Fabrication of 50 nm scale Pt nanostructures by block copolymer (BCP) and its characteristics of surface-enhanced Raman scattering (SERS)

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Surface-enhanced Raman scattering (SERS) represents an important phenomenon that can solve the low signal intensity of Raman spectroscopy, applied as a bio and chemical sensor and analyzer. The SERS effect can be varied with the substrate structure. In this study, we investigated the effect of various Pt nanostructures (e.g., Pt nanoholes, Pt nanorods, and Pt nanotubes) on the sensitivity of SERS. We fabricated 50 nm-scale Pt nanostructures with different heights with a self-aligned block copolymer (BCP) process composed of the self-assembly of BCP, Pt atomic layer deposition, and reactive ion etching of a silicon substrate and Pt. Our investigation of the SERS effect with rhodamine 6G showed a significant dependence on the shape (but not the height) of the nanostructure. Among the different Pt nanostructures investigated, Pt nanotubes (possessing the structural characteristics of nanoholes and nanorods) showed the highest SERS effect, while Pt nanoholes showed the lowest SERS effect.

Introduction

Until the discovery of the unique optical properties of metal nanostructures that can cause the amplification of optical processes in Raman scattering, called surface-enhanced Raman scattering (SERS), Raman spectroscopy had not been actively investigated nor applied to various fields (e.g., biochemistry, forensics, food safety, medical diagnostics, etc.) due to its low signal intensity (despite investigations for bio and chemical sensing applications and analysis).1–4 Ag and Au represent the most commonly used nanostructured metals. In addition, Raman scattering signals can be enhanced by other metals (including transition metals); among these, several research groups have investigated and confirmed the SERS effect of Pt.5–6

Electromagnetic and chemical enhancement generally explain the dramatic increase of the Raman scattering signals.7–9 Especially, the collective oscillation of electrons in the metal surface originates the electromagnetic enhancement, dependent upon the size, shape, and distance of the metal nanostructures.10–13 Due to the geometric dependence of the SERS effect on the metal nanostructures, many researchers study various fabrication methods for the different metal nanostructures on the substrate. Particularly, low dimensional nanostructures with 10–100 nm size (e.g., nanodot, or nanotube) have been shown to enhance SERS intensity, due to the dimensional confinement caused by the local electromagnetic field enhancement between nanostructures.14

To obtain better uniform and regular nanostructures, researchers have widely investigated E-beam lithography (EBL) for the top-down fabrication of uniform low dimensional nanostructures, because EBL can precisely control the dimension of the nanostructure (e.g., size, shape, and spacing) between structures.15,16,17,18 Despite of these advantages, EBL presents challenges for practical applications, due to its high fabrication costs and its limitation to a localized area. Researchers have also investigated bottom-up nanostructure fabrication methods using solution-based self-assembly of metal nanoparticle arrays, using AgNO3 and AuCl3 for large-area metal nanostructure processing.19–21

Involving a relatively simple process and low cost production, the solution-based method nevertheless exhibits problems related to non-uniform size and irregular distribution of nanoparticles. Such disordering can not only reduce the SERS
effect, but also decrease the accuracy of the signal intensity.\textsuperscript{22} Researchers have also investigated other top-down metal nanostructure fabrication methods, using the anodized aluminum oxide (AAO) and the nano-imprint lithography (NIL) techniques; however, these methods showed difficulties in forming differently-shaped metal nanostructures and with repeatability.\textsuperscript{23–24} Block copolymer (BCP) lithography with covalent bonding represents an alternative approach capable of forming (a few–tens of) nanometer scale polymer array patterns (e.g., dot, cylinder, and lamella) on the substrate through the self-assembly of the monomers, by controlling the mole fraction between the monomers. Due to the advantages of BCP lithography (e.g., simplicity, low cost, and large area processing), many researchers study this technique for making various top-down nanostructures, including one dimensional nanostructures using BCPs as the template.\textsuperscript{25–27} However, due to the characteristics of the materials involved, certain problems must be resolved to achieve the desired nanostructure.

In this study, we used BCPs to obtain more uniform and regular nanostructures. To improve the pattern transfer during etching, we investigated a surface treatment method using sulfur-containing plasma to harden the BCP mask. We fabricated various Pt nanostructures using a top-down self-aligned nanostructure array fabrication method (i.e., self-aligned BCP processing), composed of atomic layer deposition (ALD) of Pt and reactive ion etching (RIE) of Si and Pt, with BCP as the template. Using this method, we could fabricate uniform and large area Pt nanostructures with an outside diameter about 40 nm (e.g., Pt nanoholes, Pt nanorods, and Pt nanotubes) having different heights. Using these variously-shaped Pt nanostructures (despite a SERS effect lower than Ag or Au), we investigated the effect of the shape and size of the metal nanostructure on the amplification of the Raman intensity.

Results and discussion

Fig. 1 shows the schematic diagram of the self-aligned BCP processing sequence for the fabrication of Pt nanostructures (e.g., Pt nanoholes, Pt nanorods, and Pt nanotubes). Depending on the types of Pt nanostructures, we used three to five processing steps composed of BCP lithographic patterning, etching, and Pt ALD. For the BCP lithographic patterning, we used PS-b-PMMA; then after the PS hardening using the SF\textsubscript{6} plasma (described in the Experimental section), we finally used a 40 nm diameter PS hole array pattern as the mask for the fabrication of the Pt nanostructures. For this experiment, we etched the silicon up to 90 nm using the sulfurized PS hole array mask, with the results shown in Fig. 2. To obtain different etch depth, we varied the etch time. As shown in Fig. 2, depending on the etch time, we etched about 30, 50, and 90 nm deep silicon with a silicon by varying the etch time from \( \sim 1 \) min, \( \sim 1.5 \) min, \( \sim 3 \) min, respectively, while we could observe almost vertical and smooth silicon etch profiles (after the etching of the silicon using the sulfurized PS hole array as the etch mask). After the silicon etching but before the Pt ALD, the remaining PS mask could be easily removed by an oxygen plasma (as described above), because we carried out the Pt ALD at a temperature of 200 °C.

Fig. 3 shows the SEM micrographs (cross-section, top, and tilted views) for (a) 30 nm, (b) 50 nm, and (c) 90 nm silicon holes, after deposition of Pt using the ALD with a MeCpPtMe.
precursor. When we investigated the structure of Pt deposited by ALD using XRD (X-ray diffraction) and TEM (transmission electron microscopy), it was a polycrystalline Pt with the preferred orientation of (111) (ESI Fig. S2†). To deposit 12 nm thick Pt on the 40 nm diameter silicon holes, we used 240 cycles (0.5 Å per cycle) of ALD. From the remaining Pt on the cross-sectional and tilted views of the SEM micrographs, we could identify Pt deposition to the bottom of the silicon, even for the 90 nm deep silicon hole. The deposition of 12 nm thick Pt in the 40 nm diameter silicon holes decreased the hole size. We could identify the remaining hole size after the deposition of Pt from the top views. The measured diameter of the Pt nanoholes was uniformly 15–16 nm, due to the decrease of hole diameter of 24 nm.

For the formation of Pt nanorods (instead of Pt nanoholes with 12 nm thick Pt), we deposited 25 nm thick Pt (after the silicon hole formation in Fig. 2) by using 500 ALD cycles (instead of 240 ALD cycles). After the 25 nm thick ALD deposition, we filled all the silicon holes in Fig. 2 with Pt (SEM micrographs are shown in Fig. S3†). After the deposition of 25 nm thick Pt, we etched a 25 nm thick Pt layer covering the top of the silicon substrate using an Ar/SF6 gas mixture of Ar (27.5 sccm)/SF6 (5 sccm), 13.56 MHz 50 W of bias power, and 4.5 mTorr of operating pressure for 4 min 30 s. Therefore, we selectively etched the Pt using only bias power, mostly with an Ar+ ion bombardment, until exposing the silicon under the top Pt layer. After the exposure of the silicon substrate, we selectively etched the silicon surrounding the Pt nanorods to Pt using 8 mTorr SF6 gas with 50 W of 13.56 MHz bias power. Fig. 4 shows the SEM micrographs (cross-section, top, and tilted views) of the (a) 30 nm, (b) 50 nm, and (c) 90 nm height Pt
nanorods, by etching the surrounding silicon from 20 s to 1 min to expose Pt nanorods with different heights. Different contrast views (showing the tilted and side views) of the Pt nanorods in the SEM micrographs indicated that all were fully exposed from the silicon substrate.

To form Pt nanotubes (instead of Pt nanorods), after the deposition of 12 nm thick Pt by Pt ALD as in Fig. 3, we etched the top 12 nm thick Pt layer on the silicon wafer (by the Pt etching process described above) for 2 min 30 s, using the Ar/SF₆ plasma to expose the silicon surface. We also selectively etched the silicon surrounding the Pt nanotubes to Pt using the SF₆ plasma (similar to the case of the Pt nanorods in Fig. 4) to expose the Pt nanotubes. Fig. 5 shows the SEM micrographs (cross-section, top, and tilted views) of the (a) 30 nm, (b) 50 nm, and (c) 90 nm height Pt nanotubes, by etching the silicon for different times to expose Pt nanotubes with different heights. The SEM micrographs showed that all the Pt nanotubes were fully exposed from the silicon substrate. We observed the cross-section of the 50 nm height Pt nanotubes using TEM, and we measured the composition of the Pt nanotubes using the EDS installed in the TEM; the results are shown in Fig. 6 for (a) cross-sectional TEM micrograph, and (b) EDS data of Pt. As shown in Fig. 6(a) and (b), we could observe a Pt wall about 12 nm thick. Also, as shown in Fig. 6(a), the outside wall of the 50 nm high Pt nanotube was relatively straight, due to the anisotropic etch profile of silicon etched using the PS hole array pattern; however, the inside of the Pt nanotubes obtained by 12 nm thick Pt ALD on a 40 nm diameter silicon hole was curved. Therefore, the inside diameter of the Pt nanotubes was larger than 15–16 nm, especially at the center area of the Pt nanotubes, possibly due to the etching of a Pt hole sidewall during the top Pt layer etching using Ar/SF₆. Also, as shown in Fig. 6(a), we also etched the bottom center of the Pt nanotubes by an energetic reactive ion beam during the Pt etching (different from Pt nanoholes), while the silicon etching following after the top Pt layer etching (for the exposure of the Pt nanotubes) revealed the bottom side of the Pt nanotubes. Through the etching of Pt and silicon, we fabricated the open-ended Pt nanotubes, as shown in Fig. 6. For different types of Pt nanostructures having a height of 90 nm, we compared the Raman intensities of rhodamine 6G with the concentration of 10⁻⁸ M on the silicon substrate, with the results shown in Fig. 7. The SERS effect grew larger according to the sequence of Pt nanoholes, then Pt nanorods, then Pt nanotubes, by showing 3 times, 5 times, and 3 × 10³ times higher Raman intensity, respectively, compared to that observed on a flat Pt surface; therefore, among the Pt nanostructures investigated, the highest SERS effect could be observed for the Pt nanotubes. When we investigated the SERS effects on the different nanostructure heights of 30, 50, and 90 nm for Pt nanoholes, Pt nanorods, and Pt nanotubes, the SERS effect appeared almost linearly proportional to the height of the Pt nanostructures [ESI; Fig. S4 for Pt nanoholes; Fig. S5 for Pt nanorods; and Fig. S6 for Pt nanotubes†]. Differences in the wetting characteristics of rhodamine 6G solution on the surface of the different Pt nanostructures offered one possible explanation for the

Fig. 5  SEM micrographs (cross-section, top, and tilted view) showing Pt nanotubes of (a) 30 nm, (b) 50 nm, and (c) 90 nm height. 12 nm thick Pt was deposited in the 40 nm diameter silicon holes to form 15–16 nm Pt holes. After the Pt ALD, 12 nm Pt was blanket etched to expose the silicon surface and followed by selective silicon etching to reveal the Pt nanotubes.
di different SERS enhancement factors for the different Pt nanostructures. However, the almost linear increase of Raman intensities with the increase of Pt nanostructure height appears to indicate that the differences of Raman intensities among the Pt nanostructures did not directly relate to the differences in the wetting characteristics of rhodamine 6G solution on the Pt nanostructure surfaces. We also investigated the SERS effect using a different regent such as methylene blue and the results were similar to rhodamine 6G. Therefore, we believe that the differences in the SERS enhancement factors among the Pt nanostructures investigated in this study rather related to the differences in the nano-gap between nanostructures, causing different localized electromagnetic field enhancement. 28-30

Experimental section

Direct self-assembly of BCP

For the Pt nanostructure formation, we carried out BCP lithography on a silicon wafer to form 40 nm scale vertical hole array patterns. First, we treated the silicon wafer with a random copolymer; PS−r−PMMA [poly(styrene-co-methyl methacrylate), $M_n = 6000 \text{ g mol}^{-1}$, $M_w/M_n = 1.25$, Polymer Source Inc.]. We spin-coated 1.0 wt% of PS−r−PMMA solution dissolved in toluene on the silicon wafer, annealed in a vacuum at 160 °C for 12 h; following, we washed the wafer with toluene to remove the unattached excess polymer, forming hydroxyl-terminated silicon surface. We spin-coated 2 wt% of BCP; PS−b−PMMA [poly(styrene-b-methyl methacrylate) with a PS volume fraction ($f_{\text{PS}}$) of 0.79, $M_n = 160 \text{ kg mol}^{-1}$, $M_w/M_n = 1.16$, Polymer Source Inc.] dissolved in toluene on the hydroxyl-terminated silicon wafer, annealing at 250 °C for 24 h in a vacuum for the phase separation of PS and PMMA, as well as to have a PMMA cylinder array in the PS matrix. We selectively removed the PMMA cylinders by a magnetically-enhanced inductively-coupled plasma (ICP) etcher (ESI; Fig. S1†), using 3.5 mTorr Ar/O$_2$ (24 sccm/6 sccm) and by applying 13.56 MHz 15 watts to the substrate only. We kept the substrate at room temperature. After the removal of the PMMA cylinders from the PS matrix, a PS hole array about 40 nm in diameter and 60 nm high (a typical BCP lithographic pattern) formed on the silicon wafer.

Sulfurization

Before etching the silicon wafer with the PS hole array pattern, we treated the PS pattern with a SF$_6$ plasma to harden the PS by sulfurization in order to increase the etch selectivity of the thin PS pattern over the silicon (ESI; Fig. S2†). For the sulfurization process, we plasma treated the PS hole pattern using the ICP system with 50 W 13.56 MHz power, 8 mTorr of operating pressure, and 76 sccm SF$_6$ for 2 min, without biasing the substrate. The sulfurization process with the SF$_6$ plasma after 2 min decreased the PS mask height to about 50 nm.

Etching and deposition

Using the SF$_6$ plasma-treated PS hole pattern as the etch mask, we etched the silicon with the ICP etcher (Fig. S1†). We etched the silicon masked with the SF$_6$ plasma-treated PS hole pattern using a chlorine plasma using the ICP etch system under the following conditions: 13.56 MHz 50 W of ICP power, 13.56 MHz 80 W of bias power, 48 sccm Cl$_2$, and 6.7 mTorr of operating pressure. After the silicon etching, we also removed the PS hole mask using the ICP etcher using an oxygen plasma under the following conditions: 13.56 MHz 50 W bias power, 50 sccm O$_2$, and 5 mTorr of operating pressure for 1 min.

We carried out Pt atomic layer deposition (ALD) on the silicon nanostructures using a commercial ALD system (SNTEK, SN 13-20). We used MeCpPtMe$_3$ (C$_5$H$_4$CH$_3$Pt(CH$_3$)$_3$, Sigma Aldrich Inc.) as the Pt precursor, and we deposited 0.5 Å per cycle at the substrate temperature of 200 °C. For the self-aligned BCP processing, we carried out Pt etching using the same ICP etcher with an Ar/SF$_6$ gas mixture; Ar (27.5 sccm)/SF$_6$ (5 sccm), 13.56 MHz 50 W of bias power, and 4.5 mTorr of operating pressure. For the silicon etching selective to Pt, we etched the silicon with a SF$_6$ plasma under the following conditions: 45 sccm of SF$_6$, 8 mTorr of operating pressure, and 13.56 MHz 50 W of bias power.

Characterization

We observed top, cross-sectional, and tilt views of the BCP pattern and fabricated Pt nanostructures by using scanning electron microscopy (SEM; Hitachi, S-4700). For the measurement of hole pattern edge roughness, we used a metrology analysis program (SuMMiT, EUV Tech. Inc.). For SERS, we dropped one drop of rhodamine 6G (R6G; Alfa Aesar, J62315) with a concentration of 10 $^{-6}$ M on the Pt nanostructures using a pipette, then dried in the air before the Raman measurement. We measured the Raman spectra by using a high resolution dispersive Raman spectroscopy system (Horiba Jobin-Yvon, Model LabRAM HR UV/vis/NIR). Measuring conditions were 514 nm, 7 mW laser; the focused spot size was 1.54 µm$^2$, and the acquisition time was 10 s. We investigated the cross-section of the fabricated Pt nanotubes using transmission electron microscopy (TEM; Jeol, ARM 200F), after cutting the Pt
nanotubes using a focused ion beam (FIB; Seiko, SMI3050TB). Using the micro energy dispersive X-ray spectrometer installed in the TEM (micro EDS; Aztec, Inca), we also identified the components of the Pt nanotube structure. Also, the structure of the Pt deposited by ALD was investigated using TEM and X-ray diffraction (XRD; D8 Discover, Bruker).

Conclusions

In this study, using a self-aligned BCP processing composed of atomic layer deposition (ALD) of Pt, reactive ion etching (RIE) of Si and Pt, and direct self-assembled BCP as the etch mask, we could successfully fabricate different Pt nanostructures, such as Pt nanoholes (~15 nm inside diameter), Pt nanorods (~40 nm outside diameter), and Pt nanotubes (>15 nm inside diameter and ~40 nm outside diameter) having different heights from 30 nm to 90 nm. Using these different Pt nanostructures formed on the silicon substrates, we investigated the effect of the shape and size of the metal nanostructure on the SERS effect of rhodamine 6G with the concentration of \(10^{-6}\) M. For the Pt nanostructures having a height of 90 nm, the SERS effect grew larger following the sequence of Pt nanoholes, then Pt nanorods, then Pt nanotubes, by showing 3 times, 5 times, and \(3 \times 10^3\) times higher Raman intensity, respectively, compared to that observed on a flat Pt surface. Even though the SERS effect for Pt nanotubes investigated was not significantly high due to the use of Pt as the nanostructure, we believe that uniform and regular nanostructures for SERS enhancement can be easily fabricated with self-aligned BCP processing and by the use of sulfurization of the PS mask. In addition, these techniques could also be applied to cheaply and uniformly obtain various other nanostructures on the silicon substrates over a large area.

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Notes and references

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