

Surface-enhanced Raman scattering of rhodamine 6G on nanowire arrays decorated with gold nanoparticles

Jianing Chen^{1,2}, Thomas Mårtensson³, Kimberly A Dick³,
Knut Deppert³, H Q Xu^{1,3}, Lars Samuelson³ and Hongxing Xu^{2,3}

¹ School of Physics and Optoelectronic Technology, Dalian University of Technology, Dalian 116024, People's Republic of China

² Beijing National Laboratory of Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

³ Division of Solid State Physics, Lund University, S-22100 Lund, Sweden

E-mail: hxxu@aphy.iphys.ac.cn

Received 5 March 2008, in final form 5 May 2008

Published 28 May 2008

Online at stacks.iop.org/Nano/19/275712

Abstract

We investigate the surface-enhanced Raman scattering (SERS) of rhodamine 6G (R6G) adsorbed on Au nanoparticles attached to InP nanowires. We find that nanowire arrays act as frameworks for effective SERS substrates with a significantly higher Raman signal sensitivity than a planar framework of Au nanoparticles adsorbed two-dimensionally on a flat surface. The SERS signal displays a clear polarization-dependent effect when the nanowires are arranged in a row. We also find that the SERS signal increases with time during continuous laser illumination. The plasmon-enhanced optical forces between Au nanoparticles may either move pairs of nanoparticles closer together or attract adsorbed molecules by moving them to the junctions of Au nanoparticle aggregates. Such effects by plasmon optical forces may cause the observed increase of the SERS signal with continuous laser illumination.

1. Introduction

Surface-enhanced Raman scattering (SERS) was first reported more than 30 years ago by Fleischmann *et al* [1] and Jeanmaire and Van Duyne [2], and is now widely used to acquire Raman signals from small quantities of molecules, even down to the single-molecule level. Because of its high sensitivity, SERS has developed into an important spectroscopic tool in many fields [3–6]. It is generally believed that the two mechanisms that contribute to SERS are electromagnetic (EM) enhancement [7, 8] and chemical enhancement [9, 10]. For the EM mechanism of enhancement, the SERS intensity can be enhanced substantially when two or more nanoparticles are brought closely together [6, 7]. The small areas or cavities formed between those closely neighbored nanoparticles are called 'hot' sites, where the Raman signal is locally enhanced due to the excitation of the surface plasmon resonance. The polarization of the incident light also plays an important role, since the electromagnetic field is greatly enhanced when polarized parallel to the axis of a particle dimer, while the field is diminished for a perpendicular polarization [11].

With the development of fabrication techniques for structures on the nanometer scale, the synthesis and design of nanowires (NWs) have received much attention for their applications in electronics, photonics, and biology [12–16]. In this paper, SERS in nanowire frameworks is explored; the three-dimensional (3D) nanowire framework serves to hold more efficient metal nanoparticles clusters in order to increase number of SERS hot sites, creating a highly sensitive SERS substrate.

2. Experimental details

Nanowire samples were prepared on n-type InP(111)B wafers. Electron beam lithography and metal lift-off were used to pattern InP(111)B substrates with gold particles. Using the gold particles as growth seeds, vertically free-standing InP(111)B nanowire arrays were then grown by metal–organic vapor phase epitaxy [14]. The wires have a length of $\sim 2 \mu\text{m}$ and an uppermost diameter of $\sim 50 \text{ nm}$. The distance between neighboring nanowires is about 120 nm (figure 1). The lower

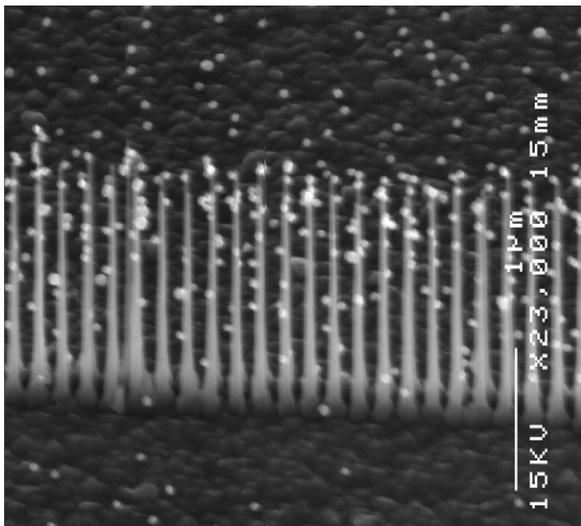


Figure 1. A 45° tilted scanning electron microscopy image of an InP nanowire row, grown on an InP(111)B wafer from deposited aerosol phase Au nanoparticles. The Au nanoparticles, with a diameter of ~50 nm (the white dots), are seen spread over the sample.

limit on wire pitch was mainly determined by the resolution of the electron beam lithography process. The nanowires were then decorated with aerosol phase gold nanoparticles [17]. These size-selected nanoparticles of about 50 nm in diameter were generated by an evaporation/condensation method [18]. After the decoration step, a droplet of 4×10^7 M R6G solution was placed on the nanowire sample, and dried before Raman measurements. The Raman spectra were collected in a backscattering geometry through a 100× objective HORIBA Jobin Yvon Raman spectrometer. The wavelength of laser excitation was 633 nm. The polarization of the incident light was set by rotating a half-wave plate mounted in the light path. Raman mapping was obtained by scanning the sample using step motors mounted on the microscope, with a step length of 300 nm.

3. Results and discussions

In figure 1, a row of NWs with deposited Au aerosols is shown. The Au nanoparticles are clearly seen as small white dots on both nanowires and the wafer surface. The free-standing nanowires are well separated. Figure 2 shows scanning electron microscopy (SEM) images of a nanowire row and a nanowire array after a droplet of R6G solution was applied on the substrate surface and dried; some nanowires are tilted and bound together because of the capillary force of the R6G solution as it dries. The capillary force changed the configuration of the nanowire row and array from separate pillars to a 'shrub'. In this configuration, Au nanoparticles on the nanowires may come very close, forming SERS hot sites. The Raman mapping shows that hot sites do indeed exist in such nano-shrubs. Normally, large SERS takes place in the interstices between metal nanoparticles with distances of less than 5 nm. From previous studies, it was reported that the intensity is greatly enhanced when nanoparticles are placed

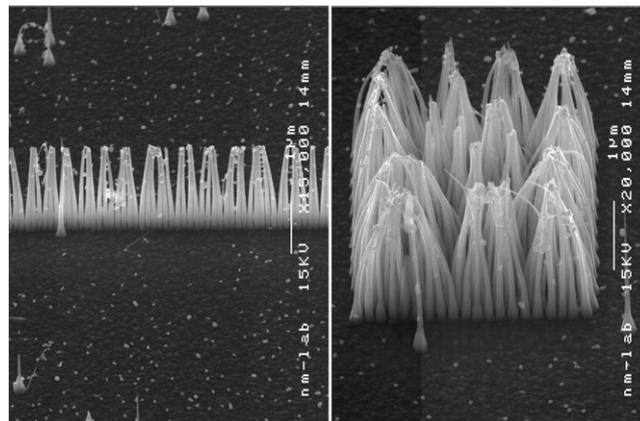


Figure 2. SEM images of a nanowire row (left) and a nanowire array (right) decorated with aerosol phase Au nanoparticles after a droplet of R6G solution was applied and then dried. The wires are bent because of the capillary force of the R6G droplet as it dries.

closely together, and the intensity can be built up by more than 11 orders of magnitude under certain conditions [7]. In principle, the quasi-one-dimensional template property of the nanowire allows efficient clustering of the Au nanoparticles favorable to SERS, if the incident polarization is parallel to the axis of the nanowire. In the backscattering experimental configuration used here, the focused light beam from the side of the objective lens has the component of the incident polarization parallel to the standing nanowire on the substrate, which benefits the SERS. But, the overall polarization effect of the incident light is perpendicular to the axis of a single standing nanowire in a polarization unfavorable configuration. However, the NW array serves as a 3D framework to carry more Au nanoparticles to create more 'hot sites' by those particles either between neighboring nanowires or along the nanowires than a flat surface, in order to enhance the SERS activity compared to a two-dimensional (2D) system.

Figure 3 shows a typical Raman mapping image of a nanowire row. The bright spots are believed to be the hot sites formed by nanoparticles. Almost no detectable R6G Raman signal can be collected from the surface of the wafer, although there are many Au nanoparticles present. The reason could be that the deposited Au nanoparticles on the wafer are well separated, and seldom aggregate [19] to create hot sites for strong SERS enhancement. The enhanced electromagnetic field around a single Au nanoparticle is too weak to enhance the Raman signal of the adsorbed molecules to a detectable level. The detected Raman signal is only acquired from the area where the nanowires exist, which provides evidence that 3D NW structures serve as nanoparticle holders that have more nanoparticle aggregations than a 2D system. Such a 3D system could offer stronger couplings between metal nanoparticles and form a better SERS substrate than a 2D system. Both coupling the excitation frequency to the particle plasmon resonance and alignment of the particles are essential to gain higher SERS enhancement of the nanoparticle clusters. On increasing the quasi-linear alignment of the Au particles along the nanowire, the coupling between the nanoparticles may shift the Au particle plasmon resonance from typically 550 nm (50 nm Au

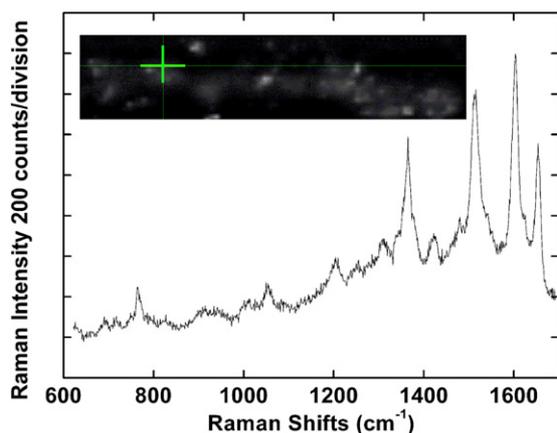


Figure 3. Raman mapping image of a nanowire row (inset) and typical Raman spectrum of a bright spot (green cross site) in the Raman mapping image. The accumulation time for each Raman spectrum is 10 s, and the Raman mapping image is taken by scanning with the scanning step of 300 nm and an integration time of each spot 10 s. The total time for each Raman mapping image is about 50 min. Considering the size of the laser spot to be about $2 \mu\text{m}$, each spot actually experiences the laser illumination during the scanning about $(2000/300)^2 \times 10 \approx 440$ s.

particles) to a position closer to 633 nm (laser used in the experiment), which can greatly increase the SERS efficiency.

From previous study, it is known that the polarization of incident light can strongly influence SERS [11, 20–22]. Different polarizations of the incident laser were used in the Raman mapping. A series of Raman mappings with different polarizations was obtained, as shown in figure 4. Six mapping images are shown with polarization of 0° , 30° , 60° , 90° , 120° , 150° in sequence, where 0° represents the polarization parallel to the nanowire row. From 0° to 60° , the averaged Raman mapping intensity decreases; it

then starts to increase. It is clear that the averaged Raman intensity is weakest when the polarization of the incident light is perpendicular to the nanowire row, although individual bright spots are still observed. This is not surprising since the randomly deposited Au nanoparticles may form hot aggregates in any direction. The polarization perpendicular to the axis of the NW row may in some cases be parallel to the axis of individual hot dimers, producing a strong SERS signal. However, the averaged Raman intensity is always higher when the incident polarization is nearly parallel to the nanowire row. This indicates that more hot sites are formed along the axis of the NW row when the NWs are bent together by the capillary force, as shown in figure 2. The photonic effect by far-separated nanoparticles along the nanowire row may also enhance the local field, and result in an increase of SERS signals in the parallel polarization [23, 24].

It is interesting that, for every series of Raman mappings, the averaged intensity of each Raman mapping increases with the number of the series, although the polarization effect may initially decrease the Raman signals, as shown in figure 4. Since only the incident polarization is changed for the different Raman mapping in the series, while the laser illumination is always on, the total illumination time for each Raman mapping is proportional to the corresponding number in the series. In figure 4, for example, the last Raman mapping has five times more laser illumination time than the first since it is also illuminated when the polarizations are changed in the previous five Raman mappings. This trend of increased SERS signals over time may be caused by the formation of additional aggregates due to the plasmon-assisted enhanced optical force under the continuous laser illumination [25]. At the same time the adsorbed molecules may be also trapped in the junctions of nano-aggregates by the gradient optical forces owing to the huge enhanced local field in the cavities between nanoparticles [26]. Since

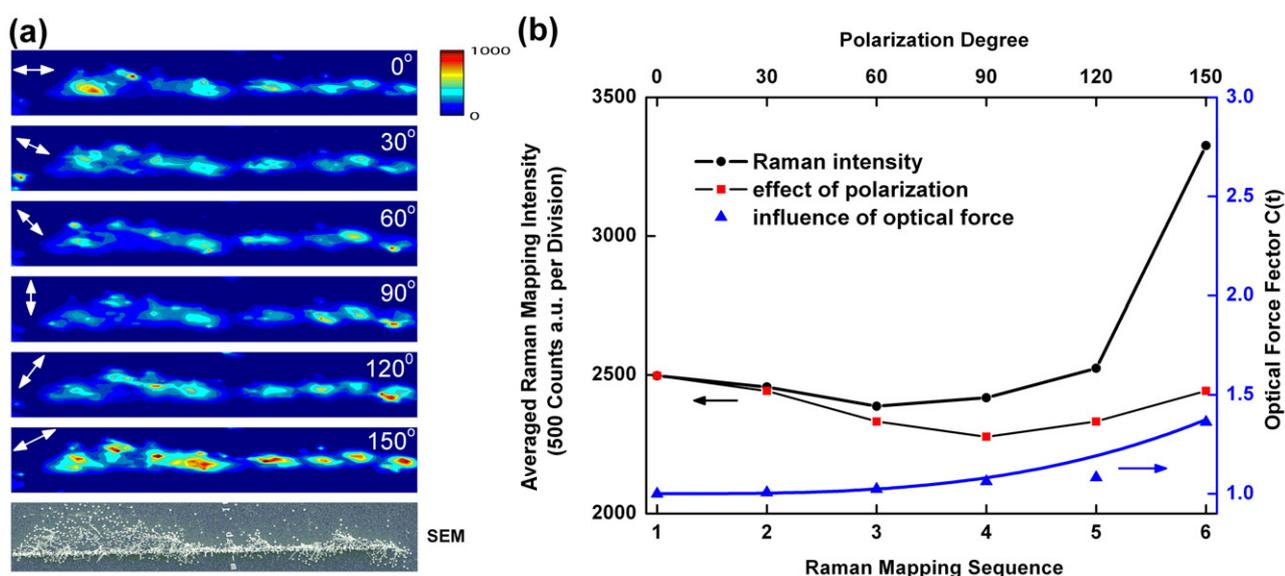


Figure 4. (a) Raman mapping images of a nanowire row at different polarizations of the laser excitation with the corresponding SEM image given at the bottom. (b) The corresponding averaged Raman intensities. Each Raman mapping image is obtained by scanning with the time of about 50 min.

the interaction distance of the plasmon-assisted optical force between metal nanoparticles can be hundreds of nanometers, much larger than the interparticle distance in our experiments, it is possible to move nanoparticles close. Hence the optical force on nanoparticles may play an important role in creating hot aggregates with increased illumination time. The longer the time the sample is illuminated, the closer the distance is between the occasionally formed nano-aggregates. With this insight, the intensity increase with the serial number should be caused by a combination of the optical forces and the effect of the polarization.

The SERS intensity can be written as $I(t, \theta) = C(t)I(\theta)$, where $C(t)$ is the effective coefficient due to the influence of the optical force, and $I(\theta) = K \cos^2(\theta) + M$ (K and M are coefficients) is the assumed polarization-dependent Raman intensity only if the influence of the optical force is ignored. It is generally agreed that the electromagnetic enhancement of SERS has two components. The first part is the local electromagnetic (EM) field intensity enhancement, which is $|\frac{E_{\text{loc}}}{E_0}|^2$, where E_{loc} is the local electric field and E_0 is the incident electric field, while the second part is the Raman emission enhancement driven by the antenna effect of metal nanostructures, which is again similar to $|\frac{E_{\text{loc}}}{E_0}|^2$. That is why we get roughly $|\frac{E_{\text{loc}}}{E_0}|^4$ for the total SERS enhancement [3, 4]. However, this rough estimation is mainly valid to estimate the maximum EM enhancement, but may not be valid for the weaker EM enhancement, e.g. the EM enhancement for the unfavorable incident polarization. For the simplest clustering of close-packed metal nanoparticles, i.e. two particles, the first part of the EM enhancement, the local intensity enhancement, is $|\frac{E_{\text{max}} \cos(\theta)}{E_0}|^2$, where E_{max} is the maximum electric field in the cavity between two nanoparticles when the incident polarization is parallel to the axis of the two nanoparticles. This part of the EM enhancement has $\cos^2(\theta)$ dependence on the incident polarization. Since the induced electric field in the cavity between two nanoparticles (this part dominates the total SERS enhancement) always aligns to the axis of the two particles, regardless of the incident polarization, the molecule located in the cavity will have the same Raman emission behavior, which is determined by the antenna effect of metal nanostructures, but not by the incident polarization. The second part of SERS enhancement, i.e. the Raman emission enhancement, remains as $|\frac{E_{\text{max}}}{E_0}|^2$, without polarization dependence. So the total EM enhancement should be $|\frac{E_{\text{max}}}{E_0}|^4 \cos^2(\theta)$, which still has $\cos^2(\theta)$ dependence on the incident polarization. We demonstrated recently that more complex clustering of nanoparticles also has the same $\cos^2(\theta)$ effect. Recent observation of the depolarization ratio $\cos(2\theta)$ of the Raman scattered light indicates a similar content [20, 21]. Since the fluctuations of SERS normally took place, and the $\cos^2(\theta)$ and $\cos^4(\theta)$ dependences are quite close, it might be hard to resolve the $\cos^2(\theta)$ and $\cos^4(\theta)$ dependences clearly by experimental observation alone [11]. In figure 4, the estimated $C(t)$ and $I(\theta)$ are shown together with the experimental data. The increase of $C(t)$ with the time accumulation of laser illumination (t is proportional to the number of the series N) indicates that the plasmon-assisted optical forces can move the nanoparticles closer,

since the enhancement of SERS is roughly determined by the interparticle distance d as $(1/d)^4$ [27]. Considering that the Au nanoparticles are distributed three-dimensionally in the arrays/lines of the nanowires with different interparticle distances, the averaged effect of the optical force could be $C(t) \propto (1/d)^\beta$, where $\beta \leq 4$ and d is the effective interparticle distance, which decreases with illumination time, $1/d \propto t \propto (N - 1)$. The fitting in figure 4 (the blue line) $C(t) = 1 + 0.003 \times (N - 1)^3$ should indicate that the plasmon-assisted optical force plays an important role in our experiment.

4. Summary

In this paper nanowire structures serving as a framework to hold gold nanoparticles were used for the study of surface-enhanced Raman scattering. In such 3D structures, Au nanoparticles can come close enough to each other to create hot sites for huge enhancement of the SERS signal. From the Raman mapping, it is clear that strong Raman signals are acquired from the nanowire regions, but not for Au nanoparticles adsorbed on the surface of the wafer. The polarization dependence of SERS on rows of nanowires was also investigated. The Raman signal intensity is strong when the incident polarization is parallel to the nanowire row and weak for the perpendicular polarization. The facts that the weakest mapping intensity is not at 90° polarization and that the intensity of the measurement of Raman mapping after long laser illumination is much higher indicate that the plasmon-assisted optical forces may play an important role. The optical forces can either drive a molecule to move to the junction of the aggregates of Au nanoparticles or pull Au nanoparticles adsorbed on a nanowire closer together to create more 'hot' sites. Both effects can cause the observed increase of SERS enhancement with continuous laser illumination.

Acknowledgments

We acknowledge the Nanometer Structure Consortium at Lund University, the Swedish Research Council (VR), the Swedish Foundation for Strategic Research (SSF), Knut and Alice Wallenberg Foundation, Ministry of Science and Technology (MOST) of China (Grant No. 2006DFB02020), and the 'Bairen' project of the Chinese Academy of Sciences for their support and funding.

References

- [1] Fleischmann M, Hendra P and McQuillan A 1974 *Chem. Phys. Lett.* **26** 163
- [2] Jeanmaire D L and Van Duyne R 1977 *J. Electroanal. Chem.* **84** 1
- [3] Kneipp K, Kneipp H, Itzkan I, Dasari R and Feld M S 1999 *Chem. Rev.* **99** 2957
- [4] Moskovits M, Tay L L, Yang J and Haslett T 2002 *Top. Appl. Phys.* **82** 215
- [5] Otto A 1984 *Light Scattering in Solid IV* ed M Cardona and G Guntherodt (Berlin: Springer) p 289
- [6] Xu H X, Bjerneld E J, Käll M and Börjesson L 1999 *Phys. Rev. Lett.* **83** 4357

- [7] Xu H X, Aizpurua J, Käll M and Apell P 2000 *Phys. Rev. E* **62** 4318
- [8] Moskovits M 1985 *Rev. Mod. Phys.* **57** 783
- [9] Moskovits M 2005 *J. Raman Spectrosc.* **36** 485
- [10] Campion A and Kambhampati P 1998 *Chem. Soc. Rev.* **27** 241
- [11] Xu H X and Käll M 2003 *ChemPhysChem* **4** 1001
- [12] Cui Y, Wei Q Q, Park H K and Leiber C M 2001 *Science* **293** 1289
- [13] Drachev V P, Thoreson M D, Khaliullin E N, Davsiion V J and Shalaev V M 2004 *J. Phys. Chem. B* **108** 18046
- [14] Mårtensson T, Borgström M, Seifert W, Ohlsson B J and Samuelson L 2003 *Nanotechnology* **14** 1255
- [15] Samuelson L 2003 *Mater. Today* **6** 22
- [16] Thelander C *et al* 2006 *Mater. Today* **9** 28
- [17] Bayer K, Dick K A, Krinke T J and Deppert K 2007 *J. Nanopart. Res.* **9** 1211
- [18] Magnusson M H, Deppert K, Malm J-O, Bovin J-O and Samuelson L 1999 *Nanostruct. Mater.* **12** 45
- [19] Krinke T J, Deppert K, Magnusson M H, Schmidt F and Fissan H 2002 *J. Aerosol Sci.* **33** 1341
- [20] Etchegoin P G, Galloway C and Le Ru E C 2006 *Phys. Chem. Chem. Phys.* **8** 2624
- [21] Jiang J, Bosnick K, Maillard M and Brus L 2003 *J. Phys. Chem. B* **107** 9964
- [22] Tong L M, Li Z P, Zhu T, Xu H X and Liu Z F 2008 *J. Phys. Chem. C* **112** 7119
- [23] Zhao K, Xu H X, Gu B H and Zhang Z Y 2006 *J. Chem. Phys.* **125** 081102
- [24] Zou S L and Schatz G C 2005 *Chem. Phys. Lett.* **403** 62
- [25] Svedbery F, Li Z P, Xu H X and Käll M 2006 *Nano Lett.* **6** 2639
- [26] Xu H X and Käll M 2002 *Phys. Rev. Lett.* **89** 246802
- [27] Xu H X, Wang X H, Persson M P, Xu H Q, Käll M and Johansson P 2004 *Phys. Rev. Lett.* **93** 243002