Physically Self-assembled Ag Nanorod Arrays for Tunable Plasmonic Sensors

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We have established a process to fabricate Ag nanorod arrays with tunable morphology, hence tunable plasmonic properties. Based on a dynamic oblique deposition (DOD) technique, the nanorods are aligned in a way where their major axis is quasi-parallel. The aspect ratio of the nanorods is adjusted by choosing an appropriate DOD condition to show plasma resonance in the wavelength region around the Raman scattering of 785 nm. The nanorod arrays thus tuned provide intense surface enhanced Raman scattering useful for practical applications to biochemical sensors. [DOI: 10.1380/ejssnt.2005.280]

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I. INTRODUCTION

For applications of the local field enhancement due to local plasmons in noble metal nanoparticles to biochemical sensors such as surface enhanced Raman scattering (SERS) sensors, controlling both the shape and the arrangement of the nanoparticles is important[1]. It is well known that the well-ordered 2D periodic arrays of triangular nanoparticles prepared by nanosphere lithography show the plasma resonance within a rather narrow wavelength region, and the sharp corners of the triangle lead the strong SERS. Although the nanosphere lithography enables the tuning of the size of the nanoparticles, the number density of the particles is fixed geometrically. Some applications such as a Raman imaging may require more SERS active spots to improve space resolution. The drastic enhancement of the local field is also expected at the end of the elongated particles[2]. For the light from visible to near IR region, actually, the SERS has been observed on the aggregates or the arrays of the elongated metal nanoparticles so-called nanorods whose width and aspect ratio are a few 10 nm and 2–5, respectively[3–5]. Taking account of the gap enhancement of the local field[6], in-line alignment of the nanorods is more desirable than side-by-side alignment[4] or random aggregation[5]. At the very early stage of the history of SERS studies, virtue of the in-line nanorod arrays has been already reported for the Ag nanorod arrays prepared on the lithographically produced templates[3]. Even today, however, it is not easy to produce sub-μm patterns over large area at low cost.

The recently popularized dynamic oblique deposition (DOD) is a physical self-assembly growth technique that can produce 3D nanostructures with a controllable porosity and shape[7, 8]. Contrary to the ordinary chemical self-assembly, physical one is very robust in that practically any material or combination of materials can be used for fabrication. Recently, we have demonstrated the direct formation of the Ag nanorods with a quasi-parallel major axis on a template layer of SiO$_2$ having strongly anisotropic surface morphology by using DOD technique[9, 10]. In this paper, we report that these physically self-assembled Ag nanorod arrays show the fairly high sensitive SERS as well as the polarization dependent plasma resonance tunable by the condition of the DOD.

II. EXPERIMENTAL

As schematically shown in Fig. 1(a), a template layer of SiO$_2$ with anisotropic surface morphology was prepared by the serial bideposition (SBD) technique[11] on a glass substrate in a DOD apparatus with a base pressure of $2 \times 10^{-6}$ Pa. A tablet of SiO$_2$ (purity 99.9%) was evaporated from an electron beam (EB) source 48 cm from the substrate, under a pressure of $8 \times 10^{-5}$ Pa. Vapor flux of SiO$_2$ was typically 0.5 nm/s. During the serial bideposition, the deposition angle, $\alpha$, measured from the surface normal, was fixed at an angle chosen between 72$^\circ$ and 86$^\circ$, while the azimuthal angle, $\phi$, was changed rapidly by 180$^\circ$ with each deposition of a 10-nm-thick layer. After repeating 15 cycles of the serial bideposition, SiO$_2$ layers with an approximate thickness of 300 nm were obtained. Under these deposition conditions, it is expected that the isolated columns grow perpendicular to the surface since the thickness of each SiO$_2$ layer (10 nm) is comparable to the width of the SiO$_2$ columns. In addition, the columns are bundled in the direction perpendicular to the plane of incidence of the SiO$_2$ vapor and subsequently form the anisotropic surface morphology. Onto the fabricated template layer, Ag was evaporated from a tungsten basket located in the deposition plane of SiO$_2$, at a distance of 12 cm from the center of the substrate as shown in Fig. 1(b). The pressure during the Ag deposition was $2 \times 10^{-5}$ Pa,
and the vapor flux of Ag was 0.1–0.2 nm/s. The deposition angle of Ag, \( \alpha_{Ag} \), was selected between 52° and 79°, while the azimuth remained unchanged during the Ag deposition. The amount of deposited Ag was 5–13 nm in average thickness, which was so minute that the Ag layers remained discontinuous on the template. Due to the shadowing of the surface corrugation, Ag deposits only on higher parts of the surface selectively and cannot reach the valley between the columns of the template. As the result, it is expected that Ag forms the nanorods on the bundled surface as shown by red color in Fig. 1(b). The morphologies of samples were observed by a scanning electron microscopy (SEM).

The optical transmittance of the samples was measured using a single-beam spectrophotometer in a wavelength range 300 < \( \lambda \) < 1500 nm at normal incidence. The incident light had either \( p \)- or \( s \)-polarization in which an electric field vibrates parallel or perpendicular to the deposition plane, respectively.

Raman spectroscopy was performed by using a near-IR confocal Raman microscope (HORIBA Jobin Yvon, The LabRam 1B) at an excitation wavelength of 785 nm and a power of 15 mW. The microscope uses a 60× objective, NA of which is 0.7, and a confocal pinhole of 1.1 mm in diameter. In order to achieve \textit{in situ} measurements of the SERS on Ag nanorod arrays immersed in water solution of 4,4′-bipyridine (BiPy), we made a small cell (6 mm in diameter with a spacer of silicone rubber of 0.5 mm in thickness) on the sample directly. After the cell was filled with the BiPy solution, it was sealed with a cover glass.

III. RESULTS AND DISCUSSION

A. Tuning of Morphology and Plasmonic Properties for SERS

Figure 2 shows typical morphology of the Ag nanorod arrays. The samples were prepared at different \( \alpha \), while \( \alpha_{Ag} \) and the average thickness of Ag are fixed at 70° and 10 nm, respectively. The ordinary secondary electron images are shown in the upper row, and the images in the bottom row are the backscattered electron images. Note that the samples were not coated with the conductive coatings to prevent charging up. In the ordinary secondary electron images, which are insensitive to compositional distribution, the surface corrugation elongated perpendicular to the incident direction of SiO\(_2\) vapor is observed. On the top of the surface corrugation, inhomogeneous distribution of the contrast is recognized. This suggests the existence of the inhomogeneous distribution of materials. In fact, Ag is distinguished from the SiO\(_2\) template in the backscattering electron images as shown in the images shown in the bottom row in Fig. 2. Many bright spots are attributed to Ag. Clearly, Ag exists on the top of the elongated columns of the template due to the shadowing effect of the surface corrugation. As a result, Ag was elongated and became the nanorods aligned in quasi-parallel to each other.

At the smaller deposition angle of \( \alpha = 72° \), the columns are closely packed. On the other hand, at the larger deposition angle of \( \alpha = 82° \) and 86°, strong atomic shadowing creates a porous nanostructure with isolated columns. The shape of the Ag nanorods also changes depending on \( \alpha \). Clearly, the nanorods on the template of \( \alpha = 82° \) and 86° is more elongated than that of \( \alpha = 72° \). The average aspect ratios of these three samples are 2.1 (\( \alpha = 72° \)), 3.5 (\( \alpha = 82° \)) and 3.0 (\( \alpha = 86° \)). We have confirmed that other DOD conditions also affect the morphology of the nanorod arrays. Therefore, the morphologies of Ag nanorod arrays can be controlled by the DOD conditions such as \( \alpha \), \( \alpha_{Ag} \) and thicknesses of Ag and template. As is well known, the plasma resonance of free electrons in the nanoparticles is sensitive to their shapes\([12, 13]\). In fact, our nanorod arrays show the significant dichroism due to the anisotropic plasma resonance and their resonance wavelength depends on the DOD conditions\([9, 10]\). In other words, the plasmonic properties can be controlled by the DOD conditions.

For the applications to the SERS sensors, it is required that the plasma resonance is tuned to the wavelength of the excitation laser and the scattered light. In this study, the resonance wavelength of 750–950 nm is preferable for the detection of the typical Raman bands, since we used the laser of the wavelength of 785 nm for the excitation. Figure 3 shows the absorbance spectra of \( p \)- and \( s \)-polarization for the samples designed for the SERS measurements. The absorption of \( p \)-polarized light reaches its peak at approximately 360 nm while the absorption of \( s \)-polarized light reaches its peak at 860 nm. Evidently,
anisotropy in the optical absorption has been successfully achieved, and the absorption peaks are attributed to the plasma resonance of the free electrons in the Ag nanorods. In the wavelength range of the Raman excitation and scattering, the strong enhancement of the local field is expected, since the plasma resonance is achieved for the s-polarized light in this region. These plasmonic properties correspond to the morphology of Figs. 2 (b) and (b')). Since the DOD based nanorods formation require no other process than the physical vapor deposition, on-demand tuning of the plasmonic properties to the various excitation wavelengths is easy to be realized.

Figure 4 indicates the Raman scattering spectra of the BiPy solution of 1 mmol/ℓ on the nanorod array and glass substrate. Intense peaks are only found in the spectra measured on the Ag nanorod array and are attributed to the SERS of BiPy on the noble metal nanoparticles[14]. This SERS spectrum was measured within 10 min after the sample was immersed in the BiPy solution, which is the time to set the sample on the microscope. Contrary to that the some other types of the SERS substrates require long time for the molecule to be adsorbed at the hot spots[15], our dosing time is quite short. This is likely to be attributed to the high density of the nanorods in our samples. Moreover, the SERS spectrum in Fig. 4 was
measured 3 months after the nanorod arrays was fabricated. For 3 months between the nanorods preparation and the Raman measurements, the nanorod arrays were kept in a standard desiccator. Almost the same spectrum was obtained further 3 months later. Therefore, the nanorod arrays prepared by the DOD are extremely stable.

In order to estimate an enhancement factor, we measured the SERS spectra of the BiPy solution down to 1 µmol/ℓ and the normal Raman scattering (NRS) spectrum for pyridine solution of 1.3 mol/ℓ. Assuming that the volumes contribute to the SERS and the NRS is 1 µm×1 µm×10 nm and 1 µm×1 µm×10 µm, respectively, the enhancement factor was roughly estimated as the order of 10⁹. Although the reliability of this value of the enhancement is not so high due to the lack of knowledge of the number of the adsorbed molecules, we can conclude that the nanorod arrays prepared by the DOD have the useful SERS activity for the practical applications.

IV. CONCLUSION

We have succeeded in fabricating the arrays of Ag nanorods directly on a glass substrate by the DOD. Discontinuous Ag islands are deposited obliquely on the template layer of SiO₂, which has a strongly anisotropic surface morphology created by SBD at an oblique angle. The morphology of the nanorods such as the aspect ratio has been controlled by choosing the appropriate DOD conditions. This enables the tuning of the plasmonic properties to the superior SERS. For the Raman scattering at the excitation of 785 nm, we have successfully prepared the nanorod arrays showing the plasma resonance in the wavelength region between 750-950 nm. These nanorod arrays provide the intense SERS spectra even just after they are immersed in the BiPy solution. Furthermore, the nanorod arrays presented here are stable and their enhancement factor is fairly high, so that they will be applied practically to the biochemical sensors with high reproducibility.

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