffraction have pushed the optical microscope to its fundamental limits. For conventional optical microscopes, a fundamental limit is imposed by the physical nature of light, and this limit represents a lower bound to the spatial resolution that can be obtained with these instruments, which is often called the Abbe's barrier or the far-field diffraction limit [1].

In Abbe's treatment, one seeks to find the circumstances under which a microscope resolves the lines of a grating that are spaced p apart. He examined the limiting case for the smallest resolvable spacing, p_{min} , and found it to be a function of

the wavelength of radiation λ and the collection angle α that subtends with respect to the object normal, namely,

$$p_{\min} = \frac{\lambda}{2n \cdot \sin \alpha}, \quad (2.1)$$

where n is the refractive index of the medium that may be a liquid or even a solid. Abbe's treatment suggests that the limit of resolution for a conventional microscope is only slightly smaller than the wavelength of the probe radiation.

If we consider an infinitesimal dipole with frequency ω in front of a lens, the electric field will be given by,

$$E(r, t) = \sum_{k_x, k_y} E(k_x, k_y) \times \exp(-i\omega t) \times \exp(ik_x x + ik_y y + ik_z z) \quad (2.2)$$

with dispersion relationship,

$$k^2 = (2\pi / \lambda)^2 = k_x^2 + k_y^2 + k_z^2 = \omega^2 c^{-2} \quad (2.3)$$

Note that k , λ , and c are the wave vector, wavelength of light, and speed of light, respectively.

For $\omega^2 c^{-2} > k_x^2 + k_y^2$, we have $k_z = +\sqrt{\omega^2 c^{-2} - k_x^2 - k_y^2}$, the function of the lens here is to apply a phase correction to each of the Fourier components so that at some distance beyond the lens the fields reassemble to a focus, and an image of the dipole source appears.

For $\omega^2 c^{-2} < k_x^2 + k_y^2$, we have $k_z = +i\sqrt{k_x^2 + k_y^2 - \omega^2 c^{-2}}$, (2.2) carries an exponential decaying term. This evanescent wave decays exponentially as z increases. This means

that the evanescent field exists only in the near-field region. No phase correction will restore them to their proper amplitude. In order to get such information, the object should be observed in near-field region.

In the far-field region, since the propagating waves are limited to $k_x^2 + k_y^2 < \omega^2 c^{-2}$, the maximum resolution of optical microscopy can never be greater than,

$$\Delta \approx \frac{2\pi}{k_{\max}} = \frac{2\pi c}{\omega} = \lambda \quad (2.4)$$

2.2 Scanning near-field optical microscopy (SNOM)

As discussed in the earlier section, the information of fine structures on a sample is only confined in the near-field region. Therefore, the capability of picking up that information is of great importance in imaging a fine object. Dated back to 1928, E. H. Synge published a series of articles that first conceptualized the idea of an ultra-high resolution optical microscope [2,3], which is shown in Figure 2.1.

Figure 2.1. Schematic diagram of the conceptual near-field microscope proposed by E. H. Synge.

Synge's proposal suggested a new type of optical microscope that would overcome the diffraction limit, but required fabrication of a 10 nm aperture (much smaller than the wavelength of visible light) in an opaque screen. A stained and embedded specimen would be ground optically flat and scanned in close proximity to the aperture. While scanning, light that illuminated one side of the screen and passed through the aperture would be confined by the dimensions of the aperture, and could be used to illuminate the specimen before undergoing diffraction and resolution degradation. As long as the specimen remained within a distance less than the aperture diameter, an image with a resolution of 10 nm could be generated. In addition, Synge accurately outlined a number of technical difficulties that building a near-field microscope would present. Included in these were the challenges of fabricating the small aperture, achieving a sufficiently intense light source, specimen

positioning at the nanometer scale, and maintaining the aperture in a close proximity to the specimen. His proposal, although simple and visionary in concept, was far beyond the technical capabilities at that time.

Experimental verification of the feasibility of Synge's idea was only realized in 1972 when E. A. Ash and G. Nicholls demonstrated the near-field resolution of a sub-wavelength aperture scanning microscope operating in the microwave region of the electromagnetic spectrum [4]. In their experiment, periodic features on a metal grating sample were measured with 3 cm microwaves passing through a small aperture. The achieved spatial resolution was $\lambda/60$. These exciting results illustrated the feasibility of Synge's idea and brought about interests in carrying out similar experiments using visible radiation.

Extension of Synge's concepts to the visible spectrum presented significantly greater technological difficulties in aperture fabrication and positioning, which could not be solved at that time. It was not until 1981 that the scanning tunneling microscope (STM) was developed [5], which launched a worldwide research effort using scanning probes. In 1984, Pohl's laboratory at IBM Zurich first reported sub-diffraction limited optical measurements [6] using the idea outlined by E. H. Synge and initiated the development activity, which has resulted in the modern SNOM instrument.

Besides SNOM with aperture, there is another approach that uses apertureless tip. J. Wessel proposed the concept of using optical field confinement by surface plasmons of a metal particle to achieve a spatial resolution higher than diffraction limit [7]. Fischer and Pohl were probably the first to show the SNOM by using a small protrusion of an otherwise flat gold film [8]. There are many reported works that show the high-resolution optical microscopy by employing apertureless technique [9-14].

There are many methods to produce the aperture SNOM tips with reasonable optical throughput. The most conventional way to obtain the tips is heat pulling of an optical fiber [15]. An alternative way is by chemical etching [16]. Focused ion beam (FIB) milling was also attempted to obtain the SNOM tip [17,18]. Another important category of SNOM tips is semiconductor-based cantilevered SNOM tips, fabricated by semiconductor microprocessing techniques [19,20]. For the apertureless SNOM tips, a sharp STM tip or metal-coated atomic force microscope (AFM) tip is normally used [21-23].

In SNOM experiment, the tip is brought to the sample surface by either a cantilever or a tuning fork. The number of possible configurations of SNOM appears to be only limited by the imagination of near-field microscopists. Typically, there are six configurations as shown in Figure 2.2, i.e. (a) collection mode, wherein the laser is delivered to the sample by a lens and the transmitted or reflected signal is collected by

the tip; (b) illumination mode, wherein the laser is delivered to the sample surface by the tip and the signal transmitted or reflected is collected by a lens in far-field; (c) illumination and collection mode, wherein the laser is delivered to the sample by the tip and the signal is also collected by the same tip; (d) collection mode using total internal reflection; (e) scattering SNOM using a dielectric tip, where illumination can be below or above the sample; and (f) is for metal probes, where field enhancement can occur at the apex of the probe.

Figure 2.2. The different types of SNOM configurations. Configurations a-d are aperture-based SNOM configurations, providing (a) collection mode, (b) illumination mode, (c) illumination/collection mode, and (d) collection mode using total internal reflection. Configuration (e) is for scattering SNOM using a dielectric tip, where illumination can be below or above the sample. Configuration (f) is for metal probes, where field enhancement can occur at the apex of the probe.

Compared to other scanning probe microscopes (SPMs) like STM or AFM, SNOM allows more contrast mechanisms, e.g. intensity contrast, polarization contrast, and wavelength contrast. Besides optical images, SNOM also provides topographical image simultaneously. In addition, optical contrast is the way in which we observe the world around us. Therefore, SNOM images are more natural compared to other SPM images. Furthermore, the spectroscopic capability allows investigating material structural properties in the nanometer scale. Due to these unparalleled merits, SNOM has been extensively used in biology [24,25], thin film characterization [26,27], semiconductor [28,29], and storage [30,31]. The spatial resolution of SNOM is not determined by the wavelength of probe radiation like in conventional optical microscopy. It is solely determined by the aperture size or the radius of the SNOM tips.

2.3 Raman spectroscopy and microscopy

When light of a certain wavelength interacts with a molecule, most photons are elastically scattered and therefore have the same energy as the incident photons (Rayleigh scattering). However, a very small fraction (approximately 1 in 10^7 photons) is inelastically scattered, which means that the energy of the scattered photon is different than the energy of the incident photon. This effect is called the Raman effect and was discovered by Sir Chandrasekhara Raman in 1928 [32]. The importance of the Raman effect lies in the fact that the energy shift between the exciting and the

Raman scattered photon is caused by the excitation (Stokes Raman scattering) or annihilation (anti-Stokes Raman scattering) of a molecular vibration [33]. This energy shift is characteristic and therefore a fingerprint for the type and coordination of the molecules involved in the scattering process. Figure 2.3 shows the typical Raman spectrum from silicon substrate.

Figure 2.3. Typical Raman spectrum from silicon substrate, showing peaks from Anti-stokes, Rayleigh, and Stokes scatterings.

Raman spectroscopy can be easily incorporated to perform in-situ measurements, such as temperature, pressure, electric field, and magnetic field. Polarized Raman spectroscopy can also be easily realized by using a half-wave plate and a polarizer in the optical path. Due to the availability of different laser wavelengths, photoluminescence can be avoided by selecting a proper laser wavelength. By properly choosing laser wavelength, resonance Raman can be achieved, in which low concentration or very weak signal can be observable under Raman spectroscopy. And

by properly coating the sample with certain metals, the sensitivity of Raman spectroscopy can be increased by surface enhancement, which is critically important for interface and monolayer characterization. Because of these advantages, Raman spectroscopy has been extensively used in chemical identification, structure and phase identification, strain/stress analysis, and contaminant identification. All these applications are important for a wide range of scientific researches and manufacturing.

For conventional Raman microscopy, the laser beam is focused on one chosen point on the sample, and the Raman spectrum of this particular point is collected using an objective lens. The laser beam is moved point by point and the Raman spectrum from each point is collected. By deconvoluting one particular vibration from the whole spectrum, it is possible to obtain a microscopic image of the distribution of the component associated with this vibration. This Raman mapping technique is utilized extensively to study the distribution of various components in biological samples and on the surfaces of solids such as minerals. Use of a confocal microscope can improve the spatial resolution, in which a pinhole (25 to 100 μm in diameter) is used to reject out-of-focus signals [34]. However, the spatial resolution of confocal Raman microscopy is still limited by diffraction of light, as discussed in the earlier section. The typical spatial resolution of today's confocal Raman system is about 500 nm depending on the wavelength, objective lens, and pinhole used. On the other hand, scientific research and manufacturing require higher and higher spatial resolution,

which is far beyond the diffraction limit of light. For example, research in life science has proceeded to the molecular level, in which conventional optical methods cannot resolve the fine structures in a cell. In the field of nano-materials, the properties of a single particle, e.g. quantum dot, are often desirable, which require a spatial resolution much higher than that of the conventional Raman system. Nowadays, semiconductor devices have shrunk to a scale less than 65 nm. Therefore, stress and strain analysis on such a scale is beyond the capability of the conventional micro-Raman microscope. Therefore, the development of Raman nanospectroscopy is essential in order for Raman technique to stay relevant for the future research and technology.

2.4 Surface-enhanced Raman scattering (SERS)

As discussed previously, Raman scattering is intrinsically weak, especially for low concentration sample. Resonance Raman and surface-enhanced Raman techniques can be employed. Here we will discuss about the surface-enhanced Raman scattering (SERS). SERS was discovered by Fleischmann et al. in 1974 who observed intense Raman scattering from pyridine adsorbed onto a roughened silver electrode surface from aqueous solution [35]. Since then, SERS research has been progressing aggressively in many fields that include electrochemistry [36], biomolecules [37], medical applications [38], and sensors [39]. Even single molecule detection has been reported by using SERS [40-42].

SERS has been observed for a very large number of molecules adsorbed on the surfaces of relatively few metals in a variety of morphologies and physical environments. Silver, gold, and copper have been the dominant SERS substrates. The largest enhancements occur for surfaces that are rough on the nanoscale (10-100 nm). These include electrode surfaces roughened by oxidation-reduction cycles [43], island films deposited on glass surfaces at different temperatures [44], films deposited by evaporation or sputtering in vacuum onto cold substrates [45], colloids [46], and arrays of particles prepared by lithographic techniques [47,48], it has been thought that surface roughness was required for SERS. Besides these, enhancement is also observed on metal nanowires [49-51].

In SERS experiments, there are two enhancement mechanisms, chemical and electromagnetic enhancements [52]. The chemical enhancement is believed to be due to the charge transfer to the new electronic states that arise from chemisorption of adsorbate to the metal surface. This new electronic states serve as resonant intermediate states in Raman scattering. Normally the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of adsorbate are symmetrically displaced in energy with respect to the Fermi level of the metal. In this case, charge from the molecule can transfer to the metal, or vice versa, at about half the energy of the intrinsic intra-molecular excitations of the adsorbate. Molecules commonly studied by SERS typically have their lowest-lying electronic excitations in the near ultraviolet that would put the charge transfer excitations of this sample model

in the visible region of the spectrum. The electromagnetic enhancement is from the contribution of surface plasmons. Plasmon is the collective oscillation of the electron gas of a conductor, and if it is confined to the near surface region it is called a surface plasmon. Surface plasmon can either be propagating on a flat metal surface, or localized on the surface of metallic particles. The schematic diagram of surface plasmon propagating along the metal surface is illustrated in Figure 2.4. Excitation of surface plasmons by light meets the difficulty as the dispersion relation of surface plasmons is at the right side of the light line and they do not intercept each other [53]. This means that the incident electromagnetic waves always have insufficient momentum to excite surface plasmons for any angle of incidence. In order to couple photons into surface plasmons it is necessary to add momentum by some means. One main method is to employ a non-flat metallic surface region that can provide momentum according to available spatial frequencies provided by the surface profile [54]. On the other hand, defects or rough metallic surface can contain a broad spectrum of spatial frequencies that can be used for exciting surface plasmons with arbitrary wavenumber [55]. Another method is to increase the momentum of the incident light in a dielectric prism, consider its total internal reflection inside of the prism, and to project the evanescent field onto the metallic surface [56,57]. If the component of the wavenumber in the prism parallel to the reflecting side of the prism is matched to that of surface plasmons then energy can be transferred to the surface plasmons. The electromagnetic field of the light at the surface can be greatly enhanced under conditions of surface plasmon excitation. The amplification of both

the incident laser field and the scattered Raman field through their interaction with the surface is part of the electromagnetic enhancement mechanism.

Figure 2.4. Schematic diagram of the electric field associated with surface plasmon propagating along a metal-dielectric interface [53].

Researchers in this area have attempted to develop many new technological innovations including high sensitivity chemical and biological detection systems [58] and labeling schemes for authentication and tracking purposes [59]. However, progress has been hampered by the inability to fabricate substrates with the high sensitivity, tunability, robustness, and reproducibility necessary for truly practical and successful SERS-based systems. These limitations have been due in part to a relative lack of control over the nanoscale features of Raman substrates that are responsible for the enhancement. With the advent of nanotechnology, new approaches are being developed to overcome these issues and produce substrates with higher sensitivity, stability, and reproducibility [60].

Besides the works done on molecules detection, SERS can also be used to enhance the Raman signal of thin strained silicon sample [61,62]. Thin metal layer is coated on the sample surface and due to the local-mode plasmons that localize on the

metal roughness, the Raman signal from the surface layer will be enhanced. In Chapter 8, local-mode and localized surface plasmons will be utilized to enhance the Raman signal from thin strained silicon sample, and also polarized-SERS will be utilized to even further enhance the strained silicon signal based on the depolarization effect of the near-field signal. The depolarization is explained by considering a SERS-active surface to be a heterogeneous collection of roughness features and the opportunity for multiple scattering. SERS also plays a very important role to the development of apertureless scanning near-field Raman microscopy, which will be discussed in the next section.

2.5 Scanning near-field Raman microscopy (SNRM)

As the spatial resolution of conventional Raman microscopy is limited by the diffraction of light, a lot of efforts have been made to achieve Raman nanospectroscopy. The success of SNOM in achieving sub-diffraction limit spatial resolution has a positive impact on the development of high-resolution Raman microscopy, which is also known as scanning near-field Raman microscopy (SNRM). As both SNOM and Raman microscopy are optical techniques, it is just natural to combine both of them to obtain structural information of samples in nanometer scale.

As in SNOM, there are two common methods in SNRM; they are aperture and apertureless SNRM. The former method has been plagued by the poor signal to noise

ratio of the near-field Raman signal, wherein an optical fiber with a small aperture (50 – 100 nm) is used to deliver the laser light and the fiber is kept at a close distance (~tens of nanometer) above the sample surface [63-66]. Raman signal is collected in the far field through either a microscope objective or a lens. The scattered light (Raman signal) is coupled into a Raman spectrometer where the Raman spectra are recorded at each point on the sample by scanning the fiber tip across the sample surface. An NSRM image is constructed using these spectra.

The laser emerging from such a fiber tip is extremely weak (typically 100 nW) due to the low optical throughput of the fiber tip. Although extensive efforts have been devoted to fabricate fiber tips with higher throughput, the throughput is still very low, especially for tips with an aperture less than 100 nm [67-69]. In addition, the Raman signal is intrinsically weak (typically about 1 in 10^7 photons). A typical Raman spectrum takes several minutes to collect using the aperture near-field Raman method, making it prohibitive to construct a Raman image this way. The Raman images (no more than 32 x 32 pixels) of modest signal to noise ratio reported in references took about 10 hours to be completed [70,71]. This approach has been largely abandoned for Raman imaging by researchers now. The schematic diagram of this approach is shown in Figure 2.5a.

In the apertureless method, the laser is focused on the tip apex to create a strongly confined optical field [72-78]. A metal or metal-coated tip is put into the laser spot on

the sample. With suitable metal tip in close proximity to the sample, Raman signals from the sample can be enhanced by several orders of magnitude. In this case, the Raman enhancement is a result of local field enhancement by the tip, or increased polarizability of the sample due to the interaction between the tip and sample. This approach can overcome the low optical throughput of the aperture SNRM. It also has higher spatial resolution, can use different tip materials, wider spectral response range, and more imaging modes. Hence, this method is the preferred choice for performing near-field Raman microscopy and 10 nm spatial resolution has been achieved [79]. The schematic diagram of the apertureless near-field Raman microscopy is shown in Figure 2.5b.

Figure 2.5. The schematic diagram of (a) aperture and (b) apertureless near-field

Raman microscopies

However, apertureless SNRM also has several challenges. As mentioned in the previous chapter, the success of apertureless SNRM experiments depends on the

reproducibility of fabricating a “hot” tip, where strongly enhanced electromagnetic field can be excited on the apex of the tip. The reproducibility of this “hot” tip is still poor, due to the mismatch between the frequency of the excitation laser and the resonance frequency of the tip [80]. Due to the diffraction limit, the laser spot focused on the tip apex also causes an intense background (far-field signal) that should be eliminated to achieve better signal to noise ratio. Apertureless SNRM also faces wear-tear and oxidation problems. These challenges need be overcome for this method to be used for large-scale applications in nano-science and nano-technology. Recently, in order to improve the near-field Raman signal, the polarization effects have been studied to minimize the far-field signal in apertureless SNRM from Si-based sample [81-83]. Another promising approach in controlling the geometry of the tip is by using nanowire. Si nanowire with gold cap was shown to be a good candidate to achieve controllable and reproducible “hot” tip for successful apertureless SNRM experiments [84,85].

2.6 Optical nanojet

Many research groups have used dielectric microspheres, e.g. polystyrene (PS) or silica (SiO_2) microspheres, in many research areas. Some of the many applications of dielectric microsphere are micro-objective lens [86], solid immersion lens (SIL) [87], hard mask in photolithography [88], and a focusing lens for nanopatterning [89].

Besides those applications mentioned above, simulation studies have shown that sub-diffraction limit focus beam can be achieved by using dielectric microsphere. Z. G. Chen *et al.* could be attributed to be the first to evidence optical nanojet in their high-resolution finite-difference time-domain (FDTD) numerical modeling [90]. They showed that when circular dielectric cylinders illuminated by a plane wave, localized nanoscale photonic jets could be generated. These optical jets have beam waists smaller than the diffraction limit and propagate over several optical wavelengths without significant diffraction. It is called a photonic nanojet because of the similarity to the jet in fluids. Figure 2.6 shows the simulated optical nanojet emerging from a $3\mu\text{m}$ dielectric microsphere. Their study was then followed by X. Li *et al.*, who demonstrated a three dimensional photonic nanojet from a dielectric microsphere using FDTD modeling as well [91]. It was shown that the photonic nanojet had sub-diffraction limit spatial resolution as well as a strong backscattering intensity from a nanoparticle. This phenomenon could be important for the fields of nanotechnology and nanobiotechnology, and it may have applications for observation of manipulation of nano-objects such as antibodies in biology. S. Lecler *et al.* also observed similar photonic nanojet in their numerical calculation using Mie theory. It was concluded that with a dielectric sphere, it is possible to create a photonic jet [92].

Figure 2.6. Optical nanojet emerges from 3 μ m dielectric microsphere.

All those numerical studies were also followed by some experiments. A. Heifetz *et al.* demonstrated an experimental confirmation of backscattering enhancement induced by a photonic jet [93]. In their experiment, they used microwave instead of visible light. They also scaled the original conceptual dimensions of the dielectric microsphere and its adjacent nanoparticle. They successfully confirmed the existence of the photonic jet and the enhanced backscattering caused by an adjacent particle. Another experiment was carried out by P. Ferrand *et al.* [94]. They studied the photonic nanojets created by different sizes of single polystyrene microspheres deposited on a glass coverslip illuminated by a plane wave with a wavelength of 520 nm using a conventional confocal microscope. Groups of microspheres in contact were also investigated and showed that each sphere produced its nanojet independently, with negligible influence from the neighboring spheres.

In the next section, it will be shown how the photonic nanojet can be used for ultra high-resolution Raman microscopy.

2.7 Microsphere near-field Raman microscopy

We have developed a new approach, which we believe is a disruptive approach to near-field Raman microscopy. In this method, the laser is focused to a sub-diffraction limit spot by a dielectric microsphere. Besides being used as the excitation source for Raman spectroscopy, the same incident laser beam is also used to hold the microsphere just above the sample surface, through the well-known optical tweezers mechanism [95, 96]. Simulation studies on optical nanojet based on plane wave incident light have shown that sub-diffraction limited focusing can be achieved, as mentioned in the previous section. In our lab, a scanning near-field Raman microscopy using a dielectric microsphere has been developed [97]. Here we show the capability of trapping a dielectric microsphere to achieve high-resolution Raman imaging. This technique has many advantages over the previous near-field Raman techniques. K. J. Yi *et al.* reported the Raman signal collected with closely-packed dielectric microsphere is much stronger than that without microsphere, by 2-7 times depending on the diameter of microsphere used [98]. This is a critical advantage over the aperture SNRM. As the laser light is focused on the sample through the microsphere, there is no far-field signal in our setup, which has been one of the challenges in apertureless SNRM. There is also no requirement to use a metal or metal-coated probe, e.g. metal-coated AFM tip, to perform the experiment. The instrumentation of this technique will be discussed in details in Chapter 3. With this system, we have succeeded in mapping near-field Raman images on advanced

metal-oxide-semiconductor (MOS) devices. The experimental results will be presented and discussed in details in Chapter 6. The strong near-field signal and the simplicity in carrying out the experiment make this technique attractive, easy and fast. The reproducibility is also excellent, close to the 100% level. We show that this technique can also work on different types of samples.

2.8 References

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Chapter 3

Instrumentation and samples

3.1 Brief description of the whole system

The developed scanning near-field Raman system is based on the commercial WITec CRM200 system. The schematic diagram of the whole system is shown in Figure 3.1. This WITec system is a compact system that is capable of being used for confocal microscopy, atomic force microscopy (AFM), scanning near-field optical microscopy (SNOM), and confocal Raman microscopy. However, in this section, we shall just focus on the capability of the system to do confocal Raman microscopy and atomic force microscopy, before we move on to the discussion on the scanning near-field Raman microscopy in the later chapter.

Figure 3.1. Schematic diagram of WITec CRM200 confocal Raman and AFM system.

1. 532 nm Nd:YAG laser, 2. linear attenuator, 3. fiber coupler, 4. white light, 5. edge/notch filter, 6. video camera, 7. holographic bandpass filter, 8. 50:50 beamsplitter, 9. z-stage, 10. objective lens, 11. piezostage, 12. single-mode optical fiber (diameter 3.5 μm), 13. multimode optical fiber (diameter 25 μm , 50 μm , and 100 μm), 14. APD/CCD/spectrometer, 15. data acquisition, shear-force feedback, and scan controllers, 16. vibration isolation table, 17. computer.

3.2 Confocal Raman microscopy

In the WITec CRM200 system, a normal white light source is used to illuminate and focus on the sample. The white light is directed to a 50:50 beamsplitter and is focused to the sample using an objective lens. The reflected white light is collected by the same objective lens and the optical image is recorded with a video camera.

For Raman experiments, double frequency Nd:YAG laser (532 nm) with a Gaussian profile is used. Typical Gaussian profile is shown in Figure 3.2. The optical path for the laser is shown in green color in Figure 3.1. The laser is coupled into a single mode fiber (diameter 3.5 μm) and is directed to a holographic bandpass filter. The single mode fiber supports only a single transversal mode (TEM_{00} , Gaussian beam), which can be focused to a diffraction-limited spot. The laser is then focused onto the sample. The scattered lights (shown as green and orange lines in Figure 3.1) are collected by the same objective lens and directed to spectrometer equipped with CCD and APD using a multimode optical fiber (diameter 25 μm , 50 μm , and 100 μm). The core of the multimode fiber acts as a pinhole for confocal microscopy. An edge filter is used to block the Rayleigh light (green line) and only the Raman light (orange line) together with a very small fraction of Rayleigh signal will go to the 1800/600/150 grooves/mm grating and detected using either a TE-cooled charge-coupled-device (CCD) or avalanche photodiode (APD). Using optical fiber for beam delivery and signal collection is very convenient. The laser, the spectrometer,

and the detectors can be placed far away from the microscope body. This will minimize the noises caused by the laser, spectrometer, and the detectors, which will be discussed in the later section. For polarized Raman experiments, a $\lambda/2$ plate can be inserted after the bandpass filter to tune the polarization direction of the laser. Thus, the laser beam after this plate does not shift while the polarization direction is tuned.

Figure 3.2. Typical Gaussian beam profile.

The sample is put on a scan table that can be moved coarsely along x - and y -axes. It also can be finely moved with a piezostage that has 100 μm of travel distance along x - and y -directions and 20 μm in the z -direction. During the Raman imaging, the sample is scanned under the focused laser. The Raman spectra from every spot of the sample are recorded and Raman images using peak intensity, peak position, or peak width can be generated after data analysis. The stage movement and data acquisition are controlled using ScanCtrl Spectroscopy Plus software from WITec GmbH, Germany. Data analysis is done using WITec Project software.

3.3 Atomic force microscopy

Besides confocal Raman microscopy, the WITec system can also be used to do AFM. Figure 3.3 shows the more detailed schematic diagram of the AFM. A near-IR laser is used as the deflection beam. This is to prevent the interference of the beam with the excitation laser while performing simultaneous AFM-Raman microscopy.

This system is a sample scanning system, where the cantilever remains at a constant position with the optics while the sample is scanned on the piezostage. The near-IR laser will be focused to the back to the cantilever and reflected back to the four-quadrant position-sensitive photo-detector (PSPD). Through the feedback from the PSPD (depending on the laser spot on the PSPD), the piezostage stage will move up or down in the z -direction to trace the surface topography of the sample while the sample is being scanned in the x - y directions. By using an AFM, it is possible to obtain atomic resolution of surfaces. In addition to that, AFM can also be used to image other surface properties such as adhesion, stiffness, magnetic properties, conductivity and others, depending on different operating modes and types of AFM probes.

Figure 3.3. Schematic diagram of the beam path of the WITec AFM system. 1. near-IR laser, 2. collimator, 3. 4-quadrant position-sensitive photo-detector (PSPD), 4. beamsplitter, 5. dichroic mirror, 6. objective lens, 7. piezo-controlled inertia drive, 8. AFM tip, 9. scan table. (Partially from WITec Manual)

3.4 Vibration control

Since the desired spatial resolution of the system is in nanometer scale, vibrations should be minimized as much as possible. As shown in Figure 3.1, the Raman microscope is placed on top of a vibration isolation table. Then, the whole system is placed on the optical table. The optical table can be floated by compressed air. The main vibration for the whole setup is caused by the cooling fans of the laser head and white light. Using optical fiber for beam delivery and signal collection is very convenient as the laser head can be placed on a different table to minimize the noise.

The spectrometer and the detectors are also detached from the microscope body and isolated from the optical table and put on a separate table. Raman signals collected by the objective lens are directed to the spectrometer using multimode fiber. Since the cooling fan of the white light can introduce noise as well, whenever imaging is on going, the white light should be turned off. With these measures, noise can be suppressed drastically. Hence, high-resolution imaging can be achieved.

3.5 Various samples used in the experiments

As a few topics of interest were covered in this thesis, various samples were needed depending on their objectives. In the following sub-sections, the details of each sample will be described.

3.5.1 Embedded SiGe (eSiGe)/Si periodic lines sample for near-field Raman

As a starting point, the developed microsphere near-field Raman technique was tested using different sizes of polystyrene microsphere. The microspheres were purchased from Polysciences, Inc. In this experiment, embedded SiGe/Si periodic lines sample to simulate *p*-type metal-oxide-semiconductor (PMOS) test structure with ~150 nm channel length with embedded $\text{Si}_{0.72}\text{Ge}_{0.28}$ was used. This sample is from the collaboration with North Carolina State University (NCSU). The sample was grown using ultrahigh vacuum rapid thermal chemical vapor deposition

(UHV-RTCD) system using disilane (Si_2H_6), germane (GeH_4), hydrogen (H_2), and chlorine (Cl_2) as gaseous precursors [1]. Figure 3.4a shows the electron micrograph of the eSiGe/Si periodic lines sample, with the schematic diagram of the cross section view shown in Figure 3.4b.

Figure 3.4. (a) Electron micrograph of the sample. (b) Schematic diagram of the cross section view of the eSiGe/Si periodic lines sample.

3.5.2 Si/SiO₂ sample and bi-layer graphene for spatial resolution determination

In order to determine the spatial resolution of our scanning near-field Raman microscope, a sample with sharp edge can be used, e.g. Si/SiO₂ structure or bi-layer graphene on SiO₂/Si substrate. Before scanning, real-time observation of the Raman peak intensity was done to ensure the focus was on the sample surface.

The electron micrographs of the Si/SiO₂ sample are shown in Figure 3.5a and b. The illustrated cross section view of the sample is shown in the inset of Figure 3.4b. The patterned structure was prepared using advanced device technology, involving photolithography, trench formation, oxidation, and chemical-mechanical-polishing (CMP) to flatten the surface. While scanning across this sample, it was observed that there was a sudden increase in Raman intensity at the edge of the trench (edge effect), which will be discussed in Chapter 5.

Figure 3.5. (a) and (b) are electron micrographs of the Si/SiO₂ sample. Inset is the illustration of the cross-section view at the dash line.

To eliminate any ambiguity in determining the spatial resolution caused by the edge effect, we also scanned the edge of a very thin 2-layer graphene sheet on SiO_2/Si substrate. Thickness of a graphene sheet is ~ 0.3 nm. The graphene sample was prepared by micromechanical cleavage on a silicon wafer with a 300 nm of SiO_2 capping layer [2]. The optical microscope was used to locate the 2-layer graphene sheet and the thickness was further confirmed by either Raman spectroscopy or contrast spectroscopy [3,4]. 2-layer graphene sheet was chosen instead of monolayer graphene sheet in determining the spatial resolution was purely because the Raman intensity of 2-layer graphene sheet was much stronger than it is of monolayer graphene. Figure 3.6a shows the optical image of the graphene sample. As mentioned previously, Raman spectroscopy was employed to determine the thickness of the graphene, in which the spectra are shown in Figure 3.6b. Figure 3.6c shows the Raman image plotted by the intensity of G band. Figure 3.6d shows the cross section of the Raman image from the dash line in Figure 3.6c, showing distinct difference in the Raman G-band intensity from the different thicknesses of graphene sample. By doing so, the 2-layer graphene sheet can be identified easily. So 2-layer graphene sheet is an ideal sample because it has strong enough Raman signal, it has a sharp edge, and most importantly it is thin such that there is no ambiguity in determining the spatial resolution caused by the edge effect.

Figure 3.6. (a) optical image of 1-, 2-, and 3-layer graphene. (b) Raman spectra of different layers graphene sheets and HOPG. (c) Raman image plotted by the intensity of G-band. (d) Cross section of Raman image, which corresponds to the dash line.

3.5.3 Different thicknesses of SiO₂ layer on Si for decay length determination

To determine the decay length, the distance between the microsphere and the bulk silicon can be adjusted using different thicknesses of SiO₂ layer on silicon substrate. Various sample with SiO₂ thicknesses ranging from 8 nm to 500 nm were prepared. Those samples with SiO₂ thickness less than 50 nm were grown using furnace at 950 °C in ambient. But for samples with thickness ranging from 50 nm to 500 nm were grown using plasma-enhanced chemical vapor deposition (PECVD) at 250 °C. Figure 3.7 shows the schematic diagram of the sample, with d is the thickness of the SiO₂ layer.

Figure 3.7. Schematic diagram of SiO₂/Si sample with SiO₂ thickness d .

3.5.4 PMOS transistors with eSiGe stressors for microsphere near-field Raman imaging

Besides the eSiGe/Si periodic lines to simulate the PMOS transistors, we also used the real transistor structures in our experiment. The electron micrographs of the transistor samples are shown in Figure 3.8a and b. As can be seen on the schematic diagrams below the micrographs, the transistors consist of poly-Si gate, Si₃N₄ spacer, SiO₂ isolation, and also eSiGe source drain stressors. The purpose of using eSiGe stressors is to compressively strain the silicon channel, such that the hole mobility in the channel can be improved significantly, which is advantageous for PMOS transistors.

The patterned wafers used in this study were prepared using advanced 65 nm device technology. After spacer formation and Si recess etch, the wafer was cleaned and the epitaxial SiGe growth was performed on a commercially available low-pressure chemical vapor deposition (LPCVD) system. We also show the

capability of the microsphere near-field Raman microscopy in studying the strain on the channel below the poly-Si gates, which is compressively strained by the eSiGe stressors. This shows the real advantage of our approach over the conventional near-field Raman techniques.

Figure 3.8. (a) and (b) are the electron micrographs of two different PMOS transistor samples. Schematic diagrams for both samples are shown directly below the electron micrographs.

3.5.5 Carbon nanotubes (CNT) and gold nanopattern samples

In order to show the capability of the microsphere near-field Raman microscopy not limited to transistor samples, other samples were also used. We have also performed near-field Raman imaging on gold nanopatterns and carbon nanotubes on silicon substrates.

Here are the details in preparing the gold nanopattern sample. Polystyrene microspheres of diameter $0.5\text{ }\mu\text{m}$ were purchased from Polysciences, Inc. The colloids were used as received and mixed with high purity de-ionized water to a density of

approximately 10^{10} beads/ml. 20 μ l of this solution were drop-coated on Si substrate. The polystyrene microspheres will self-assemble to form monolayer after drying, as shown in Figure 3.9a. Gold thin film with a thickness of ~ 100 nm was deposited onto the silicon substrate using DC magnetron sputtering. The sample was sonicated for one minute in chloroform to remove the polystyrene microspheres. The sample was then annealed in Argon ambient at 400 $^{\circ}$ C for 30 minutes. The size of the gold nanopatterns is ~ 100 nm, as shown in Figure 3.9b.

Figure 3.9. Electron micrographs of (a) closely-packed polystyrene microspheres and (b) gold nanopatterns on silicon substrates.

Carbon nanotubes sample was also prepared on silicon substrate. The purified HiPCO single-walled carbon nanotubes (SWNTs) were purchased from Carbon Nanotechnologies. 10 mg of HiPCO SWNTs was dispersed in 100 ml D₂O solution with 1 wt % sodium dodecyl sulfate (SDS). The dispersion was then treated by probe sonication (Sonics & Materials Inc., Model: VCX 130) at a power level of 250 W for 30 minutes, followed by ultra-centrifugation at 140,000 g-force for four hours. The

supernatant was drop-cast on silicon substrate and dried in air. Individual (or small bundled) tubes on the substrate were then obtained after rinsing with pure water. The near-field Raman images of these two samples will be shown in Chapter 5.

3.5.6 Strained silicon on top of relaxed SiGe layer for surface sensitive study using polarized Raman spectroscopy

Last but not least, for surface sensitive study using polarized Raman spectroscopy, a sample consists of 20 nm strained silicon layer grown on 1 μm relaxed $\text{Si}_{0.75}\text{Ge}_{0.25}/2$ μm graded $\text{Si}_{1-x}\text{Ge}_x$ ($x = 0$ to 0.25)/bulk silicon was used. The schematic diagram is shown in Figure 3.10. The thin silicon layer on top is tensile strained silicon. This is due to the bigger lattice constant of the relaxed SiGe layer below than that of the silicon layer. This type of sample is very important for NMOS transistor because the channel of NMOS transistor needs to be tensile strained, in contrary to PMOS transistor, such that the electron mobility in the channel can be improved.

This sample is ideal for the surface sensitive study using the polarized Raman spectroscopy. This is because the Raman signal from the top and bottom layers are separated, so that the surface enhancement factor can be defined accurately.

Figure 3.10. Schematic diagram of 20 nm strained silicon layer grown on 1 μm relaxed Si_{0.75}Ge_{0.25}/2 μm graded Si_{1-x}Ge_x (x = 0 to 0.25)/silicon substrate.

3.6 References

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Chapter 4

Hardware preparation, laser trapping mechanism, and Brownian motion

4.1 Microsphere near-field Raman microscopy

For the microsphere near-field Raman microscopy [1], sample needs to be placed in a sample cell with diluted microspheres in water. During scanning, only one microsphere is trapped and pushed down by the laser beam. The illustration of the typical sample cell with a trapped microsphere is shown in Figure 4.1. Mechanism of trapping will be discussed in the later section.

Figure 4.1. Detailed description of the typical sample cell: (1) water immersion lens (60X NA=1.2), (2) water, (3) focused laser, (4) cover glass, (5) microsphere, (6) sample, and (7) sample cell.

As mentioned in Chapter 3, there are three sizes of multimode fiber available for our system. They are 25 μm , 50 μm , and 100 μm . The choice of the fiber size as

pinhole is important for imaging. In one hand, we want the signal to be as high as possible, but on the other hand we want to have highest spatial resolution possible. For the near-field Raman imaging, 25 μm fiber is always being used to achieve the highest spatial resolution possible.

4.2 Fabrication of sample cells

As the method used in our near-field Raman involving trapping of microsphere in liquid, there is a need to have a container in which the sample will be immersed in the microsphere solution. There were many considerations in fabricating the container, or we would call it *sample cell* from now on.

As the first attempt, we fabricated a sample cell made of glass. Microscope slides were cut into pieces. The pieces were then glued together to form a cavity at the center such that the sample and the solution can be kept inside. Figure 4.2a shows the picture while near-field imaging was on going, and Figure 4.2b shows the picture of the sample cell made of microscope slides. The drawback of this sample cell was the solution would seep through the glued regions, causing it to dry easily.

Figure 4.2. (a) Illustration (b) Picture of the typical sample cell made of glass stack. (c) Picture of the aluminium sample cell. (d) Picture of the improvised aluminium sample cell with adjustable sample plate.

To prevent the solution from drying easily, we fabricated another sample cell made of aluminium plate. It was made by dimpling such that a cavity was formed at the center of the plate. The picture of the aluminium sample cell is shown in Figure 4.2c. By using this type of sample cell, we could overcome the problem. Both glass and aluminium sample cells can only accommodate samples with certain thicknesses. In order to accommodate samples with different thicknesses, sample cells with different cavity depth need to be made.

Another improvisation was done to the sample cell. An adjustable plate was added so that the distance from the sample surface to the cover glass could be adjusted. This is to accommodate samples with various thicknesses. Figure 4.2d shows the picture of the sample cell with the adjustable sample plate at the center. The sample cell can be adjusted up and down by rotating it. Besides aluminium, to reduce the weight of the sample cell, other materials can also be used. We have also fabricated a sample cell from Teflon and it is shown in Figure 4.3.

Figure 4.3. Sample cell made of Teflon.

So various materials can be used to fabricate the sample cell, e.g. glass, aluminium, and Teflon, to name a few. The design of the sample cell will depend on the dimension of the sample. The sample cells shown in Figure 4.2d and 4.3 are also suitable when cross section imaging of sample is required.

4.3 Laser trapping mechanism

From simulation and experimental studies, as discussed previously in Chapter 2, an individual dielectric microsphere can enhance the backscattered intensity by small particles, and photonic nanojet with sub-diffraction limit spatial resolution can be achieved [2-6]. Based on these, the microsphere near-field Raman microscopy was developed [1]. In this section, we shall discuss the principle in trapping the dielectric microsphere, which is based on optical tweezers.

Ashkin and coworkers introduced optical tweezers in 1986 [7], where a focused light was used to trap and move particles around repeatedly. This technique provides a unique approach in controlling the movement of small particles and has played a revolutionary role in physics [8-13] and biology [14-21]. Some reviews of optical tweezers have been published recently [22-24]. For illustration, imagine a microsphere with refractive index larger than that of the surrounding medium, placed off-axis in a focused Gaussian beam as shown in Figure 4.4a. A pair of rays “ a ” and “ b ” (ray “ a ” has higher intensity than ray “ b ”) strike the microsphere about its center with the initial momentum “ Pa ” and “ Pb ”, respectively. The rays will refract through the particle and this refraction results in a change in momentum of the rays, “ ΔPa ” and “ ΔPb ” respectively. According to Newton's 3rd law, there will be an equal and opposite change in momentum on the microsphere. Hence, we have “ $-\Delta Pa$ ” and “ $-\Delta Pb$ ” as illustrated in Figure 4.4a. This will give rise to forces F_a and F_b in the

direction of the momentum change.

The net force can be resolved into two components, scattering force (F_{scat}) that pushes the particle in the direction of the incident light, and gradient force (F_{grad}) that tries to pull the microsphere into the center of the light intensity. For a microsphere at the center of the beam, the rays are refracting through the microsphere symmetrically, resulting in no net lateral force ($F_a = F_b$), and there is no net gradient force component. For a particle with an index of refraction lower than that of the surrounding medium (e.g. water droplets in oil), the refraction through the particle reverses, $F_a < F_b$, and such a particle should be pushed out of the beam.

Figure 4.4. (a) Origin of F_{scat} and F_{grad} for high index sphere placed off-axis from TEM₀₀ beam. (b) The schematic diagram of how the microsphere is being trapped by the laser beam, while the sample in the sample cell is being scanned by the piezostage.

To have a three-dimensional trapping, an objective lens with a high NA is required. This is to create a steep intensity gradient that causes a gradient force in the z -direction. This force will oppose the scattering force. Hence, the particle can be stably trapped within three dimensions. However, in our microsphere near-field Raman microscopy, three-dimensional trapping is not necessary. We just need to

make sure the microsphere is being trapped and in contact with the sample surface during scanning.

As mentioned previously, in our setup the dielectric microsphere needs to be in “contact” with the sample surface during scanning. The scattering force will push the microsphere in the direction of the incident light. L. E. Helseth [25] and N. Shojiro *et al.* [26] have shown approaches to determine the scattering force. We can estimate how strong force a laser beam will exert on a polystyrene microsphere. Since radiation pressure σ is just force divided by area, we can write the average radiation pressure as $\sigma=F/A$. We also know that the magnitude of the force on the surface must be equal to the change in energy ΔE of the light beam per change in its position Δx (since the light beams transfers all its energy to the surface, and energy is as we know conserved), such that,

$$\sigma = \frac{F}{A} = \frac{1}{A} \times \frac{\Delta E}{\Delta x} \quad (4.1)$$

We may now manipulate this expression by writing,

$$\sigma = \frac{1}{A} \times \frac{\Delta E}{\Delta x} = \frac{1}{A} \times \frac{\Delta E}{\Delta x} \times \frac{\Delta t}{\Delta t} = \frac{1}{A} \times \frac{\Delta E}{\Delta t} \times \frac{\Delta t}{\Delta x} \quad (4.2)$$

Since the power is given by $P=\Delta E/\Delta t$, velocity of light is $c=\Delta x/\Delta t$, and the intensity on the surface is given by power P (of the light beam) per area A , i.e. $I=P/A$, we can now write,

$$\sigma = \frac{1}{c} \times \frac{P}{A} = \frac{I}{c} \quad (4.3)$$

We therefore see that the radiation pressure is simply proportional to the intensity of the light beam. And we can write the force as,

$$F = \sigma \times A = \frac{1}{c} \times \frac{P}{A} \times A = \frac{P}{c} \quad (4.4)$$

In our setup, for ~3 mW laser on the microsphere (the power of the laser can be adjusted using a linear attenuator), with $c=3 \times 10^8$ m/s scattering force to push the microsphere can be estimated to be just about 10^{-11} N or 10 pN. This is a very small force. However, it does play an important role at the microscopic scale, where such small forces can be used to push particles around, in our case to push the dielectric microsphere to the sample surface.

During mapping, the movement of piezostage is controlled using ScanCtrl Spectroscopy Plus software from WITec GmbH, Germany. The laser beam is fixed, so the position of the trapped microsphere is fixed as well. The software can control the speed of forward and backward scans of the piezostage. This is very important in order not to lose the microsphere during scanning. The mapping mechanism is illustrated in Figure 4.4b.

4.4 Brownian motion

As the microspheres are suspended in liquid, they are subjected to the Brownian motion, which is the random motion of particles in liquid caused by the bombardment of the particles by molecules of the liquid. Brownian motion was first observed by a Scottish botanist called Robert Brown in 1827 when he was studying plant pollens

jiggling around in the liquid under the microscope [27]. Review of Brownian motion has been published recently by M. D. Haw [28].

This phenomenon was later explained by Einstein in his paper on Brownian motion published in 1905 [29]. From Stokes-Einstein formula, the diffusion coefficient D of spherical particles of radius r in a fluid of viscosity η at temperature T is shown in equation (4.5) with k is the Boltzmann's constant.

$$D = \frac{kT}{6\pi\eta r} \quad (4.5)$$

The displacement of the spherical particle is shown in equation (4.6) below.

$$\lambda = \sqrt{2Dt} \quad (4.6)$$

From both equations, we can see that the distance traveled by the particle grows with the square root of time. Besides that, it also depends on temperature, viscosity of the fluid, the size of particle, and time. So the particle will be less active at lower temperature, more viscous fluid, and the bigger its size. It will also keep moving, as long as the liquid does not dry up.

In the microsphere near-field Raman microscopy, the effect of Brownian motion to the microsphere is important. In Chapter 6, experimental results on the effect of viscous solution, i.e. sugar solution, to the spatial resolution of the technique will be presented.

4.5 AFM probe with a dielectric microsphere

Besides using laser to trap the microsphere, it is also possible to attach a microsphere to a holder, e.g. an AFM probe. By doing so, the concern of worsening of spatial resolution due to Brownian motion can be eliminated, since the microsphere is no longer in liquid.

The AFM probe that we used is the one with the tip visible from the top, so that the AFM cantilever will not block the incoming laser. This commercially available probe is known as ATEC (Advanced Tip at the End of Cantilever) probe from Nanosensor. Figure 4.5a shows the typical SEM micrograph of the probe (taken from Nanosensor website).

Figure 4.5b shows the model of nano-manipulators (Kleindiek Nanotechnik, MM3A-EM) that are used to help attach a 3 μm microsphere to the AFM tip. There are a few steps needed to attach a microsphere on the AFM tip. Firstly, solution with microspheres was dropped and dried on a glass slide. Secondly, a sharp tip, e.g. a tungsten tip that was fabricated using electrochemical-etching method, was used to pick up the microspheres using a nano-manipulator under an optical microscope. Thirdly, the tungsten tip with microspheres was fixed, and another tungsten tip that was mounted to another nano-manipulator used to pick up one microsphere from the previous tungsten tip. Lastly, with the help of the manipulator the single microsphere

was transferred to the AFM tip. To make sure that the microsphere could attach well to the AFM tip, epoxy was carefully applied to the end of the tip. The AFM probe with microsphere was later baked in an oven at 150°C for 30 min to harden the epoxy. Figure 4.5c shows the optical image of an AFM probe that is successfully attached with a single 3 μm microsphere.

Before scanning, real-time observation of the Raman peak intensity was done to ensure the focus was on the sample surface. The AFM probe with the microsphere is brought near to the sample surface. The position of the probe will be later finely moved using piezo-controlled inertia drive until the maximum Raman intensity from the sample is achieved. Finally, the sample is being scanned on the piezostage.

This approach serves as an alternative approach to the near-field Raman imaging with optically trapped microsphere. Besides, by using an AFM tip there will be no Brownian motion that can affect the spatial resolution. It can prevent sample damage or contaminations from the liquid. It is also more stable, and potentially topography image of the sample can be obtained simultaneously if the AFM feedback system is being used. However, in this report we shall only focus on the approach without the feedback system, as the other approach with feedback system still remains work in progress.

Figure 4.5. (a) typical SEM micrograph of the tip (from Nanosensor). (b) high precision nano-manipulators (Kleindiek Nanotechnik, MM3A-EM) used to attach a microsphere to the AFM tip. (c) optical image of an ATEC tip that was successfully attached with a single $3\ \mu\text{m}$ microsphere.

4.6 References

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Chapter 5

Beam width and decay length determination

5.1 Line scan with different sizes of microsphere

As a starting point, different sizes of microsphere were trapped and scanned across eSiGe/Si periodic lines. Figure 5.1a shows the electron micrograph of the sample with marked position *X* and *Y* on Si and eSiGe lines, respectively. Figure 5.1b shows the typical Raman spectra recorded on top of Si (*X*) and eSiGe (*Y*) lines, respectively, obtained using 3 μm polystyrene microsphere. On *Y* (eSiGe line), we can observe a small Raman peak (509.4 cm^{-1}) that comes from Si-Si phonon vibrations of the eSiGe line. While on *X*, there is no SiGe peak observed.

Figure 5.1. (a) Scanning electron micrograph of the eSiGe/Si lines sample with marked lines *X* and *Y* indicating Si and SiGe lines, respectively. (b) Typical Raman spectra from *X* and *Y* lines obtained using 3 μm polystyrene microsphere. Scale bar is 1 μm .

Figure 5.2a shows the line profiles of the integrated intensity of Si-Si vibrations from eSiGe line obtained by scanning different sizes of polystyrene microspheres (diameter = 0.5 μm , 1 μm , and 3 μm) across the sample. As a comparison, we also show the line profile when no microsphere is used. From Figure 5.2a, it is clear that without the microsphere, the eSiGe lines cannot be resolved. Note that the profiles have been translated vertically for better viewing. Figure 5.2b shows the line profiles of the integrated intensity of Si-Si vibrations from eSiGe and Si lines obtained by scanning 0.5 μm microsphere across the sample. Due to the weak SiGe signal, eSiGe profile has been magnified for better viewing. The peak in the eSiGe line profile is the valley in the Si line profile, and vice versa. The line profiles show excellent correspondence with the sample structure with good S/N ratio. Besides this, the results also give a confirmation of the high spatial resolution of the microsphere near-field Raman microscope. The spatial resolution will be quantified in Section 5.2.

Figure 5.2. (a) The line profiles of the integrated intensity of Si-Si vibrations from eSiGe line with and without microsphere. (b) The line profiles from eSiGe and Si lines obtained by scanning 0.5 μm microsphere across the sample. The line profiles show excellent correspondence with the sample structure with good S/N ratio.

Besides the improved spatial resolution, enhancement of Raman intensity was also observed, depending on the size of microsphere and the NA of objective lens being used. Enhancement of Raman intensity by different sizes of microsphere with different NA of objective lens will be discussed separately in Chapter 7.

From these experiments, we observed that the smaller the size of microsphere, the faster it would move in liquid due to Brownian motion. An attempt to reduce the Brownian motion with sugar solution will be presented in Chapter 6. It is also difficult to view the small microsphere under optical microscope, making it difficult to make sure there is only one microsphere being trapped during scanning. So, for the microsphere near-field Raman imaging, 3 μm microsphere will be used. It is more stable to be trapped under optical tweezers and it is reasonably clear under the view of the objective lens.

5.2 Spatial resolution determination using scanning-edge method

To quantify the spatial resolution of a near-field Raman microscope, we need to determine the full-width at half-maximum (FWHM) of the Gaussian beam. This can be done by scanning the beam across a sample that is considerably smaller than the beam width, e.g. a carbon nanotube [1-4], or by scanning the beam across a sample with sharp edge, e.g. Si/SiO₂ structure or bi-layer graphene on SiO₂/Si substrate [5].

For the former method, the FWHM of the beam can be determined straightforwardly, but for the latter method, which is known as scanning-edge method, the intensity profile needs to be fitted with an error function as shown in equation (5.1) below [6]. However, both methods serve the same purpose, to determine the FWHM of the beam. Hence, the spatial resolution of the near-field microscope can be quantified.

$$I(x) = \frac{P}{2} \left\{ 1 - \operatorname{erf} \left(\frac{\sqrt{2}(x - x_0)}{w} \right) \right\} \quad (5.1)$$

P is the total power contained in the laser beam, x is the position of the scanning edge, x_0 is the center of the beam and w is the $1/e^2$ half-width. The spot size of the beam - the full-width at half-maximum (FWHM), can be determined from equation (5.2).

$$FWHM = \sqrt{2 \ln 2} w \quad (5.2)$$

G. Veshapidze *et al* have shown in their study that, in the analysis of Gaussian beam spot size data using scanning-edge method, it is more accurate to directly fit the data with equation (5.1) than to fit the derivation of the data to a Gaussian function [6].

In characterizing the spatial resolution of the microsphere near-field Raman microscope, we used the scanning-edge method due to samples availability. As mentioned in Chapter 3, we used both Si/SiO₂ structure and bi-layer graphene on SiO₂/Si substrate to determine the spatial resolution. Details on the samples have been described in Chapter 3. Before scanning, real-time observation of the Raman peak

intensity was done to ensure the focus was on the sample surface. The typical Raman spectra for both silicon and bi-layer graphene are shown in Figure 5.3.

Figure 5.3. Typical Raman spectra of (a) silicon and (b) bi-layer graphene.

Using the first sample, the trapped 3 μm polystyrene microsphere was scanned across the Si/SiO₂ structure with 10 nm step size. The integrated intensity of Si-Si phonon vibrations from the silicon (Figure 5.3a) was fitted with the equation (5.1). The Si-Si Raman intensity vs position is shown in Figure 5.4a with the fitting result. The spot size of the beam - the full width at half maximum (FWHM), was calculated from equation (5.2) to be 78 nm.

Note that there is a sudden increase of silicon intensity at the edge of the trench. This edge effect can be attributed to increase in Raman scattering volume due to more exposed Si surface at the interface of Si/SiO₂. E. Bonera *et al.* have also suggested in their experiments that the increase in the Raman intensity at the edge may be due to the change in polarization of incoming beam at the focus induced by inhomogeneities

of the surface [7,8].

To eliminate any ambiguity in determining the spatial resolution caused by the edge effect, we have also scanned the edge of a very thin 2-layer graphene sheet on SiO₂/Si substrate. The integrated G-band intensity of the graphene sheet vs position is shown in Figure 5.4b with the fitting result. The calculated spot size is 84 nm. Spatial resolutions obtained from both samples are comparable. Hence, we can conclude that both samples are suitable for the spatial resolution determination.

The high resolution achieved in our approach comes from the tight focusing of incoming beam and collection of Raman signal in the near-field region. The incoming beam will be focused by the microsphere to a sub-diffraction limit focus size as discussed previously in Chapter 2. On top of that, during imaging, the microsphere is pushed by the scattering force of the incoming beam to the sample surface. In this way, the collection is done in the near-field region in which the detailed information of the sample exists. Hence, high spatial resolution can be achieved with this approach.

Figure 5.4. (a) Si-Si Raman intensity vs position with the best fit to equation (5.1) to determine the laser spot size. The spot size of the beam - the full-width at half-maximum (FWHM), was calculated to be 78 nm. (b) Integrated G-band intensity vs position of a 2-layer graphene sheet. The calculated spot size is 84 nm.

5.3 Decay length determination using different thicknesses of SiO₂ layer on silicon substrate

To determine the decay length, the distance between the microsphere and the bulk silicon was tuned by growing different thicknesses of SiO₂ layer. The methods of preparation have been described in Chapter 3. Figure 5.5 shows the Raman enhancement factor (E_f), which is defined in equation (5.3) below, versus the SiO₂ thickness (d).

The Raman enhancement factor, E_f , is defined as,

$$E_f = \frac{(I_{Si\ peak} - I_{background})_{(with\ PS)}}{(I_{Si\ peak} - I_{background})_{(without\ PS)}} \quad (5.3)$$

Red curve in Figure 5.5 is the fitting result to equation (5.4) below,

$$y(d) = y_0 + Ae^{\left(\frac{-d}{t}\right)} \quad (5.4)$$

where d is the SiO_2 thickness, y_0 and A are constants, and t is the decay length. Inset shows the schematic diagram of the sample. The silicon intensity exponentially decays to a constant value with a decay length (t) of ~ 140 nm.

Figure 5.5. Raman enhancement factor vs SiO_2 thickness. Red curve is the fitted data to equation (5.4). Inset shows the schematic diagram of the sample.

The short decay length provides an advantage of this technique over normal far-field Raman imaging, as background signal can be minimized. As comparison, in far-field configuration with the same incoming laser ($\lambda = 532$ nm), the decay length on Si is ~ 1 μm . This is evident when Raman imaging on PMOS transistors is performed, as will be shown in the next chapter.

5.4 Conclusion

In conclusion, different sizes of microsphere were trapped using optical tweezers and scanned across eSiGe/Si periodic lines. The line profiles from different sizes of microsphere confirmed microsphere near-field Raman microscopy has better spatial resolution than far-field Raman microscopy (without the microsphere). All near-field line profiles show excellent correspondence with the sample structure with good S/N ratio. Smaller spheres are not favorable because they are difficult to view under microscope and they are very active in liquid due to Brownian motion. To quantify the spatial resolution, a 3 μm microsphere was trapped and scanned across Si/SiO₂ structure and bi-layer graphene on SiO₂/Si substrate. We have achieved sub-diffraction limit spatial resolution of $\sim 80\text{ nm}$ ($\sim \lambda/7$). Decay length was also estimated to be $\sim 140\text{ nm}$.

5.5 References

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Chapter 6

Results from microsphere near-field Raman microscopy

6.1 1D near-field Raman mapping on PMOS transistors

Many studies and publications on near-field Raman imaging have been focused on the imaging of carbon nanotubes and DNA samples [1-3]. We would like to take this opportunity to show the capability of near-field Raman imaging to study real transistor samples.

In this section, we focus on the study of PMOS transistors with SiGe source drain stressors and poly-Si gate, in which the channel is under compressive strain by the SiGe stressors. The patterned wafers used in this study were prepared using advanced 65 nm device technology as elaborated in Chapter 3. We also show the capability of our technique in studying the strain on the channel below the poly-Si gates, which is compressively strained by the embedded SiGe stressors [4].

Straining the silicon can suppress the inter-valley scattering and reduce the effective carrier mass. Hence, it results in an improvement of the effective carrier mobility in the Si channel. Semiconductor industry has used mechanical strain as an alternative to physical scaling in improving the transistor performance [5]. Appropriate strain applied to the channel region can significantly improve transistor

performance. However, in complementary metal-oxide-semiconductor (CMOS) transistor, n-MOS and p-MOS need to be strained differently. The compressive strain is known to be beneficial for p-MOS and the tensile strain is known to improve the n-MOS performance [6,7]. That is why a technique to characterize strain with sub-100 nm resolution reliably is high in demand.

Figure 6.1a and 6.1b show the Raman spectra recorded in the SiGe line region and on top of the poly-Si line, respectively. Each spectrum was fitted with three Lorentzian peaks. In Figure 6.1a, the Raman peaks from SiGe line correspond to Si-Si phonon vibrations from the SiGe (510.4 cm^{-1}), tensile-strained Si just below the SiGe (518.9 cm^{-1}), and the Si substrate below (520.6 cm^{-1}), respectively. Similarly, in Figure 6.1b, the Raman peaks correspond to Si-Si phonon vibrations of poly-Si (516.3 cm^{-1}) and bulk Si below (520.6 cm^{-1}), and another one is from compressively strained silicon in the channel region (522.1 cm^{-1}).

Figure 6.1. The Raman spectra from (a) SiGe and (b) poly-Si lines with fitted peaks using Lorentzian function. In spectrum a, the Raman peak at 510.4 cm^{-1} corresponds to Si-Si phonon vibrations from SiGe, while the peaks at 518.9 and 520.6 cm^{-1} belong to tensile-strained Si just below the SiGe and the bulk Si substrate, respectively. In spectrum b, the Raman peaks at 516.3 , 520.6 and 522.1 cm^{-1} correspond to Si-Si phonon vibrations of poly-Si, bulk Si substrate and compressively strained Si in the channel region, respectively.

The strain value in the channel can be calculated from the Raman peak positions. A compressive strain will result in the blue shift of the strained Si peak compared to that of the unstrained Si. According to I. De Wolf [8], the uniaxial stress can be calculated from the Raman shift according to,

$$\sigma(\text{MPa}) = -434\Delta\omega(\text{cm}^{-1}) \quad (6.1)$$

From the stress (σ) values, the strain (ϵ) value can be calculated from the relation, $\epsilon = \sigma/E$, where E is the Young's modulus of Si $\langle 110 \rangle$ along the channel, which is 170

GPa [9]. Hence, the strain can be calculated as follows,

$$\varepsilon(\%) = -0.26\Delta\omega(\text{cm}^{-1}) \quad (6.2)$$

As shown in Figure 6.1b, the peak at 522.1 cm^{-1} is attributed to be from the compressed channel region. There is a blue shift of 1.5 cm^{-1} from the unstrained silicon peak (520.6 cm^{-1}). A blue shift of 0.023 cm^{-1} would represent a compressive strain of 10 MPa. From equation (6.1), the shift of 1.5 cm^{-1} in the channel corresponds to a compressive stress of 651 MPa; and from equation (6.2), it corresponds to a compressive strain of 0.39 %.

Figure 6.2 shows the SEM image of the device sample together with the detailed illustration diagram of the device structure below. From Figure 6.2 we can see the line profile of the integrated intensity of Si-Si phonon vibrations from the SiGe (yellow color), and the Si-Si peak position from the bulk Si (purple color) scanned across the device. The results show excellent correspondence with the device structure with good S/N ratio.

Figure 6.2. Scanning Electron micrograph with cross-section view diagram of periodic poly-Si lines and SiGe stressors. Line-scan of Raman Si-Si intensity from SiGe is shown in yellow color, and the Si-Si peak position from the bulk Si is in purple color. The line scans show excellent correspondence with the structure.

Figure 6.3 shows the SEM image of another sample together with the detailed illustration diagram of the device structure below. From Figure 6.3 we can see the line profile of the integrated intensity of Si-Si phonon vibrations from the SiGe (green color), scanned across the device. The line scan only shows the position of the SiGe stressors labeled as (-5, -3, -1, 1, 3, 5) in blue color. The result also shows excellent correspondence with the device structure with good S/N ratio.

Figure 6.3. Scanning Electron micrograph with cross-section view diagram of periodic poly-Si lines and SiGe stressors. Line-scan of Raman Si-Si intensity from SiGe is shown in green color. The line scans show excellent correspondence with the eSiGe stressors labeled as (-5, -3, -1, 1, 3, 5) in blue color.

6.2 2D near-fied Raman mapping on PMOS transistors

Figure 6.4a shows the $4.0 \times 1.3 \mu\text{m}^2$ near-field Raman image from the intensity of Si-Si phonon vibrations from the SiGe of the structure shown in Figure 6.2. For comparison, Figure 6.4b shows the image from confocal Raman setup (far-field imaging). It is clear that our near-field technique can resolve the periodic lines with excellent repeatability, but far-field technique cannot resolve the lines at all. The fact that it took only about six minutes to carry out the mapping means high-resolution Raman imaging using our technique can be performed in reasonable time.

Figure 6.4. (a) and (b) are $4.0 \times 1.3 \mu\text{m}^2$ near-field and confocal Raman images of the periodic poly-Si lines and SiGe stressors obtained in about six minutes, respectively, generated from the Si-Si peak intensity from SiGe.

6.3 2D near-field Raman mapping of gold nanopatterns & CNTs on silicon substrate

We have also performed Raman mapping on gold nanopatterns. Gold nanopatterns were fabricated on silicon substrate with the size of ~ 100 nm. The fabrication method has been elaborated previously in Chapter 3.

Figure 6.5a and 6.5b show the $5.0 \times 5.0 \mu\text{m}^2$ (100x100 points) near-field and confocal Raman images of gold nanopatterns, respectively. Figure 6.5a shows the Raman image from the Si-Si peak intensity. Darker regions correspond to the gold nanopatterns. It can be clearly seen that the gold nanopatterns with the size of ~ 100 nm can be clearly resolved using our technique. The near-field Raman image

corresponds well to the electron micrograph as shown in the inset of Figure 6.5a. The confocal Raman image of the gold nanopatterns shows no details of the patterns, as shown in Figure 6.5b. This proves the capability of our technique to various samples.

Figure 6.5. (a) and (b) are $5.0 \times 5.0 \mu\text{m}^2$ near-field and confocal Raman images of the gold nanopatterns, respectively, generated using Si Raman peak intensity from the substrate. The white dots illustrate the gold nanopatterns on the substrate. Inset shows the SEM image of the gold nanopatterns with the size of the nanopatterns is $\sim 100 \text{ nm}$.

We have also tried the near-field technique on carbon nanotubes (CNTs). Figure 6.6 shows the near-field Raman image from the G band intensity.

Figure 6.6. Near-field Raman image of carbon nanotubes (CNTs), generated using G band peak intensity. Inset shows the Raman spectrum of CNTs. Scale bar is 1 μm .

6.4 Reduction of Brownian motion with sugar solution

In order to reduce the Brownian motion of the microsphere, one alternative solution that is easily made is sugar solution. In this experiment, different amount of sugar was dissolved in de-ionized water by weight. The 3 μm microsphere was trapped and scanned across the Si/SiO₂ lines sample in sugar solution with different sugar concentration (0% - 40%). The beam widths were characterized using the scanning-edge method as discussed previously in Chapter 5. The Si-Si intensity profiles were fitted with equation (5.1) and the beam widths were calculated using equation (5.2).

Figure 6.7a shows the beam widths (FWHM) with different sugar concentration

in de-ionized water. The higher the sugar concentration is, the viscosity increases exponentially as shown in Figure 6.7b [10]. As can be seen in Figure 6.7a, the spatial resolution starts to improve, as the sugar solution viscosity gets higher. This can be attributed to the reduction in movement of the microsphere due to Brownian motion. Spatial resolution of ~ 66 nm can be achieved with 30% sugar solution. As we increased the viscosity of sugar solution further (i.e. 40%), the microsphere became more difficult to be trapped as the drag force on the microsphere increased. Further increased of the viscosity (i.e. 50%) had made the optical trapping not possible as the trapping force was not able to overcome the drag force.

Figure 6.7. (a) Beam width (FWHM) with the function of sugar concentration in de-ionized water. (b) Viscosity of sugar solution at different concentrations [10].

In the next section, the attempt to completely remove the Brownian motion will be presented. AFM tip with attached microsphere will be used to perform the near-field Raman imaging.

6.5 1D and 2D near-field Raman mapping on Si/SiO₂ lines and PMOS transistors using AFM tip with a single microsphere

As mentioned in Chapter 4, we have also developed a near-field Raman microscopy by using a single microsphere attached to an ATEC tip. Once the microsphere is attached on to the tip, the tip will be attached to a piezo-controlled holder. So the microsphere can be controlled such that the incoming laser will be aligned to the center of the microsphere. While the tip with the microsphere was approaching the sample, real-time observation of the Raman peak intensity is needed to ensure the focus is on the sample surface.

Figure 6.8a and 6.8b show the integrated Si-Si peak intensity of the Si/SiO₂ lines sample, which has been elaborated in Chapter 3. Figure 6.8a shows the comparison between near-field and far-field profiles on small Si lines, with near-field profile shows a much higher spatial resolution. Figure 6.8b shows the profiles on bigger Si lines. The edges of the near-field profile are much sharper, which suggests a better spatial resolution. Besides the good spatial resolution, near-field profiles also show a higher Raman intensity.

Figure 6.8. (a) and (b) are the comparison between near-field and far-field Raman line profiles of small and big Si lines, respectively, using AFM tip with a single microsphere.

Figure 6.9a shows the near-field Raman image from the intensity of Si-Si phonon vibrations from the same PMOS transistors sample that was shown in Figure 6.2. This image was obtained by using an objective lens with a small numerical aperture ($\text{NA} = 0.4$). At the moment, higher NA objective lens are not possible, due to the short working distance between the lens and the sample. As comparison, Figure 6.9b shows the image from confocal Raman microscope (far-field imaging) using a much better objective lens ($\text{NA} = 0.95$). It is clear that our near-field technique can resolve the periodic SiGe lines, but far-field technique cannot resolve them at all.

Figure 6.9. (a) and (b) are near-field and confocal Raman images of the periodic poly-Si lines and SiGe stressors, respectively, generated from the Si-Si peak intensity from SiGe. Scale bar is 0.8 μm .

This approach shows a great potential in achieving high-resolution Raman image. It is expected to be more stable, since there is no Brownian motion that can worsen the spatial resolution. It is also very useful for sample that cannot be immersed in liquid. Further improvement can be done, e.g. by using an objective lens that has higher NA and longer working distance, so that there is a room for the AFM tip and microsphere. And better spatial resolution can be obtained.

6.6 Near-field white light microscopy

Apart from the microsphere near-field Raman imaging shown in the previous section, with the similar configuration we also can perform microsphere near-field white light imaging. To direct the light source (tungsten halogen lamp, excitation range from 350 to 850 nm) to the microsphere and sample, a 50:50 beamsplitter (labeled with “(8)”) was put in the optical path, as shown in Figure 3.1 Chapter 3. The

reflected light was collected using backscattering configuration (with a 25 μm multimode optical fiber) and directed to a 150 grooves/mm grating and detected with a TE-cooled charge-coupled-device (CCD).

To show the capability of this novel approach, we used gold nanopattern on Si sample. The sample was prepared using polystyrene microspheres with diameter of 1 μm . The details of sample fabrication are similar to those elaborated earlier in Section 3.5.5, except no annealing was done after pattern formation.

Figure 6.10a shows the optical spectrum of the light source with the excitation range from 350 to 850 nm. The deep around 532 nm in the optical spectrum is caused by the holographic bandpass filter for Raman experiment. Figure 6.10b is the near-field Raman image from the Si-Si peak intensity using small NA lens ($\text{NA} = 0.4$), and the darker regions correspond to the gold nanopatterns. Figure 6.10c to 6.10f are the near-field white light images obtained by integrating the white light intensity in different spectral ranges, as indicated on each image. From these near-field images, we could see the gold nanopatterns clearly, which correspond well with the near-field Raman image. As comparison, by removing the microsphere, we would get the far-field images, as shown in Figure 6.10g to 6.10j. Similar method was used to generate these images, which was by integrating the white light intensity in the ranges shown on each image. It is clear that our near-field technique can resolve the periodic gold nanopatterns, but in far-field technique the gold nanopatterns cannot be resolved.

Hence, we confirm the high spatial resolution of this near-field white light microscopy.

Figure 6.10. (a) The typical optical spectrum of tungsten halogen lamp, (b) Near-field Raman image. (c)–(f) Near-field white light images. (g)–(j) Far-field white light images. Details of the images are on the text. Scale bar is 2 μm for all images.

Near-field white light microscopy may have a potential in the study of metallic nanostructures and biological samples, in which the studies in different spectral regions are needed. This technique can also be extended to the development of microsphere fluorescence microscopy.

6.7 Conclusion

In this chapter, we have shown the microsphere near-field imaging on different types of samples, starting from PMOS samples, gold nanopattern, and CNTs on silicon substrate. We showed the capability of the microsphere near-field technique in

studying the strain on PMOS transistors with eSiGe source drain stressors. In this sample, the silicon channel was compressively strained by the SiGe stressors and was calculated to be 0.39 %, which corresponds to a compressive stress of 651 MPa.

With sugar solution, we showed it is possible to improve the spatial resolution further by reducing the Brownian motion of the microsphere. Spatial resolution of ~66 nm could be achieved with 30% of sugar solution. However, further increasing the concentration will make the solution too viscous and trapping may be not possible. To eliminate the Brownian motion, AFM tip with a single microsphere was used to image Si/SiO₂ lines and PMOS transistors. Comparisons of the near-field images with far-field images, confirmed the superiority of the microsphere near-field technique than far-field microscopy. Both developed near-field Raman techniques, show great potential in producing high-resolution Raman image. They are non-destructive, high reproducibility (almost 100%), fast (strong signal), and easy to use compared to other conventional near-field Raman techniques, e.g aperture and apertureless methods, that have been discussed in Chapter 2.

Apart from near-field Raman imaging, the microsphere approach can be also be used in white light microscopy. The microsphere near-field white light microscopy showed a better resolution compare to far-field microscopy. This technique may have a great potential in the study of nanostructures and biological samples, in which different spectral information are needed. Based on this work, it can also be extended

to the development of microsphere fluorescence microscopy.

6.8 References

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Chapter 7

Individual dielectric microsphere for the enhancement of Raman spectroscopy

7.1 Introduction

Apart of using SERS for Raman signal enhancement, in this chapter we will discuss on the Raman signal enhancement using an individual dielectric microsphere. Dielectric microspheres, e.g. polystyrene (PS) or silica (SiO_2) microspheres, have been used in many research areas. H. J. Münzer *et al.* have successfully created nanopatterns on silicon and glass surfaces by irradiating laser pulses to the PS microspheres [1]. M. Sasaki *et al.* have showed that a microsphere manipulated by optical tweezers can be used as a micro-objective [2]. This micro-objective can observe area that cannot be observed using conventional microscope. The use of microspheres in optical tweezers works, e.g. for studying DNA, also has been reported [3,4]. M. H. Wu *et al.* have used PS microspheres to generate submicron features using projection photolithography [5]. PS microspheres also have been used to fabricate solid immersion lens (SIL) to improve spatial resolution in microscopy [6]. L. H. Mak *et al.* even went further to attach a microsphere on a cantilever [7]. And just recently, E. McLeod *et al.* have showed nanopatterning using optically trapped microspheres [8].

Recent theoretical study by X. Li *et al.* showed that by illuminating dielectric sphere, it is possible to focus visible light to sub-diffraction limit spot size, on what they called as photonic jet [9]. The photonic jet is a narrow, high-intensity beam that propagates into the background medium from the shadow-side surface of a plane-wave illuminated lossless dielectric cylinder or sphere of diameter comparable to the wavelength. It is also interesting to note that they showed photonic nanojet has a very high resolving power. It can be used to detect sub-nanometer size particles using visible light. S. Lecler *et al.* also reported on the three dimensional properties of photonic nanojet [10].

Through the formation of photonic jet, dielectric microspheres can focus light into sub-diffraction limited size at the shadow surface of the sphere. Taking advantage of this feature of photonic jet, backscattering enhancement of metal particles [11] and detection of deeply sub-wavelength pits in data-storage disks [12] have been realized at microwave frequency. Photonic jet driven enhancement of optical spectra signals is expected as well. Enhancement of two-photon fluorescence [13] and Raman scattering by closely packed dielectric microspheres has been reported recently [14]. P. Ferrand *et al.* even showed the direct imaging of photonic nanojets [15].

Motivated by these, in this chapter, we present the one-to-one correspondence study between different sizes of individual PS microsphere and the enhanced Raman signal of crystalline Si. Different numerical aperture (NA) effect on the enhancement

will be discussed as well. This work is also helpful for choosing an appropriate size of dielectric sphere in microscopy, where individual dielectric particle is favorable because it is easy to be manipulated and available in various sizes. As another example, the enhanced Raman spectrum of 4-MBA molecules by individual sphere is shown as well.

7.2 Experimental

Polystyrene (PS) microspheres ($n=1.59$ at $\lambda=532$ nm) [16] with different diameters ($d = 0.203, 0.356, 0.465, 0.530, 0.914, 2.790, 3.156, 4.650$ and 10.320 μm) were purchased (Polysciences) in suspension. The suspension was further diluted in deionized water and sonicated for 10 minutes. After that, a few drops of the different suspension were dispersed on clean (001) silicon substrates, and were let dry to obtain individual sphere with inter-sphere distance larger than 50 μm . The configuration for Raman experiments has been discussed in Chapter 3. In this study, several microscope objective lens ($\text{NA} = 0.4, 0.55, \text{ or } 0.95$) were used.

Beam diameters (Γ) for different NA objective lens were determined by scanning-edge method across a Si/SiO₂ structure (Figure 7.1d) [17]. Figure 7.1a to 7.1c show the line profiles across the structure for different NA objective lens. The line profiles were fitted with equation (5.1). From w obtained from equation (5.1), Γ

can be determined from equation (7.1), where the Gaussian intensity drops to $\sim 1.9\%I_0$.

$$\Gamma = 2\sqrt{2}w \quad (7.1)$$

The beam diameters (Γ) are measured to be $2.83 \mu\text{m}$, $0.94 \mu\text{m}$, and $0.58 \mu\text{m}$, respectively.

Figure 7.1. Laser intensity when it was scanned across a Si/SiO₂ structure for different NA objective lens: (a) NA0.4, (b) NA0.55, (c) NA0.95, and (d) the schematic diagram of the Si/SiO₂ structure.

7.3 Results and discussion

Figure 7.2 shows a typical Raman spectra of crystalline silicon substrate, silicon substrate with a PS microsphere ($d = 3.156 \mu\text{m}$), and a PS microsphere on glass slide, with NA = 0.4 objective lens. The power and the integration time were kept the same for the enhancement experiments. The Raman spectrum of silicon substrate exhibits a strong first-order Raman peak at 520 cm^{-1} . After adding the PS microsphere, the intensity of the Si peak can be enhanced obviously. There is no Raman peak of PS microsphere at 520 cm^{-1} . This shows that the observed enhancement is not due to the superposition of PS peak with silicon peak.

Figure 7.2. (a) Raman spectra of (a) crystalline silicon substrate without PS microsphere, (b) crystalline silicon substrate with $3.156 \mu\text{m}$ PS microsphere, and (c) PS microsphere on glass slide.

Various sizes of PS microspheres were dispersed on the Si substrates. The

purpose is to study the effect of the size of PS microspheres to the enhancement in Raman spectroscopy. From equation (5.3) in Chapter 5, the Raman enhancement factor, E_f , from different sizes of PS microspheres can be obtained, which is plotted in Figure 7.3 as a function of the PS diameters with different NA of objective lens.

Figure 7.3. Raman enhancement factor E_f as a function of the PS diameters for different objective lens (a) NA = 0.4, (b) NA = 0.55, and (c) NA = 0.95, respectively. Black and red dots represent the experimental and simulation results, respectively.

For NA = 0.4, as can be seen in Figure 7.3a, E_f increases with the PS diameters and can reach as high as ~ 11 by using $3.156 \mu\text{m}$ PS microsphere, and then decreases for larger microspheres. To understand the size dependence better, we have calculated

the E_f for the other objective lens by changing the NA to 0.55 and 0.95, and the corresponding results are shown in Figure 7.3b and 7.3c, respectively. Similar to Figure 7.3a, maximum points occur in Figure 7.3b and 7.3c as well, at which strongest enhancement of Raman scattering is obtained for $d = 0.914 \mu\text{m}$ and $0.530 \mu\text{m}$ for $\text{NA} = 0.55$ and $\text{NA} = 0.95$, respectively. It is interesting to note that the maximum enhancement for each NA occurs when the microsphere diameter is approximate to the beam diameter (Γ), which was calculated in the earlier section.

To understand the enhancement mechanism, numerical simulations of the light propagation through the dielectric microsphere were carried out using the software COMSOL Multiphysics® for $\text{NA}=0.4$. The simulated intensities ($|E|^2$) are shown in Figure 7.4a, 7.4b, and 7.4c for PS microspheres with diameter of $0.530 \mu\text{m}$, $3.156 \mu\text{m}$, and $4.650 \mu\text{m}$, respectively. As can be seen in Figure 7.4, the incoming light is focused in the forward direction along the propagation direction near the shadow surface of the microspheres, forming the photonic jet. The simulated $|E|^2$ at the shadow surface of the microspheres for different diameters of microsphere and NA are plotted in Figure 7.3 for direct comparison with experimental results. The simulated results are consistent with the experimental results. This indicates that the Raman enhancement by an individual PS microsphere is from the localized electric fields within the nanojets in the vicinity of the microsphere along the propagation direction of the incident laser.

Figure 7.4. Simulated distributions of the $|E|^2$ for the different diameters of PS microspheres using the software COMSOL Multiphysics[®]. The microsphere diameters are 0.530 μm , 3.156 μm , and 4.650 μm .

As the diameter of the microsphere increases, more and more light will be focused to the sample. This explains the increase of E_f and it reaches a maximum when the diameter is approximate to the beam diameter. As the microsphere gets bigger, the nanojet starts to emerge and moves away from the microsphere. This was also observed by X. Li *et al.* [9]. Hence, the light that focused on the sample is reduced which will decrease the Raman intensity. Consequently, in order to get maximum enhancement, diameter of microsphere needs to be matched with the incoming beam diameter.

Enhancement of Raman scattering by PS spheres is not limited to silicon substrate. They can also be used to enhance Raman scattering of other samples, such as organic molecules. Figure 7.5 shows the Raman spectra comparison between 1 mM

4-mercaptobenzoic acid (4-MBA) molecules spin coated on thin silver film with and without a 3 μm diameter PS microsphere using NA = 0.4 objective lens. Raman spectrum of PS microsphere is also shown for reference. As can be seen in Figure 7.5, with microsphere on the top surface of 4-MBA sample, the Raman signals (labeled with dotted lines in Figure 7.5) of the molecules [18] are enhanced, which is about 32.5 times of that without the microsphere. Accordingly, the normalized Raman enhancement factor (E_{nef}) can be calculated to be ~ 500 by using equation (7.2),

$$E_{nef} = \frac{(I_{4-MBA} - I_{background})_{(with\ PS)}}{(I_{4-MBA} - I_{background})_{(without\ PS)}} \times \frac{S_{(without\ PS)}}{S_{(with\ PS)}} \quad (7.2)$$

where S is the beam diameter. $S_{without\ PS}$ is 2.83 μm from the scanning edge method, and $S_{with\ PS}$ is 0.2 μm from the simulation result shown in Figure 7.4.

Figure 7.5. Comparison Raman spectra of 1 mM 4-mercaptobenzoic acid (4-MBA) molecules spin coated on silver film without (a) and with (b) 3 μm PS spheres along with that of PS Raman spectra on glass slide with objective lens 20x, NA = 0.4. (c) Raman spectrum of PS microsphere for comparison.

7.4 Conclusion

Single dielectric microspheres have found great interest in microscopy improvement and nanoparticle detections. Understanding their size-dependent optical properties is helpful in determining their applications. One-to-one correspondence enhanced Raman scattering of silicon by individual polystyrene (PS) microsphere is studied, which is shown to depend not only on the diameter of the sphere but also on the numerical aperture (NA) of the objective lens. Maximum enhancement is observed for sphere with diameter approximate to the beam diameter while numerical simulation using COMSOL Multiphysics® reveals that photonic jet at the shadow side of the spheres contributes to the Raman enhancement. Enhancement factor of ~ 11 was achieved with $3.156\ \mu\text{m}$ PS microsphere using $\text{NA} = 0.4$ objective lens. We went further to show that individual polystyrene microsphere could be used for SERS experiment. Enhanced Raman scattering of 4-MBA molecules by single microsphere further was shown. Normalized Raman enhancement factor for the SERS was calculated to be ~ 500 .

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Chapter 8

Plasmon-enhanced polarized Raman spectroscopy for sensitive surface characterization

8.1 Introduction

As mentioned in Chapter 2, surface-enhanced Raman spectroscopy (SERS) has been a successful and powerful method for sensitive Raman detection of low concentrations of simple organic and complex biological molecules [1,2]. It has been successfully used to detect low molecule concentration that cannot be detected by normal Raman spectroscopy [3,4]. It can also be used for thin film characterization on a substrate, e.g. the strain study on thin strained silicon film on SiGe substrate, which is one of the most important methods used to improve the microchips performance [5-7]. Tensile strained Si can be utilized by using the $\text{Si}_{1-x}\text{Ge}_x$ as a buffer layer for n-MOSFET application [8] while compressively strained silicon is achieved by using $\text{Si}_{1-y}\text{C}_y$ buffer layer for p-MOSFET [9]. In strained silicon, the inter-valley scattering will be suppressed and the effective carrier mass will be reduced, hence results in an improvement of the effective carrier mobility in the Si channel. This phenomenon enables us to achieve a higher transistor performance by a few times without reducing its physical size [10,11]. Since mobility enhancement in the strained silicon depends on the amount of strain that is being applied to the channel region [12], accurate strain determination is extremely important.

There are number of techniques that can be used for strain measurement. Techniques such as converging beam electron diffraction (CBED) [13,14], transmission electron microscopy (TEM) [15,16], and X-Ray diffraction (XRD) [17,18] have been used to study the strain in materials. Although the first two techniques have a high spatial resolution, the sample preparation is very complicated and destructive that can cause strain relaxation in certain directions. The interpretation is also not straightforward as extensive modeling is required. For XRD, localized strain determination will be difficult since the X-rays cannot be focused into a small spot easily and will penetrate deep into the silicon sample. Computer simulation tool such as finite element analysis can be used to calculate the stresses in thin film structures and underlying substrates [19,20]. In theory, all kind of materials and combinations of materials can be studied. However, some assumptions have to be made on the stress distribution or stress state. Experimental results are needed in order for the simulation results to have enough scientific validity. On the other hand, Raman spectroscopy has been a versatile technique in strain determination [21-23]. Laser used in Raman spectroscopy can be focused down to 500 nm, depending on the wavelength used. Raman peak shift is also sensitive to strain and can be used for quantitative strain determination [24,25].

The Raman signal originates from a volume defined by the wavelength and the diameter of the laser beam. A shorter laser wavelength gives information on the strain closer to the surface [26]. However, it is not practical to change laser wavelengths to

suit different thicknesses of samples. Here we will use 532 nm laser that can penetrate to certain depth and utilize surface enhancement technique to obtain the strain information closer to the surface. The total scattered light intensity integrated from the surface to a depth d , I_s , is given by [27],

$$I_s = I_0 R \int_0^d e^{-2\alpha x} dx = \frac{I_0 R}{2\alpha} (1 - e^{-2\alpha d}) \quad (8.1)$$

while that from the depth d to infinity, I_d , is given by,

$$I_d = I_0 R \int_d^\infty e^{-2\alpha x} dx = \frac{I_0 R}{2\alpha} e^{-2\alpha d} \quad (8.2)$$

where I_0 , R , and α are the incident light intensity, the Raman scattering cross section, and the absorption coefficient, respectively.

If one assumes that the penetration depth, d_p , is given by the depth that satisfies the relationship,

$$\frac{I_d}{(I_d + I_s)} = 0.1$$

(8.3) then this depth is given by,

$$d_p = \frac{-\ln 0.1}{2\alpha} = \frac{2.3}{2\alpha} \quad (8.4)$$

The optical properties (refractive index (n), extinction coefficient (k), and absorption coefficient (α)) of Si and Ge for the 532 nm (2.33 eV) wavelength are obtained from [28]. Those values for $\text{Si}_{0.75}\text{Ge}_{0.25}$ are calculated using Vegard's law based on the reported values of Si and Ge. By using equation (8.4), the penetration depths of 532 nm (2.33 eV) laser in Si, Ge, and $\text{Si}_{0.75}\text{Ge}_{0.25}$ are found to be 940 nm, 21 nm and 77 nm, respectively. These results are summarized in Table 8.1.

Table 8.1 Optical properties of Si, Ge, and Si_{0.75}Ge_{0.25} at $\lambda = 532$ nm (2.33 eV)

	ϵ_1	ϵ_2	n	k	$10^3 \alpha$ (cm ⁻¹)	d_p (nm)
Si	17.22	0.43	4.15	0.052	12.23	940
Ge	18.75	23.22	4.93	2.359	557.41	21
Si _{0.75} Ge _{0.25}	17.60	6.13	4.35	0.629	148.53	77

As can be seen in Table 8.1, due to the deep penetration of laser into silicon, a problem arises when Raman spectroscopy is employed to measure the strain in a very thin strained silicon layer grown on 1 μm relaxed Si_{0.75}Ge_{0.25}/2 μm graded Si_{1-x}Ge_x ($x = 0$ to 0.25)/bulk silicon. The details of the sample have been elaborated in Chapter 3. As the 532 nm laser will penetrate into the buffer layer, the Raman signal from this layer is very strong and overlapping with the peak position of that from the strained silicon. This makes the strain determination of the strained layer become complicated and less accurate.

To solve this problem, unlike the conventional SERS experiments where the molecular samples are deposited on top of roughened metal surface or metallic nanoparticles [29-31], N. Hayazawa *et al.* enhanced the signal from the thin strained silicon layer (30 nm) using local-mode plasmons by coating 10 nm silver thin film on top of the sample [32]. The local-mode plasmons are due to the collective oscillation of electrons at small metallic particle by the incident laser.

Apart from the local-mode plasmons, propagating surface plasmons that are excited by a large numerical aperture (NA) objective lens, can interfere with each other to produce a strong localized electromagnetic field in the focus region [33,34]. This is the localized surface plasmons, which is the collective oscillation of electrons on a 'flat' metal surface by a focused beam [35].

The objective of this part is to show the enhancement of the Raman signal by both the local-mode plasmons and the localized surface plasmons from silver thin film on a 20 nm strained silicon layer grown on a SiGe buffer layer [36]. Different thicknesses of silver thin films were investigated. Like silicon substrate [37], Raman signal from the crystalline SiGe substrate can be suppressed by utilizing polarized Raman spectroscopy. Therefore, the surface signal can be enhanced further. We show that using an analyzer at cross polarization with the laser polarization, the Raman signal from the SiGe buffer layer is reduced and the surface sensitivity is enhanced further, allowing more accurate strain determination of the thin strained silicon layer.

8.2 Experimental

The configuration for Raman experiments has been discussed in Chapter 3. The Raman spectra were collected with an OLYMPUS microscope objective lens (60X NA=1.2 WATER IMMERSION). Raman signals from the (001) face of the samples were collected by the lens in the backscattered configuration without analyzer

$[z(x,xy)\bar{z}]$ or with rotating analyzer axes with respect to laser polarization $[z(x,xy(\theta))\bar{z}]$ to a 1800 lines/mm grating and detected by a TE-cooled charge-coupled-device (CCD).

Silver thin films with different thicknesses (5 nm, 10 nm, 15 nm and 20 nm) were deposited on the samples using DC magnetron sputtering in vacuum. Silver was used because it is the most effective surface enhanced medium for SERS among all metals in the visible region [38,39]. During the experiments, a 150 μm thick cover glass ($n_r = 1.45$) was pressed onto the samples, leaving a small air gap between the cover glass and the silver film. In the later experiments, the effect of adding an analyzer was studied. An analyzer was placed after the edge filter.

8.3 Results and discussion

Figure 8.1 shows the Raman spectra from uncoated and silver-coated samples. If we look at the spectrum from the uncoated sample, there are two peaks in the spectra. The first peak at $\sim 502\text{ cm}^{-1}$ belongs to the SiGe layer underneath the strained layer while the second peak at $\sim 512\text{ cm}^{-1}$ belongs to the strained silicon layer. The second peak is used to determine the strain value as the phonon frequency is related to the lattice constant, hence the strain. However, the intensity of the strained silicon peak is much weaker than that from the SiGe layer because the strained silicon layer is much thinner compared to the SiGe layer, making strain determination using the strained

silicon peak position very difficult. This is particularly true for samples with a smaller Ge concentration in the SiGe layer where the Raman peaks due to strained silicon and SiGe overlap much more severely.

Figure 8.1. Raman spectra of strained silicon sample coated with different thicknesses of silver thin films. The dashed spectrum shows the Raman spectrum from the bulk silicon for comparison. The spectra have been shifted vertically for clarity.

Surface-enhanced Raman by silver coating was then used to enhance the signal from strained silicon. The local-mode plasmons can be excited by the natural roughness of the silver film, however, in order to excite the localized surface plasmons, the component of the incident laser wave vector parallel to the metal surface, k_{parallel} , has to be equal to the wave vector of the surface plasmons (k_{sp}). This is to satisfy the conservation of energy and momentum.

$$\omega_{\text{sp}}^2 = \frac{\omega_p^2}{2} + (ck)^2 - \left[\frac{\omega_p^4}{4} + (ck)^4 \right]^{1/2} \quad (8.5)$$

$$\omega_p = \frac{ne^2}{m_e \epsilon_0} \quad (8.6)$$

The dispersion relation for surface plasmons will not intersect with the dispersion curve for light in air, $\omega = ck$, as shown in equation (8.5) [40], where ω_p is the bulk plasma frequency of metal; n is number of conduction electrons; e is the charge of electron; m_e is the effective mass of electron and ϵ_0 is the permittivity in vacuum. This is because k_{sp} of the surface plasmons is larger than $k_{parallel}$ of incident light in air, hence the conservation of momentum cannot be satisfied. Therefore, surface plasmons cannot be excited in this way. In order to couple photons into surface plasmons, it is necessary to increase the momentum of the incident light. This can be achieved by passing the light through a medium that has higher refractive index (n_r) than the air, e.g. the cover glass, and bring it near to the metal surface. Hence, surface plasmons can be excited when $k_{parallel}$ of the evanescent wave, which is present in total internal reflection, can match the k_{sp} at a certain incident angle α , as shown in equation (8.7) [41] as follow,

$$k_{sp} = k_{parallel} = \frac{\omega}{c} n_r \sin \alpha \quad (8.7)$$

In our study, a large NA objective lens (NA = 1.2) was used to satisfy the dispersion-matching condition between light and the surface plasmons. The surface plasmon field will oscillate perpendicularly and propagate parallel to the metal surface in many directions. As discussed earlier, at the focus region the surface plasmons will interfere with each other to form strong localized electric field, i.e.

localized surface plasmons. The Raman signals induced by the plasmons are depolarized from the polarization of laser [42]. On the deposited silver films, the propagating surface plasmons are scattered at the roughness of the metal surface. This will result in the change of propagation direction and partial loss of coherence of the scattered photons. This depolarization effect is exploited in our study to increase the relative Raman peak intensity of the strained silicon layer using polarized Raman later on. This depolarization effect is exploited in our study to increase the relative Raman peak intensity of the strained silicon layer using polarized Raman later on.

The Raman spectra of samples after silver coating are shown in Figure 8.1. We observed that the intensity of the Si-Si peak from strained silicon increased after silver coating. Throughout this work, surface enhancement is defined as follow:

$$Surface_enhancement = \frac{r_{silver-coated}}{r_{uncoated}} \quad (8.8)$$

$$r = \frac{I_{strained-Si}}{I_{SiGe}} \quad (8.9)$$

where I is the intensity of the Raman signal in the corresponding layer. The optimum silver thickness was about 5 nm for the highest surface enhancement, which is 12.89 times enhanced as compared to that of the uncoated sample. As the thickness of the silver film becomes thicker, the enhancement will decrease. This is due to the exponential decay of the surface plasmons into the silver film. As a comparison, surface enhancement of only 5.23 times was obtained when cover glass was not used (in this case dry objective lens was used, NA = 0.95). The enhancement of 12.89 can

be attributed to the contributions from the localized surface plasmons and the local-mode plasmons, while the enhancement of 5.23 can be attributed to the contribution from the local-mode plasmons alone. This further demonstrates the existence of localized surface plasmons and the role of the cover glass in exciting it, as shown in equation (8.7).

To further increase the relative Raman signal of the strained silicon layer, we used the fact that the polarization of the surface enhanced Raman signal is different from that of the normal signal. Several groups have also taken the advantage of the polarization dependent of the sample to improve the sensitivity for Raman enhanced experiments [43-45]. By using different analyzer angles, we can choose the signal from different polarizations. The angle θ here represents the angle between the analyzer axis and the laser polarization, as shown in inset of Figure 8.2a. Figure 8.2a shows the Raman spectra at different analyzer angles. Figure 8.2b shows the Raman intensities of SiGe and strained silicon layers at different analyzer angles. As analyzer angle increases, both SiGe and strained silicon signals decrease. However, it can be observed that the strained silicon signal decreases at a slower rate than that of SiGe. Figure 8.2c shows the ratio of strained silicon over SiGe signals from uncoated and coated samples as a function of analyzer angle. For the uncoated sample, the ratio does not change with the analyzer angle. This is because both Raman signals from strained silicon and SiGe are polarized to the laser polarization. By coating a thin layer of silver, surface plasmons are excited by the incident laser. While the incoming

laser is polarized, the surface plasmons can cause enhanced depolarized Raman scattering from the sample, as discussed previously. So as the analyzer angle was rotated from 0° to 90° in consecutive steps of 10° with respect to the polarization of laser, which is linearly polarized at 0° , the ratio of strained silicon and SiGe signals is increased. It reaches the maximum when the angle is at 90° . The role of the analyzer here is to remove the Raman signals that are not enhanced by the surface plasmons (far-field signal). At 90° , the analyzer will remove the far-field signals, and the enhanced Raman signals due to surface plasmons, which are depolarized, will still be detected. With this approach, surface enhancement of 25.4 times can be obtained. Also can be observed from Figure 8.2a and 8.2b, even when the analyzer is at 90° , the intensity of SiGe is not completely removed. This is because the plasmon propagation length is more than the thickness of the strained silicon. Hence the SiGe signal near to the strained silicon layer still can be enhanced by the surface plasmons, but it is much weaker.

Figure 8.2. (a) Raman spectra of 5 nm silver coating at different analyzer angles with respect to the laser polarization. All the spectra have been shifted vertically for clarity.

(*) and (+) show the Si-Si LO phonon mode from the relaxed SiGe and strained silicon layers, respectively. (b) Raman intensities of SiGe and strained silicon at

different analyzer angles. (c) The ratio of strained silicon and SiGe signals for

uncoated and 5 nm silver coated sample at different analyzer angles, respectively.

Inset in Figure 8.2a shows the schematic diagram of the analyzer. $\theta = 0^\circ$ represents the analyzer axis parallel to the laser polarization.

8.4 Conclusion

In conclusion, we have shown that combination of local-mode plasmons and localized surface plasmons on thin metal surface can be used to enhance the surface sensitivity of Raman spectroscopy. This approach is very useful when the Raman signal from the surface is obscured by the signal beneath, for example in strained silicon grown on a SiGe layer. The effect from different thicknesses of silver film was studied. The optimum silver thickness was about 5 nm for the highest surface signal enhancement, which is 12.89 times enhanced as compared to that of the uncoated sample. To further increase the surface sensitivity, an analyzer was used to remove the far-field signal when it is at 90° to the polarization of laser. The near-field enhanced Raman signal which is depolarized can be detected, and surface enhancement up to 25.4 times was successfully obtained.

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Chapter 9

Conclusion and future works

9.1 Conclusion

This thesis consists of three main parts. In the first part, the scanning near-field Raman microscopy using optically trapped dielectric microsphere was realized. In this part, the detailed instrumentation and mechanism of trapping were presented. During imaging, the sample was put inside a water-filled sample cell. A 3 μm diameter polystyrene microsphere was trapped using optical tweezers and the sample was scanned by a piezostage. We have achieved spatial resolution of ~ 80 nm, which is a sub-diffraction limit spatial resolution ($\sim \lambda/7$). Decay length was also estimated to be ~ 140 nm. We have shown the microsphere near-field imaging on different types of samples, starting from PMOS samples, gold nanopattern, and CNTs on silicon substrate. We showed the capability of the microsphere near-field technique in studying the strain on PMOS transistors with eSiGe source drain stressors. In this sample, the silicon channel was compressively strained by the SiGe stressors and was calculated to be 0.39 %, which corresponds to a compressive stress of 651 MPa. With sugar solution, we showed it is possible to improve the spatial resolution further by reducing the Brownian motion of the microsphere. Spatial resolution of ~ 66 nm ($\sim \lambda/8$) could be achieved with 30% of sugar solution. However, further increasing the concentration will make the solution too viscous and trapping may be not possible. To

eliminate the Brownian motion, AFM tip with a single microsphere was used to image Si/SiO₂ lines and PMOS transistors. Comparisons of the near-field images with far-field images, confirmed the superiority of the microsphere near-field technique than far-field microscopy. Both developed near-field Raman techniques, show great potential in producing high-resolution Raman image. They are non-destructive, high reproducibility (almost 100%), fast (strong signal), and easy to use compared to other conventional near-field Raman techniques, e.g aperture and apertureless methods, that have been discussed in Chapter 2.

Apart from near-field Raman imaging, the microsphere approach can be also be used in white light microscopy. The microsphere near-field white light microscopy showed a better resolution compare to far-field microscopy. This technique may have a great potential in the study of nanostructures and biological samples, in which different spectral information are needed. Based on this work, it can also be extended to the development of microsphere fluorescence microscopy.

The second part deals with the use of different sizes of individual polystyrene microsphere to enhance the Raman signal. Enhanced Raman scattering of silicon was studied, which was shown to depend not only on the diameter of the sphere but also on the diameter of the incoming beam. The experiments were done by using different sizes of polystyrene microsphere and objective lenses with different numerical aperture. Maximum enhancement was observed for sphere with diameter approximate

to the beam diameter. Simulation studies using COMSOL Multiphysics® were carried out as well, and the simulation results showed agreement with experiment results. Besides intensity enhancement, simulation results suggested that sub-diffraction focus spot could be obtained as well. Enhancement factor of ~ 11 was achieved with $3.159\ \mu\text{m}$ PS microsphere using $\text{NA} = 0.4$ objective lens. We went further to show that individual polystyrene microsphere could be used for SERS experiment. Enhanced Raman scattering of 4-MBA molecules by single microsphere further was shown. Normalized Raman enhancement factor for the SERS was calculated to be ~ 500 . The first and the second parts show the capability of a single microsphere in increasing Raman intensity and focusing the incoming light into sub-diffraction limit spot size, which are the criteria in realizing a novel near-field Raman microscope using a single dielectric microsphere.

The final part discusses about the role of local-mode and localized surface plasmons to enhance the surface sensitivity of Raman spectroscopy. This approach is very useful when the Raman signal from the surface is obscured by the signal beneath, e.g. for sample consists of $20\ \text{nm}$ strained silicon layer grown on $1\ \mu\text{m}$ relaxed $\text{Si}_{0.75}\text{Ge}_{0.25}/2\ \mu\text{m}$ graded $\text{Si}_{1-x}\text{Ge}_x$ ($x = 0$ to 0.25)/bulk silicon. Different thicknesses of silver film were deposited on the sample using DC magnetron sputtering. The optimum silver thickness was about $5\ \text{nm}$ for the highest surface signal enhancement, which is 12.89 times enhanced as compared to that of the uncoated sample. As the thickness of the silver film becomes thicker, the enhancement will decrease. This is

due to the exponential decay of the surface plasmons into the silver film. To further increase the surface sensitivity, we used the fact that the polarization of the surface enhanced Raman signal is different from that of the normal signal. The study of different analyzer angles was carried out. The role of the analyzer here is to remove the Raman signals that are not enhanced by the surface plasmons (far-field signal). At 90° with the polarization of light, the analyzer will remove the majority of far-field signals, and the enhanced Raman signals due to surface plasmons, which are depolarized, will still be detected. With this approach, surface signal enhancement up to 25.4 times was successfully obtained.

9.2 Future works

The current work on scanning near-field Raman microscopy with optically trapped microsphere, in our opinion, still can be improved further.

Besides reducing or eliminating the Brownian motion of the microsphere, higher refractive index microsphere can also be used to improve the spatial resolution. However, it is also important to note that the ratio between the refractive index of the microsphere and the surrounding medium has to be lower than 1.4, as pointed out by A. Devilez *et al.* in their recent simulations [A. Devilez *et al.*, *Opt. Express* **17** (2009) 2089]. Simulation studies, e.g. COMSOL Multiphysics[®], can be employed to understand further the effect of refractive index of microsphere to the laser spot size.

Another possibility to improve the spatial resolution is by using radially polarized light [e.g. K. Yonezawa *et al.*, *Opt. Lett.* **31** (2006) 2151 & W. J. Lai *et al.*, *Opt. Express* **16** (2008) 15694]. It has been reported that radially polarized light can be focused to a tighter spot size [e.g. S. Quabis *et al.*, *Opt. Commun.* **179** (2000) 1]. Combination of microsphere and radially polarized light may even improve the spatial resolution further. These are the possible ways to improve the spatial resolution.

Extending the application of this technique is another goal in future research. So far, our approach has been used in semiconductor transistor samples, gold nanopatterns, and carbon nanotubes. In future, the application can be extended to bioscience, the study of graphene, etc.

The work on plasmon-enhanced Raman spectroscopy can also be further improved using radially polarized light [R. Yamaguchi *et al.*, *Jpn. J. Appl. Phys.* **28** (1989) 1730]. As calculated by H. Kano [“Near-Field Optics and Surface Plasmon Polaritons”, *Topics Appl. Phys.* **81** (2001) 189], radially polarized light is more effective in generating the localized plasmons. It will be interesting to couple the radially polarized light to our CRM200 Raman system, so that Raman signal from the surface can be enhanced more effectively.

Appendix

Publications

Journal publications

1. **J. Kasim**, T. Yu, Y. M. You, J. P. Liu, A. K. H. See, L. J. Li, and Z. X. Shen, "Near-field Raman imaging using optically trapped dielectric microsphere." *Opt. Express* **16** (2008) 7976.
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Conference publications

1. Z. X. Shen, **J. Kasim**, Y. M. You, and C. L. Du, "A novel near-field Raman and white light imaging system for nano photonic and plasmonic studies." *MRS Spring 2008 Proceeding, San Francisco, USA*.
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Book Chapter

Z. X. Shen, J. Kasim, and T. Yu, “Chapter 21: Near-field Raman imaging of nanostructures and devices.” *Advanced Nanomaterials Volume 2*, Wiley-VCH 2010.

Patent

Near-field Raman imaging using cantilever-positioned dielectric microsphere – US Patent (pending)