Automatic fabrication of high-sensitive SERS-active nanogaps between Au sea and Au islands

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Received November 25, 2018; revised December 31, 2018; accepted January 11, 2019; published online February 4, 2019

A novel and efficient method to produce surface enhanced Raman scattering (SERS)-active nanogaps was developed by double-step Au film depositions and subsequent thermal annealings. The obtained nanostructure comprises metallic sea, islands, and in particular gaps between the sea and islands whose width can be automatically adjusted <10 nm, which is difficult to be achieved by the conventional single-step metal deposition and annealing. The nanogap structure gave an increased enhancement factor up to the order of 109, whereas conventional vacant sea and Au island structure exhibited 107. The SERS-active performances are supported by increased localized surface plasmon at the nanogaps.

1. Introduction

Surface plasmons (SPs) have been attracting much research interest as a powerful means to obtain an enhanced electric field. As one of the most promising and practical application of SPs, surface enhanced Raman scattering (SERS) spectroscopy has been studied in recent years,1–3 which enables one to observe remarkably enhanced Raman signals even from diluted analytes. As it is possible to analyse aqueous solutions, SERS is expected specifically to be a new tool for biomedical fields which allows high-sensitive and quick diagnosis.4–6

Presently, a variety of metal nanostructures have been examined for SERS substrates, for instance, metal nanoparticles,7–9 metal deposition on monolayer of colloidal particles,10–12 metal deposition on a template fabricated by photolithographic technique,13–15 metal nanowires chemically synthesized,16–18 and oblique angle metal deposition.19 The amplification of the electric field by these metal nanostructures are attributed to the localized surface plasmon (LSP) mode, and, especially, superposition of electric field obtained at a nanogap typically less than 10 nm in between the metal nanostructures give a much stronger nonlinear near-field enhancement effect than that of the isolated LSP in the proximity of independent metal nanoparticles.5,20

In addition to these various precedents, metal islands or clusters made by metal film deposition and subsequent high temperature annealing have been investigated for SERS-active nanostructures.21–23 An obvious advantage of these metal sea-island structures is thought to be its simple and inexpensive fabrication process, which is suitable for industrial mass production. On the other hand, in order to achieve a high sensitivity and substantial reproducibility, the thermal annealing process must be controlled precisely with regard to the size, shape, and density of the islands,24–25 because the gap-clearance in between the islands enlarges as the annealing temperature and time increase, resulting in a decrease of near-field enhancement at the gaps.26,27

In this study, we present a unique and novel metal nanostructure comprised of Au sea, Au islands, and nanogaps in between the sea and islands, fabricated by a double-step process of metal depositions and thermal annealings. Even though the nanogaps are formed by self-organization, the gap-clearance is automatically adjusted down to <10 nm regardless of the distance between the islands, which is advantageous for high reproducibility of the optical performance necessary for utilization of SERS substrates in the analytical and diagnostic fields.

2. Experimental methods

2.1. Fabrication process

Single Au layer with nominal thickness of 9.0 nm was deposited on flat quartz substrates by vacuum sputtering method using an ion sputtering coater (E-1030, Hitachi High-Technologies), at pressure 8 Pa, current value 15 mA, and deposition rate 11.6 nm min−1. The thickness of the as-deposited Au film was measured by a scanning probe microscope (MultiMode8-HR, Bruker AXS) with a probe “Scanastyl-Air” (nominal tip radius 2 nm) at a scanning rate of 1.0 Hz. Then, the as-deposited Au films were annealed by a furnace at 300 °C for 18 min. For some samples, Au film deposition and annealing were carried out in duplicate. In the 2nd process, the deposition thickness of Au film was adjusted to the same 9.0 nm, and the annealing condition was 150 °C for 5 min. After the deposition and annealing, the surface structure of Au films were observed by a field-emission scanning electron microscope (JSM-7800F, JEOL Ltd) at an acceleration voltage of 1.5 kV and a gun-to-work distance of ca. 10 mm.

2.2. Melting point temperature (Tm) measurement

Tm of Au film samples were determined by a change in a spectrum curve of reflected light from the film surface. A film sample was set on a copper stage placed on a hot plate (temperature control accuracy 0.1 K), and in-situ measurement of surface reflectance was performed by an optical fiber probe connected with a spectrometer (USB-2000, Ocean...
Optics) by normal incident white light with spectral range of 350–1050 nm (LS-1-CAL tungsten halogen light source, Ocean Optics), while the Au film sample was heated up stepwise. A measured change in the reflection spectrum curve was defined as $T_m$, which is caused by the onset of development in the metal surface morphology.

### 2.3. Extinction and Raman spectra measurements

Extinction spectra of the Au film samples were obtained by a spectrophotometer (V-770, JASCO Corporation) with unpolarized normal incident beam. Raman spectra of the samples were examined using diluted 4,4′-bipyridyl aqueous solutions, by means of a dispersive Raman microscope (Nicolet Almega XR, Thermo Fisher Scientific) at excitation wavelength of 785 nm with laser power ca. 10 mW, hole aperture 100 μm, and accumulation 64 scans. All the Raman spectra measurements were carried out four times and their average data was used in this study.

### 3. Results and discussion

Figure 1 shows SEM images of the morphological development of Au film nanostructure by double-step deposition and annealing. Due to the small average thickness of 9.0 nm, the as-deposited Au film [1st deposition, Fig. 1(A)] exhibited semicontinuous fissure-like morphology with gap-clearance of ca. 10 nm, which typically appears in the process to the final coalescence as a continuous film. The optical behavior of these metal island clusters has been studied for decades, reporting that they exhibit SERS-active performance.

In this simple system, optical extinction and SERS intensity increases exponentially as the deposition rate is decreased. Compared with the literature, the deposition rate of 11.6 nm min$^{-1}$ in this study is rather fast. When the 1st-deposited Au film was annealed at 300 °C for 18 min, it formed a typical sea-island structure [Fig. 1(B)] created by dewetting of the molten thin metal films, analogous to those in the literature.

The morphological transition is explained by $T_m$ depression owing to the small film thickness (surface-to-volume ratio) and subsequent aggregation of molten metal driven by surface tension (vapor–liquid interfacial free energy). As a SERS-active structure, however, the distance between the islands is not sufficiently small on average, because the pseudo-hemispheroidal metal islands recede from one another, due to the strong surface tension of molten metal. Therefore, as shown in Fig. 1(B), the possibility to obtain <10 nm gap-clearance between these islands becomes very small.

In order to reduce the enlarged gap-clearance, the 2nd step of an Au layer deposition and thermal annealing was carried out in this study. Figure 1(C) shows the surface morphology after the 2nd Au deposition of ca. 9.0 nm thick onto the pre-existing sea-island structure. After the 2nd deposition, the original islands were covered with the additional Au layer of smooth surface, whereas the “sea area” resulted in the fissure-like morphology same as what appeared after the 1st deposition. An important feature here is that there are some indentations surrounding the original metal islands. The reason why these indentations appear adjacent to the edge of the islands is presumed that there is thinning of the 2nd Au film because of “shadowing” of sputtering Au particles due to the cosine rule.

The 2nd annealing at 150 °C for 5 min did not alter the surface morphology greatly but made the surrounding indentations deeper [Fig. 1(D)]. In this step, $T_m$ depression of the Au films took place again. Considering the later mentioned results of Raman intensity, these indentations are thought to have depth enough to reach the substrate surface, hence these are “nanogaps” with <10 nm clearance between the islands and the metallic sea. It is significant that these

Fig. 1. SEM images of the Au nanostructured surfaces. SEM images of nanostructured surfaces after the 1st deposition (A), 1st annealing (B), 2nd deposition (C), and 2nd annealing (D), respectively.
nanogaps are produced automatically at the preformed indentations nearby the Au islands, and the gap-clearance is spontaneously adjusted by the surface tension of liquid metal. Although the gap-clearance can be controlled by thickness of the 2nd deposition, temperature of the 2nd annealing, as well as period of the 2nd annealing, the reproducibility of the clearance of the nanogaps is very high if an appropriate conditions are once decided. An important point is that the 2nd annealing conditions (temperature and period) should be set smaller than the 1st annealing in order to prevent additional change in shape of the pre-existing islands and enlargement of the gap-clearance. It is also to be noted that there are some gaps in the metallic sea area which are thought to be the same remaining fissure-like morphology formed by the 2nd Au deposition.

The surface morphology after the 2nd annealing obtained by SPM and its height distribution are also presented in Figs. 2 and 3, respectively. The height distribution clearly exhibits that the nanostructured surface has independent peaks relating Au islands, Au sea, and nanogaps. As the height of the islands depends on the individual dewetting area of Au films in the 1st annealing process, the height of islands widely distributes 18–40 nm (peak: 26.1 nm). In contrast, the height of the metallic sea ranges 9–18 nm (peak: 12.3 nm), narrower than the islands, reflecting the lower 2nd annealing temperature which did not induce massive dewetting of the 2nd deposition film. The measured height distribution of nanogaps becomes 0–9 nm (peak: 6.3 nm) apparently representing the depth of the gaps. It should be mentioned, however, that the tip of SPM probe does not always touch the surface of the substrate because of narrowness of the nanogaps and the substantial diameter of the probe, hence it is possible that the height distribution in Fig. 3 includes small positive shift.

The cross-sectional schematic illustrations in Fig. 4 summarize the notion in the each process step of the Au nanostructure fabrication. As discussed above, the 1st as-deposited layer [Fig. 4(A)] produces sea-island structure by the 1st annealing [Fig. 4(B)], then the 2nd deposition layer covers again the whole surface [Fig. 4(C)], and finally the 2nd annealing produces the nanogaps surrounding the islands [Fig. 4(D)]. The fissure-like morphological structures in the 1st and 2nd as-deposited layers are depicted as checkered pattern in this schematics for simplification. Figure 4(E) exhibits imaginary drawing of detection of 4,4′-bipyridyl molecules at the nanogaps with a clearance typically <10 nm, under irradiation by excitation laser at 785 nm.

In general, as atoms at the surface have less cohesive energy than that in the bulk, $T_{m}$ at the surface is depressed. The Gibbs-Thomson equation describes a linear relationship between the $T_{m}$ depression and the inverse of nanostructure dimension,35,37, and in the case of a thin solid film with lateral sizes $x$ and $y$, and thickness $d$, the size-dependent melting temperature $T_{m}(r)$ is given by,38–40

$$\frac{T_{m}(r)}{T_{mB}} = 1 - \frac{2\sigma_{SL}}{\Delta H_f \rho_s} \left( \frac{1}{x} + \frac{1}{y} + \frac{1}{d} \right).$$

Here, $T_{mB}$ = bulk melting temperature, $\sigma_{SL}$ = solid–liquid interfacial free energy, $\Delta H_f$ = bulk enthalpy of fusion, $\rho_s$ = density of solid. As the $x$ and $y$ are orders of magnitude larger than $d$, the first two terms in the Eq. (1) can be neglected. Given that the Au layer is homogeneous fully-packed metal film, the appropriate thickness requires for the $T_m$ depression down to 150 °C is obtained to be ca. 1.2 nm by Eq. (1).

In this study, $T_m$ depression of as-deposited Au films was measured experimentally (Fig. 5). The resulting $T_m$
perpendicular to the substrate. The measured Tm(z) is lower than the calculated one by Eq. 1.

Even though the fissure-like morphology also increases the surface-to-volume ratio and encourages melting behavior, there is still large difference between the experimental and theoretical Tm depressions. It would possibly be most agreeable that the metal films formed by vacuum sputtering deposition consist of metal atoms and their clusters, and these clusters are thought to give minuscule sites in the metal films leading to the considerable magnitude of Tm depression. The Tm depression observed in this study is consistent with the annealing temperatures in the references much smaller than the bulk Tm.21,22,24,25,27,33)

As the vapor–liquid interfacial free energy (σVL) decreases with increasing temperature, a negative temperature coefficient dσVL/dT = −1.9 × 10^{-4} (N mK^{-1}) is known for Au.41) Hereby, σVL of Au at 300 °C and 150 °C are roughly estimated as 1283 × 10^{-3} and 1311 × 10^{-3} (N m^{-1}), respectively, which are much larger than that of water (72.3 × 10^{-3} (N m^{-1}) at 23 °C). The contact angle of liquid Au against quartz substrate at 1353 °C are reported to be 143°,41) hence, at the depressed Tm of 300 °C and 150 °C, contact angles are deduced to be large enough to produce the pseudo-hemispheroidal islands and the depressed Tm(z) exhibits that ca. 8 nm of nominal thickness is required for the depressed Tm = 150 °C, which differs from the calculated thickness by Eq. (1). Even though the fissure-like morphology also increases the surface-to-volume ratio and encourages melting behavior, there is still large difference between the experimental and theoretical Tm depressions. It would possibly be most agreeable that the metal films formed by vacuum sputtering deposition consist of metal atoms and their clusters, and these clusters are thought to give minuscule sites in the metal films leading to the considerable magnitude of Tm depression. The Tm depression observed in this study is consistent with the annealing temperatures in the references much smaller than the bulk Tm.21,22,24,25,27,33)
which forms the sea-island morphology. The nanogaps surrounding the islands in this study are spontaneously created by the large $\sigma_{VL}$.

Figure 6 exhibits extinction spectra at each process step of metal nanostructures. It has been reported that as-deposited Au films thinner than ca. 10 nm deposited at a low rate of 0.3–0.7 nm min$^{-1}$ show an extinction peak in the visible range which is attributed to excitation of LSP.21,33) In this study, however, the Au film deposited at a rate of 11.6 nm min$^{-1}$ did not give a peak in the visible range but a broad extinction spectrum increasing towards the near IR range [Fig. 6(A)], similar to the extinction curve of Au film as-deposited at a very high rate of 18 nm min$^{-1}$.21) This means the resonant wavelength by fast deposition shows red-shift with increasing deposition rate.

After the 1st annealing, the broad extinction shifted to low-wavelength range showing a sharp LSP peak at 569 nm [Fig. 6(B)]. It is analogous with the thermal annealing against the as-deposited film in the literature,21,25,33) giving a blue-shift of LSP band to around 550 nm. The formation of metal islands by thermal annealing leads to the appearance of LSP resonances similar to that of colloidal metal nanoparticles. On the basis of theoretical estimation, the resonant wavelength of Au nanoparticles with 20 nm in diameter is calculated to be 511 nm in ambient air,43) which is close to the measured extinction peaks of nanospheres with 15–30 nm.43) However, the extinction peak of Au islands appeared at 569 nm in this study, and the reason for this shift is thought to be due to the shape of the islands. It has been demonstrated that the LSP peak exhibits red-shift, when size of the particle increases,44) aspect ratio enlarges,45) and corner sharpness increases.46)

The 2nd deposition of Au layer made the extinction curve broader and shifted to red [Fig. 6(C)]. This alteration means that the 2nd deposition overlaid the broad extinction curve of the as-deposited layer [Fig. 6(A)] onto the peaky spectrum of the sea-island structure [Fig. 6(B)]. The deposition of the Au film of 9.0 nm thick with fissure-like structure onto the vacant sea area resulted in a broadening of the LSP peak and increase of resonance in the high-wavelength range.33)

Further, it is deduced that the islands coated with the additional deposition film exhibited a red-shift of the LSP peak, because of the increase in the film thickness of the islands.

The Au nanostructure after the 2nd annealing [Fig. 6(D)] indicated an extinction spectrum similar to that of after the 2nd Au deposition. As the surface morphologies of the metal nanostructures before and after the 2nd annealing basically resemble one another, the similarity in the extinction curve seems to be reasonable.

Figure 7 summarizes the Raman scattering intensities of aqueous 4,4′-bipyridyl of 100 $\mu$M measured on these metal nanostructures at 785 nm excitation. In this study, the largest peak at 1607 cm$^{-1}$, which are assigned to the stretching vibration of pyridine rings,47) was selected for comparison of the SERS intensities.

Figure 7(A) shows the SERS enhancement of the fissure-like structure by the 1st Au deposition gives Raman intensity of ca. 5.2 $\times$ 10$^4$. The SERS-active performance on the as-deposited metal films have been reported in the previous works,30–32) and the semicontinuous fissure-like morphology gave a better enhancement effect than island-like morphology.30) The Raman intensity obtained in this study is thought to be along with the literature.

On the other hand, Fig. 7(B) (after the 1st annealing) exhibits Raman intensity drastically decreased down to ca. 7.0 $\times$ 10$^3$ at 1607 cm$^{-1}$, reflecting the elongated distance in between the Au islands. It has been reported that Raman intensity decreases as annealing temperature is increased, annealing time is elongated, and island size is enlarged.21) These changes are thought to be associated with the increase in the average distance between the islands (decrease in the island area fraction).25)

The 2nd Au deposition onto the sea-island surface recovered the plasmonic resonances giving the Raman intensity of ca. 1.2 $\times$ 10$^5$ [Fig. 7(C)], larger than that of the 1st deposition, reflecting the additional electric field amplification by the fissure-like structure and the indentation surrounding the islands. As the intensity after the 2nd deposition doubled that of the 1st deposition, the SERS enhancement attributed to the indentation is supposed to be sufficiently influential.

After the 2nd annealing, the Raman intensity dramatically soared up to ca. 4.8 $\times$ 10$^5$ [Fig. 7(D)], which is far higher than that of the previous surfaces. Also it was confirmed that the limit of detection of the analyte at 1607 cm$^{-1}$ was ca. 1–10 nM. This increment is reasoned by the formation of the <10 nm nanogaps in between the metallic sea and the pre-existing islands as shown in Figs. 1(D) and 2. As SERS enhancement is dominated by “hot spots” in <10 nm nanogaps rather than quantity of gaps or total area of the metal surface structures, the increase in the Raman intensity in this study is thought to be reasonable. The function of the 2nd annealing is inferred to produce nanogaps with well-defined contours, in which as-deposited metal fraction remains.

Generally, it is difficult to fabricate <10 nm metal nanogaps by standard photolithographic technique. However, there are some studies to obtain the nanogaps, e.g. Au deposition by chemical reduction on Au nanoparticles narrowing the gap between the particles.48) Au deposition by sputtering on Si nanopillars fabricated by deep UV immersion lithography,15) or two-step controlled angle vacuum deposition of Ag on photoresist particles fabricated by electron beam.
lithography. \(^{13}\) Compared with these previous techniques, the nanogap fabrication in this study suggests a novel method to obtain <10 nm clearance with a very swift and inexpensive process. In particular, it is significant to note that the gaps surrounding the islands are automatically adjusted down to <10 nm with a sufficient accuracy.

The total SERS enhancement factor (EF) in an excitation field is obtained as a summation of products of the local SERS EFs, describing the coupling of plasmonic resonances between enhancements by incident light \((M_I)\) and Raman scattering light \((M_R)\), respectively. Accordingly, the total EF \(M_{SERS}\) is written by,\(^{49,50}\)

\[
M_{SERS}(\lambda_I, \lambda_R) = M_I(\lambda_I) \cdot M_R(\lambda_R)
\]

\[
= \sum_{i=1}^{n} \frac{E_i^I(\lambda_I)}{E_i^I(\lambda_I)} \cdot \frac{E_i^I(\lambda_R)}{E_i^I(\lambda_R)}
\]

(2)

where \(E_i^I\) and \(E_i^R\) are the amplitudes of the incident light and the local electric field, \(\lambda_I\) and \(\lambda_R\) are the wavelengths of incident and Raman scattering light, respectively, and \(n\) is the total number of analyte molecules. Therefore, as the theoretical EF is amplified by \(|E_i^I|^4\), an electric field enhancement of 10\(^3\) will ideally produce a SERS enhancement of 10\(^12\). For instance, when a molecule is symmetrically placed in between two Ag spheres of 40 nm in diameter with separation distance of 1 nm,\(^{51,52}\) the EFs \(M_I\) and \(M_R\) are calculated to be 10\(^4\)–10\(^5\) (accordingly the \(M_{SERS}\) is estimated to be 10\(^8\)–10\(^10\)). In the case of actual Raman spectroscopy measurement, however, it is not easy to obtain such a high SERS effect in arbitrary circumstances. Presumably, there are two main reasons for this discrepancy, i.e. one is distribution of the nanogap clearance, and the other is distance between “hot spots” and adhered molecules. A further investigation using the high resolution microscopic Raman imaging technique \(^{11}\) should be useful to clarify the distribution of the SERS-active hot spots.

In this study, the SERS EFs of the Au nanostructures were calculated experimentally. As the laser power and the accumulation time was the same for the both SERS and blank (flat) substrates, the equation can be simplified as follows,\(^{48}\)

\[
EF = \frac{I_{SERS}/n_{SERS}}{I_{Raman}/n_{Raman}}
\]

(3)

where \(I_{SERS}\) and \(I_{Raman}\) are the measured Raman intensities of the SERS and blank substrates, \(n_{SERS}\) and \(n_{Raman}\) are the number of effective molecules on the SERS and blank substrates, respectively.

Table I shows the obtained EFs for the samples after the 1st and 2nd annealings in this study, in comparison with the references. Au islands and vacant sea after the 1st annealing in this study exhibited 2.0 × 10\(^7\), which is close to the same conventional sea-island structure in a reference giving EF of 2.2 × 10\(^7\).\(^{26}\) These are on the basis of LSP, however, the metallic islands are isolated another and difficult to form nanogaps between themselves.

On the other hand, the SERS substrate after the 2nd annealing (Au sea and Au islands with nanogaps) shown significantly increased EF of 1.1 × 10\(^9\), which is higher than that after the 1st annealing by the order of 10\(^7\). Similarly, in the literature, Au islands grown their size by reduction of HAuCl\(_4\) onto the islands (accordingly there are nanogaps between the grown islands) exhibited increased EF of 3.2 × 10\(^9\).\(^{48}\)

Consequently, the results in this study and the literature in Table I are consistent with one another in that the shape-dependent LSP by isolated Au islands with vacant sea gives lower EFs of the order of 10\(^7\), whereas the intensified electric field at the hot spots in the nanogaps between Au sea and Au islands provides augmented EFs up to the order of 10\(^9\).

4. Conclusions

In conclusion, we have demonstrated double-step depositions and annealings of Au films aiming to produce SERS-active nanostructured surfaces. The advantageous point of this process is that the gaps between the metallic sea and the islands are automatically adjusted down to <10 nm, giving large enhancement of electric field at the gaps. The resulting Raman intensity of the metallic structure after the 2nd
The present work: Au islands and vacant sea (1st annealing)

The present work: Au islands with nano-gaps

Fang et al.: Au islands and Au sea (2nd annealing)

Khlebtsov et al.: Au islands and vacant sea

Khalentsov et al.: Au islands with nano-gaps

annealing exceeded over 5 orders of magnitude for dilute 100 μM aqueous 4,4′-bipyridyl, and its EF was 9 orders of magnitude. The novel and efficient fabrication method presented in this study is carried out on the basis of simple self-organization of the double metallic sea-island structures, which should contribute to the spread and wide utilization of SERS substrates for microanalysis in the fields such as analytical chemistry and medical diagnostics.

Table I. Comparison of enhancement factors with references.

| Author            | Nanostructure                  | Fabrication method                          | Excitation wavelength (nm) | Characteristic  | Enhancement factor | References |
|-------------------|--------------------------------|---------------------------------------------|-----------------------------|-----------------|--------------------|------------|
| The present work  | Au islands and vacant sea     | Once Au layer deposition and annealing      | 785                         | Shape-dependent | 2.0 × 10^7         | —          |
| The present work  | Au islands and Au sea         | Twice Au layer depositions and annealings   | 785                         | Shape-dependent | 1.1 × 10^9         | —          |
| Fang et al.       | Au islands and vacant sea     | Once Au layer deposition and annealing      | 785                         | Shape-dependent | 2.2 × 10^7         | 26         |
| Khlebtsov et al.  | Au islands with nano-gaps     | Au layer deposition and annealing followed by reduction of HAuCl₄ | 785                         | Shape-dependent | 3.2 × 10^8         | 48         |

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