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# Surface-enhanced Raman scattering substrate of silver nanoparticles depositing on AAO template fabricated by magnetron sputtering

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## 1. Introduction

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Raman spectroscopy, based on an inelastic scattering of photons, has been used to identify a wide variety of chemical and biological molecules by their Raman spectra. However, a conventional Raman spectroscopy suffers from a small scattering cross section. The problem can be solved by a surface-enhanced Raman scattering (SERS) technique which greatly enhances the sensitivity of the conventional Raman spectroscopy [1–6]. This powerful technique hence is applicable to detect molecular species and has recently drawn a considerable attention in researches in chemical and biological analyses. In addition, SERS offers several potential advantages over other spectroscopic techniques because of its measurement speed, high sensitivity, portability, and simple maneuverability.

Despite a considerable number of researches in the SERS technique, its mechanism is still under debated [3]. In general, enhancement factors for the SERS substrates are reported between 10<sup>6</sup> to 10<sup>8</sup> [7–10]. Note that, an extraordinarily high enhancement factor ( $\sim 10^{14}$ ) was reported on an active SERS system using colloidal silver molecules [11,12]. However, metal colloid suffers from its aggregation states. Although different analytes produce different aggregation states, they equally impose unreliable Raman

ABSTRACT

In this report, we describe a fabrication process of low-cost and highly sensitive SERS substrates by using a simple anodizing setup and a low-energy magnetron sputtering method. The structure of the SERS substrates consists of silver nanoparticles deposited on a layer of anodic aluminum oxide (AAO) template. The fabricated SERS substrates are investigated by a scanning electron microscope (SEM), a transmission electron microscope (TEM), and a confocal Raman spectroscope. We have verified from the surface morphology that the fabricated SERS substrates consist of high-density round-shape silver nanoparticles where their size distribution ranges from 10 to 30 nm on the top and the bottom of nanopores. The surface-enhanced Raman scattering activities of these nanostructures are demonstrated using methylene blue (MB) as probing molecules. The detection limit of  $10^{-8}$  M can be achieved from this SERS substrate. © 2010 Elsevier Ltd. All rights reserved.

> intensity and difficulty for standardization. Lithography is another ideal method for producing uniform and reproducible SERS substrates [13,14]. Although their enhancement factor can be achieved up to  $\sim 10^9$  [14], the lithographic technique is very expensive in a large-area production of the SERS substrates. In this work, we here report a fabrication process of low-cost and highly sensitive SERS substrates, based on a magnetron sputtering system. The magnetron sputtering technique has a primary advantage in an easy adaptation to a large-scale production. We use the magnetron sputtering system to deposit silver nanoparticles on top of a thin AAO template which is previously coated on each silicon substrate. The presence of the AAO template helps increase the surface area and prevent coalescence of the deposited silver nanoparticles. The AAO template thus maintains a high density of the silver nanoparticles to obtain a large SERS enhancement factor. Note that the silicon-based support makes the SERS substrates easier to handle than those fabricated on fragile porous alumina foils as previously reported [15].

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#### 2. Experimental details

#### 2.1. Sputtering system

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All of the metal nanoparticles in the SERS substrates are prepared by a homemade high vacuum (HV) DC magnetron

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sputtering system. Its deposition chamber reaches a base pressure at approximately  $1 \times 10^{-3}$  Pa. During the film deposition, an operating pressure is maintained at 0.4 Pa by a throttle valve. Plasma cleaning is performed for 5 min prior to the metal deposition on the silicon surface using 70 W of an RF power, 16.25 MHz of an RF frequency, and 5 sccm of an argon flow. The metal deposition is then followed with a DC sputtering power of 34 W.

#### 2.2. Preparation of AAO templates

For each AAO template, a 120 nm thick aluminum film is first deposited on a (100) silicon substrate. In an anodizing step, the substrate is connected to a power supply of an anodic electrode, and subsequently immersed in 0.3 M oxalic acid. A gold plate on the silicon substrate is used as a cathodic electrode. The anodizing current is precisely controlled by a Motech's LPS-305 digital power supply at the current of 10 mA with the voltage limit of 40 V. During this step, a large fraction of the aluminum film will be transformed into nanopores confined to 5–10 nm Al<sub>2</sub>O<sub>3</sub> side walls. The substrate is then submerged in 5 wt% H<sub>3</sub>PO<sub>4</sub> for 30 min in order to remove the Al<sub>2</sub>O<sub>3</sub> layer, thus opening cylindrical nanochannels along the top surface of the AAO film toward the silicon surface.

#### 2.3. Sputtering of silver nanoparticles

The silver nanoparticles are deposited on each AAO template by the DC magnetron sputtering system. The sputtering target is a 3-inch high-quality pure (99.99%) silver manufactured by K.J. Lesker. The deposition rate is approximately 1 nm/s as calibrated by a spectroscopic elipsometer (HS-190) manufactured by J.A. Woollam.

#### 2.4. Surface characterizations and analyses

The film thickness is verified by Hitachi's s-5200 field emission scanning electron microscope (FE-SEM). The FE-SEM is also used to examine the lateral features of the AAO nanopores and the silver nanoparticles deposited on their matrix. The cross-sectional details of the SERS structures are characterized by JEOL 2010 (200 kV) transmission electron microscope (TEM).

#### 2.5. Raman scattering characteristics

The fabricated SERS substrates are cut into several  $5 \times 5 \text{ mm}^2$  pieces. Each of these samples will be one time used to characterize reference molecules. In this report, methylene blue (MB) is selected as probing molecules on the fabricated substrates in order to determine the SERS activities. A sensitive NT-MDT NTEGRA Raman spectrometer equipped with a confocal optical microscopy system is used to characterize the Raman spectra. Prior to the measurements, a drop of methylene blue (MB) at  $5 \times 10^{-2}$  mL in volume is deposited on each SERS surface. The sample with the MB droplet is left to dry at room temperature in an air atmosphere, and is immediately measured for the Raman spectra using a 633 nm He–Ne laser excitation. In this study, the Raman scattering characteristics are conducted as the MB concentration varies between  $5 \times 10^{-8}$  M and  $5 \times 10^{-3}$  M.

## 3. Results and discussion

## 3.1. Physical characteristics of SERS substrates

Fig. 1(a) shows the top-view image of one SERS substrate taken by the FE-SEM. The image illustrates a uniform nanopore array with



**Fig. 1.** SEM images of the SERS substrates with the silver nanoparticles deposited by the magnetron sputtering for 8 seconds (a) on the AAO template (b) on the Si surface.

a pore size distribution between 30 and 40 nm, and an interpore distance around 80–100 nm. The silver nanoparticles with the diameter size around 10–30 nm are observed both on the inside and outside of the AAO nanochannels. The density of the silver nanoparticles on this particular sample is about half of that of the nanopore array at approximately  $1 \times 10^{10}$  cm<sup>-2</sup>. Without the AAO template, these nanoparticles will migrate along the substrate surface and coalesce to form a larger island as shown in Fig. 1(b). The coalescence results in the decrease in the density and the surface area of silver nanoparticles that can be bounded by the probing molecules. The coalescence hence reduces the coupling effect between the silver nanoparticles and degrades the Raman enhancement factor.

The structural details of the SERS substrates are further investigated by cross-sectional TEM images. One of the images has been selected and shown in Fig. 2. The TEM image verifies that the nanopores are completely opened from the aluminum top surface down to the silicon substrate interface. In addition, the image reveals the silver nanoparticles embedded on the bottom of the nanochannels and on the top of the AAO surface. The TEM image also indicates the difference in size distribution between the nanopaticles embedded on each layer. The silver nanopaticles on the bottom of the nanochannels range between 10 and 20 nm in size, while those on the top of the AAO range between 20 and 30 nm in size. The size difference is most likely due to a shadowing effect of sputtered material between these two locations.

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Fig. 2. Cross-sectional TEM images of the SERS substrates with the silver nanoparticles on AAO template.

#### 3.2. SERS measurements

The Raman spectra of MB at the concentration of  $5 \times 10^{-3}$  M on the different types of the substrates are presented in Fig. 3. Since the main absorption peaks of MB solution are located at 656, 610 and 293 nm [16], the resonant Raman effect from the excitation wavelength may partially improve the Raman intensities. However, this resonant effect is expected to be much smaller than SERS effect. The normal Raman spectrum of solid MB molecules adsorbed on the silicon substrate without the SERS structure is shown in spectrum (a). The peak at 520  $\text{cm}^{-1}$  corresponds to the Raman scattering of the crystalline Si substrate. The spectrum indicates that the Raman signal of MB without enhancement is not strong enough to be observed due to small amount of Raman scattering from the material deposited on the Si surface. Spectrum (b) presents the enhancement effect on the Raman scattering of the silver nanoparticles coated directly on the silicon wafer. With this sample, characteristic Raman peaks of MB become visible, indicating enhancement activity from the silver nanoparticles. For the SERS



**Fig. 3.** Raman spectra of the methylene blue droplets at the concentration of  $5 \times 10^{-3}$  M as left dried on (a) the Si substrate, (b) the silver nanoparticles deposited on the Si substrate, and (c) the silver nanoparticles deposited on the AAO template.

substrate with the silver nanoparticles embedded in the AAO template, the Raman intensities increase drastically as shown in spectrum (c). This suggests that the coalescence of the silver nanoparticles is an important factor that limits the Raman enhancement factor of these substrates. That is, the presence of nanochannels increases the surface area for the deposition of the silver nanoparticles and suppresses the coalescence. These results in further enhancement of the SERS intensities and thus allow the SERS substrates to reveal several molecular details of the MB molecules adsorbed on their surface.

Fig. 4 shows the Raman spectra of MB with the concentrations varied from 5  $\times$  10  $^{-2}$  M to 5  $\times$  10  $^{-8}$  M on the fabricated SERS substrate. One of the interesting features that should be pointed out here is the comparison in the SERS intensities between MB with the concentrations of  $5 \times 10^{-3}$  M and  $5 \times 10^{-2}$  M. At this point, the SERS intensity increases, instead of decreases, with a decrease in the MB concentration. This indicates that the enhanced Raman signal is generated only from a thinlayer of analyte molecules embedded close to the metal nanoparticles. Other additional layer of analyte molecules weakens the scattering signal, instead of the strengthening. The Raman scattering intensities decrease at concentrations below  $5 \times 10^{-3}$  M, which indicate reduction in MB monolayer film deposited on the SERS substrates. The Raman intensity almost disappears for MB at  $5 \times 10^{-8}$  M concentration compared to that of the higher MB concentrations. However, the inset shows that some of MB band peaks can still be able to observe at this ultra low concentration. This verified a high sensitivity of this fabricated SERS substrate.

## 3.3. Calculation of Raman enhancement factors

The observed MB band positions are in general agreement with the previously published results [17–21]. For quantitative comparison, we use the Raman enhancement factor which is defined as the ratio of the elastic scattering intensity per molecule between the presence and the absence of SERS. The Raman enhancement factor is written as [15–18]:

$$G = \frac{I_{\text{SERS}}}{I_{\text{Ref}}} \cdot \frac{N_{\text{Ref}}}{N_{\text{SERS}}}.$$

In this formula,  $I_{SERS}$  is the enhanced intensity of the adsorbed MB molecules on the SERS substrate.  $I_{Ref}$  is the spontaneous Raman



Fig. 4. Raman spectra of the methylene blue droplets with different concentrations on the SERS substrates. An inset shows spectrum of the droplet at 5  $\times$  10<sup>-8</sup> M.

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scattering intensity from the bulk MB molecules under the laser spot on the blank Si substrate.  $N_{\text{Ref}}$  is defined as the number of the bulk MB molecules excited by the laser without Raman enhancement effect. For a scattering volume of 1000  $\mu$ m<sup>3</sup>, N<sub>Ref</sub> is approximately  $3.3 \times 10^{11}$  molecules.  $N_{\text{SERS}}$  is the number of molecules uniformly spreading on SERS substrate under laser spot. Using a 100× objective lens, the area of laser spot is around 1  $\mu$ m<sup>2</sup>. As the maximum SERS intensity is obtained from MB at concentration of  $5 \times 10^{-3}$  M, which is corresponding to  $10^4$  monolayers of MB, the value of  $N_{\text{SERS}}$  under laser excitation is therefore  $6 \times 10^9$  molecules. We now obtain the average values of the enhancement factors for the spectrum (b) and (c) in Fig. 3 as  $4.46 \times 10^3$  and  $1.71 \times 10^4$ , respectively. Note that, if we assume a monolayer of molecules for the value of *N*<sub>SERS</sub> as reported previously [16,17], the enhancement factor of these SERS will be on the order of 10<sup>8</sup>. However, there is still no consensus that the SERS signal mainly arises from a single molecule layer covering on nanoparticle array.

#### 4. Conclusions

We have discussed the fabrication process of the low-cost and highly sensitive SERS substrates, which can be achieved by the deposition of the silver nanoparticles on the AAO templates using the magnetron sputtering system. Using the AAO templates, the coalescence of the silver nanoparticles can be suppressed. The density of silver nanoparticles deposited on the SERS substrates can be optimized to be more than  $1 \times 10^{10}$  cm<sup>-2</sup>. By using methylene blue as the reference analyte, the SERS substrates allow an excellent observation of the MB molecular details and offer the enhancement factor more than  $1.71 \times 10^4$ . In addition, the SERS substrates fabricated in this report has detectability to MB at the ultra low

concentration of 10<sup>-8</sup> M. These results suggest that the developed SERS substrates are promising in applications of chemical detections and analyses. For future work, we expect to optimize the nanochannel size and thickness of the AAO arrays which would further increase the SERS enhancement factors for this structure.

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