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In-line aligned and bottom-up Ag nanorods for surface-enhanced Raman spectroscopy

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We have demonstrated surface-enhanced Raman spectroscopy on arrays of Ag nanorods aligned in line by a dynamic oblique deposition technique. For the light polarized along the major axis of the nanorods, the plasma resonance of the Ag nanorods has been tuned to a wavelength suitable for Raman spectroscopy. The average width and the length-to-width ratio of the resulting nanorods are 56 nm and 3.5, respectively, and the nanorods align in line with small gaps of a few 10 nm. The Raman scattering for the polarized light along the nanorods is enhanced significantly as compared with that perpendicular to the nanorods. This polarization dependent Raman enhancement is attributed to the local field concentration at the ends of the nanorods. Since the preparation process is physical and completely bottom up, it is robust in its selection of the materials and is useful in providing the surface-enhanced Raman scattering sensors at low cost. © 2006 American Institute of Physics. [DOI: 10.1063/1.2205149]

Surface-enhanced Raman scattering (SERS) is one of the most attractive phenomena from the viewpoint of applications in biochemical sensors.^{1,2} The origin of the SERS is mainly attributed to the enhanced electric field localized around the metal nanostructures.³ An array of the elongated nanoparticles, so-called nanorods, is one of the strongest candidates for the SERS sensors, because the local electric field close to the end of the nanorods can be more than ten times larger than that around the nanospheres when the nanorods are excited by light polarized along their major axis.⁴ From a practical viewpoint, semiconductor lasers for Raman measurements are often linearly polarized so that the local field associated with them is enhanced efficiently if the nanorods are aligned parallel to each other. In addition, the further enhancement of the SERS intensity can be expected if the ends of the nanorods are in close proximity.⁵

In the very early stages of SERS studies, the advantages of the nanorod arrays had already been reported for the Ag nanorod arrays prepared on the lithographically produced templates.⁶ Even today, however, it is not easy for the top-down process to produce sub-100-nm patterns over a large area at a low cost. On the other hand, nanorods also can be created by the chemical⁷ or physical⁸ bottom-up processes. However, they are randomly oriented⁷ or are aligned side by side⁸ on the substrate. No report exists on in-line aligned and bottom-up nanorod arrays with SERS activity.

The dynamic oblique deposition (DOD), in which the deposition angle and/or in plane direction of the substrate are changed during deposition, enables one to control the complex three-dimensional morphology.⁹ By using DOD, we have recently realized discontinuous Ag films with a large dichroism due to the plasma resonance for the purpose of

applying them to thin film polarizers.¹⁰ Although a detailed morphology of the Ag particles was not elucidated, their optical properties suggested that the alignment of the elongated Ag nanorods was quasiparallel. In this study, we investigated the morphology of these physically self-assembled Ag nanorod arrays in detail and measured their SERS properties.

These nanorod arrays were physically self-assembled by taking advantage of the self-shadowing effects in the DOD.¹⁰ First, a template layer of SiO₂ with an anisotropic surface morphology was prepared by the serial bideposition (SBD) technique¹¹ on a glass substrate in a DOD apparatus. During the SBD, the deposition angle α measured from the surface normal was fixed at an angle selected between 72° and 86°, while the azimuthal angle was quickly changed by 180° with each deposition of a 10-nm-thick layer. After repeating 15 cycles of the serial bideposition, a SiO₂ layer with an approximate thickness of 300 nm was obtained. Onto the fabricated template layer, Ag was evaporated from a tungsten basket located in the deposition plane of the SiO₂. The deposition angle of Ag, α_{Ag} , was selected between 52° and 79°, while the azimuth remained unchanged during the deposition. The average thickness (d_{Ag}) of the deposited Ag was 5–13 nm; this deposition was so thin that the Ag layers remained discontinuous on the template. We have reported that the samples thus created exhibit anisotropic plasma resonance properties depending on the deposition conditions.¹⁰ Since the plasma resonance is essential for a significant enhancement of the SERS,³ it is important to design nanorods that resonate around the wavelength of the excitation and scattered light. The DOD enables one to control the plasma resonance, and we focus in this letter on the morphology and SERS properties of the samples designed for a laser with wavelength $\lambda=785$ nm. As shown in Fig. 1, the sample prepared under the selected condition ($\alpha=82^\circ$, $\alpha_{\text{Ag}}=70^\circ$, d_{Ag}

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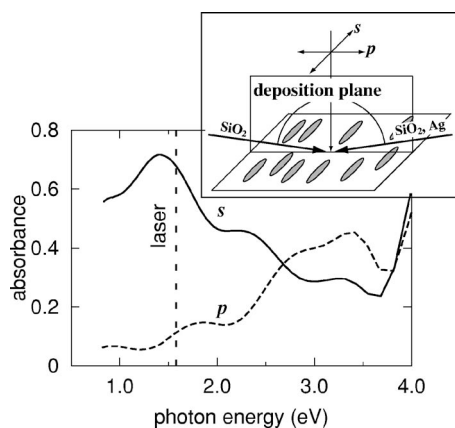


FIG. 1. The absorbance spectra of the Ag nanorod arrays tuned to the Raman spectroscopy at $\lambda=785$ nm. The incident light was either p or s polarized, where an electric field vibrates parallel or perpendicular to the deposition plane, respectively, as shown schematically in the upper right box.

=10 nm) exhibits the plasma resonance absorption for s -polarized light at 1.4 eV, which is slightly lower than the photon energy of the excitation laser ($\lambda=785$ nm) for the SERS measurements. On the other hand, the laser energy is significantly lower than that required for plasma resonance for p -polarized light. In this letter, the polarization of the incident light is defined as either p or s polarization in which an electric field vibrates parallel or perpendicular to the deposition plane, respectively, as shown in the top right box in Fig. 1. Since the nanorods are elongated perpendicular to the deposition plane as described below, p and s polarizations correspond to the polarizations perpendicular and parallel to the nanorods, respectively.

Figure 2 shows the surface morphologies of the sample under consideration. Note that the samples were observed without any conductive coatings and that the secondary electron images [Fig. 2(a)] and the backscattered electron images [Fig. 2(b)] show exactly the same area. In the secondary electron images, anisotropic surface corrugations can be observed. These corrugations correspond to the top of the bundled columns that are characteristic of the SBD films deposited at large $\alpha(\geq 75^\circ)$ and are elongated perpendicular to the deposition plane of SiO_2 .¹⁰ On the other hand, many bright spots found in the backscattered electron images are attributed to Ag. Since Ag was deposited from the bottom to top direction in Fig. 2, the Ag nanorods grow above the columns of the template as well as on the part slightly displaced toward the incident direction of Ag due to the shadowing effect of the anisotropic surface corrugation. Thus, the Ag nanorods are elongated in the direction perpendicular to the deposition plane of Ag with a quasiparallel alignment. Furthermore, one can see many gaps where the end of a nanorod is within a few 10 nm from that of another one. This seems advantageous for the plasmonic sensors such as the SERS substrates to enhance the local electric field. The averaged width and length-to-width ratio of these Ag nanorods are approximately 56 nm and 3.5, respectively. These values are also quite attractive for plasmonic applications, since they are compatible with the sizes and shapes desired for the current plasmonic applications.

Raman spectroscopy was performed using a near-IR confocal Raman microscope (HORIBA Jobin Yvon, The LabRam 1B) at an excitation wavelength of 785 nm and a

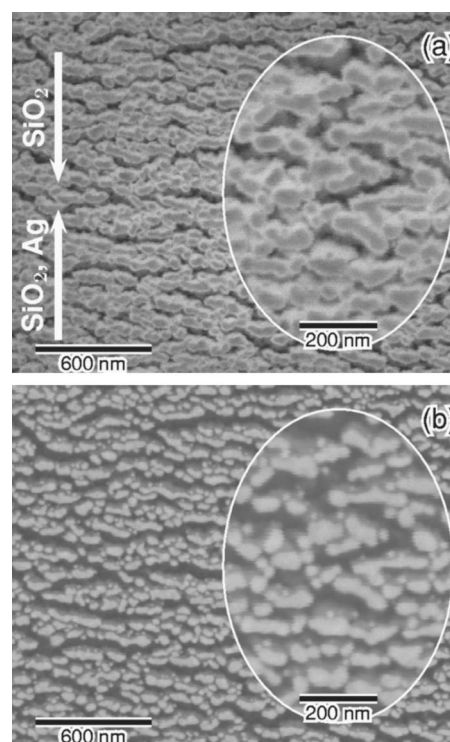


FIG. 2. Scanning electron micrographs [secondary electron images (a) and backscattered electron images (b)] of the surface of the Ag nanorod array. Arrows on the left in (a) indicate the incident directions of the vapors projected onto its surface.

power of 15 mW. The microscope uses a $60\times$ objective [the numerical aperture (NA) of which is 0.7] and a confocal pinhole with diameter 1.1 mm. In order to achieve *in situ* measurements of the SERS on the Ag nanorod arrays immersed in a 4,4'-bipyridine (BiPy) water solution, we created a small cell (6 mm diameter with a spacer of silicone rubber of 0.5 mm thickness) on the sample. After the cell was filled with BiPy solution, it was sealed with a cover glass. The excitation laser was polarized by a commercial Polaroid film with an extinction ratio of 170 at $\lambda=785$ nm.

Figure 3(a) shows the polarization dependent Raman spectra of the 1 mmol/l BiPy solution on the Ag nanorod array. The clear peaks observed for both the s - and p -polarized light are characteristic of the SERS of BiPy on the noble metal particles.¹² No peaks were observed on glass substrates without nanorods (not shown). It is remarkable that the SERS for the s -polarized light is much stronger than that for the p -polarized light. Figure 3(b) indicates the polarization dependence of the integrated intensity of the ring in plane deformation mode around 1014 cm^{-1} , where the linear background is subtracted from the scattering intensity and the angle of the polarization θ is measured from the s polarization. The SERS peak intensity changes through a period of 180° with the angle of the polarization and becomes a maximum for the s polarization, while it becomes a minimum for the p polarization. The line in Fig. 3(b) indicates the absorbance of the Ag nanorod arrays at $\lambda=785$ nm. The polarization dependence of the absorbance agrees well with that of SERS. The nanorods, which are significantly smaller than the laser wavelength, behave as a point dipole with anisotropic polarizability.¹³ Based on this simple model, it can be assumed that the extinction cross section is proportional to the square of the dipole moment as well as to the scattering

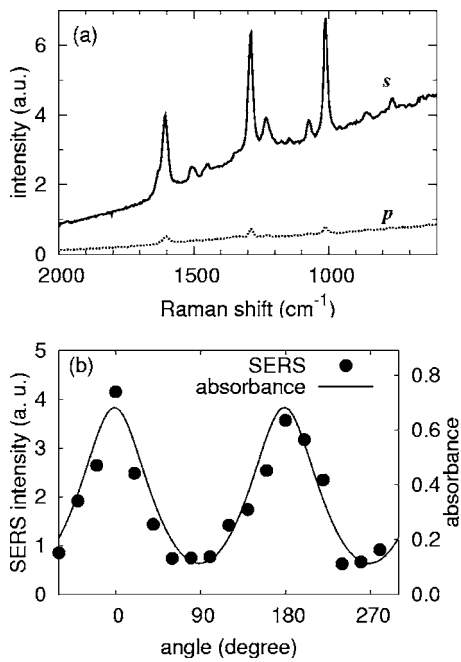


FIG. 3. Polarization dependence of (a) the Raman spectra and (b) the peak intensity at 1014 cm^{-1} . The polarization dependence of the absorbance at $\lambda=785\text{ nm}$ is also shown by a solid line in (b).

cross section. Thus, the correlation between the SERS and the absorbance is consistent with that observed by Itoh *et al.*¹⁴ for single Ag nanoparticles when the extinction by a collection of the nanorods is taken into account.¹³ Since the enhancement of the field scattered by the randomly oriented BiPy molecules is likely to be independent of the polarization of the excitation laser, the polarization dependence of the SERS reflects that of the intensity of the excitation field enhanced by the resonating nanorods. The present results indicate that the enhanced excitation field intensity is proportional to the square of the dipole moment; it is also consistent with the theoretical study in which the local field at the end of the nanorods for the longitudinal polarization becomes much larger than that for the transverse excitation.⁴

In summary, we have measured the SERS from the BiPy solution on the in-line aligned Ag nanorod arrays at λ

$=785\text{ nm}$. The physical self-assembly of nanorod arrays has been achieved only by using the DOD, and their morphology has been designed to exhibit a plasma resonance near $\lambda =785\text{ nm}$ for the polarization parallel to the major axis of the nanorods. The resulting Ag nanorods align in line with small gaps within a few 10 nm. Since both the absorbance and the SERS intensity strongly and identically depend on the polarization direction, the enhancement of the Raman scattering is attributed to the induced dipolar field around the resonating nanorods. The physically self-assembled nanorod arrays are useful for practical applications using linearly polarized excitation light from the viewpoints of the efficiency of the local plasmon excitation and the low cost of the self-assembly process.

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