Preparation of Metal Microdots and Microdiscs by Using Honeycomb Template Prepared by Self-organization

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Summary: Honeycomb-patterned films were prepared by using orderly arranged water droplets as templates. By using the honeycomb-patterned films as templates, Pt/Pd metal microdot arrays were formed on solid substrates. Silver layer was formed on the Pt/Pd layer by electroless deposition, and then, the microdiscs of Ag were obtained by removing the substrate.

Keywords: metal microdots; self-organization; templates

Introduction

Metal particles have received great interest due to their potential applications in the fields of electronics and photonics. Shape of particle is one of the important factors determining the particle properties. Anisotropic metal particles have been received great interest due to their unique electrical, magnetical, and optical properties. For example, nano-rods[1] of gold or silver shows strong plasmonic resonances. Recently, some reports show anisotropic metal structures can be applied for left-handed metamaterials.[2] These examples show shapes of the metal particles and their properties are strongly related.

There are many methods reported to prepare anisotropic metal particles. It is well known that inversed micelles, which have spherical, worm-like, and other structures, can be used as a template of metal particle preparation. Metal ions are reduced in the inversed micelles and form metal particles reflecting the template shapes.[3] Microporous films also have potential abilities for template of micro- and nano-structures. Preparation of nanotubes of organic,[4] inorganic,[5] and carbons[6] have been reported by using porous anodic alumina and microphase separation structures of block-copolymers as templates. The photolithgraphy can be used to make the template of metal particles,[7] however, it requires elaborate processes and expensive equipments.

We have reported that well-arranged micro porous polymer films can be prepared by casting amphiphilic polymer solution under humid conditions.[8] During evaporation of solvents, water droplets condense onto the surface of polymer solution, and then, microporous polymer films can be obtained by using these water droplets as templates. The amphiphilic polymers stabilize the template water droplets and prevent the water droplets from fusion.[9] By using this method, microporous films, which have hexagonally arranged pores ranging from 100 nm to 20 μm, are formed with changing preparation conditions.[10] We have reported that gold microdots were formed by metal deposition and successive removal of the honeycomb templates.[11] Hadziioannou et. al. also has reported that metal microdots can be formed by evaporation deposition.[12]

Electroless plating is a widely used method for surface metallization, and is a

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purely chemical process of reducing metal ions on catalysts introduced onto surfaces.[13] A major advantage of electroless plating is its applicability to a wide variety of materials including insulating surfaces such as glass, silicon oxide, and organic polymers. In this paper, we show preparation of periodic silver microdot arrays on solid substrate by electroplating of silver using the self-organized honeycomb-patterned films as templates. After preparation of honeycomb-patterned films, catalyst layer of platinum and palladium (Pt/Pd) was formed by sputtering. And then, silver metal microdot arrays were formed by electroless plating. The metal microdiscs were also prepared by dissolving the solid substrate.

Experimental Part

Figure 1 shows a schematic illustration of metal microdot and microdisc formation. Poly(bisphenol-A-carbonate) (PC, Mw ~ 64,000 g/mol) was purchased from Sigma-Aldrich. Amphiphilic copolymer 1 (Chart 1) was synthesized according to the literatures.[14] Ten-to-one mixture of PC and 1 were dissolved in chloroform to prepare 1.0 mg/mL solution.Three milliliter of solution was cast on a glass substrate under humid conditions, and then, an opaque film was obtained after complete evaporation of solvent. Si and glass substrates are used to measure the surface structure by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Si and glass

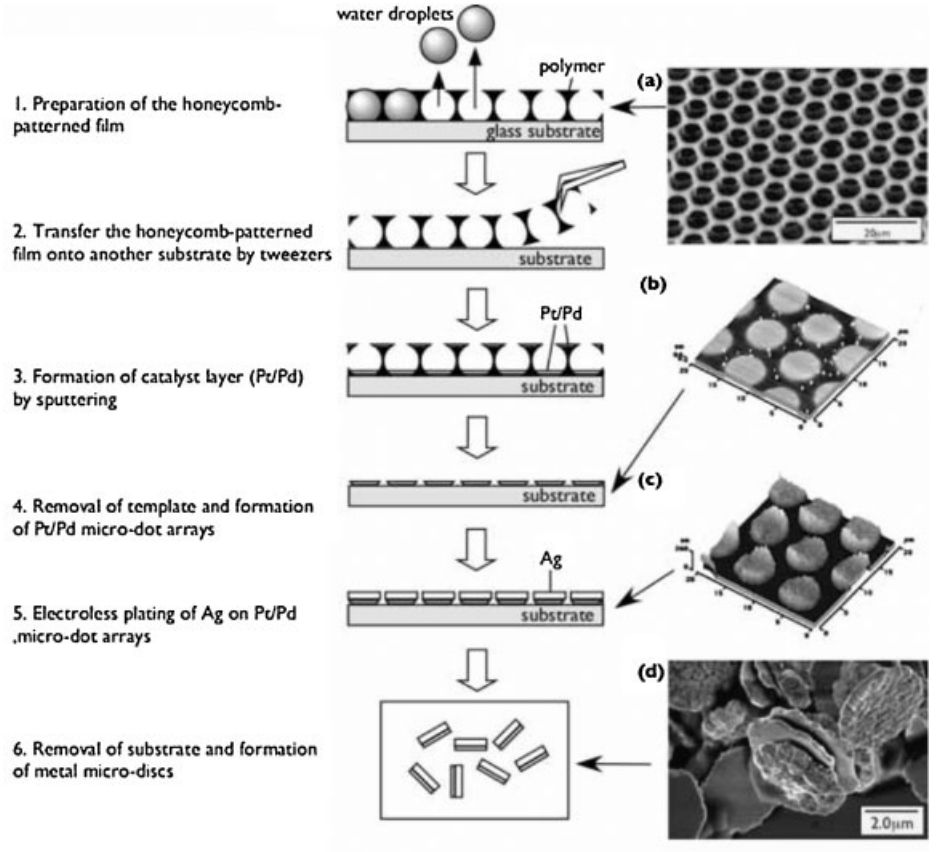

Figure 1.
Schematic illustration of formation process of micro-dots and micro-discs, a SEM image of honeycomb-patterned film (a), AFM images of Pt/Pd (b) and Ag (c) microdots on Si substrate, and a FE-SEM image of Ag microdiscs (d), respectively.

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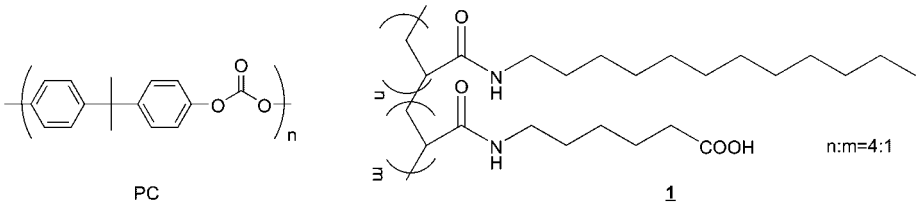

Chart 1

were cut to 4 cm squire and washed by UV-O3 treatment. Shiro Co. Ltd provided a sheet of polyolefin substrate, which can be dissolved in chloroform. The prepared honeycomb-patterned film was transferred onto Si, glass, and polymer film substrates by using tweezers. The surface structure of the film was observed by scanning electron microscopy (SEM).

The honeycomb-patterned film on a solid substrate was placed in a chamber of a discharge ion-sputtering instrument. After sputtering of Pt/Pd for 60 s, the template honeycombpatterned film was removed with adhesive tape (Scotch TapeTM, 3 M). The substrate with Pt/Pd layer was immersed in 250 mL of electro plating solution which containing silver nitrate (3.12 mmol), ammonia (377 mmol), acetic acid (90.0 mmol), and hydrazine (109 mmol). Silver was deposited onto the Pt/Pd catalyst layer according to the following chemical reactions:

$$N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^- \quad (1)$$

$$Ag(NH_3)_2 + e^- \rightarrow Ag + 2NH_3 \text{ (on Pt/Pd)} \quad (2)$$

Reaction (2) only proceeded in the presence of Pd/Pt, and silver was thus selectively deposited on the Pt/Pd surface. After immersing in the plating solution for 3 min., the substrate was rinsed by water and dried. The surface structure on the substrate was observed by SEM and AFM. The surface elemental analysis was performed by XPS. The polymer film substrate was dissolved after plating process in chloroform. After dissolving the polymer film substrate, insoluble components were precipitated and washed twice in chloroform. The structures of the insoluble components were observed by scanning transmission electron microscopy (STEM). The elemental analysis was performed by Energy dispersive X-ray spectroscopy (EDX).

Results and Discussion

Figure 1 (a) shows a SEM image of template honeycomb-patterned film. Well-ordered hexagonally arranged microporous film was formed. Figure 1(b), (c) show AFM images of Pt/Pd microstructures on a Si substrate before/after electroless plating, respectively. In this experiment, the pore size of the honeycomb-patterned film was ca.4 μm in average. The hexagonally arranged micro-dots were formed after deposition of Pt/Pd layer and removing the template honeycomb-patterned film reflecting the pore structure of template honeycomb. The average diameter and thickness of Pt/Pd layer were 3.8 μm and 20 nm, respectively. The diameters of the microdots are well consistent with the pore size of the honeycomb-patterned film. After electroless plating, the thickness of the microdots

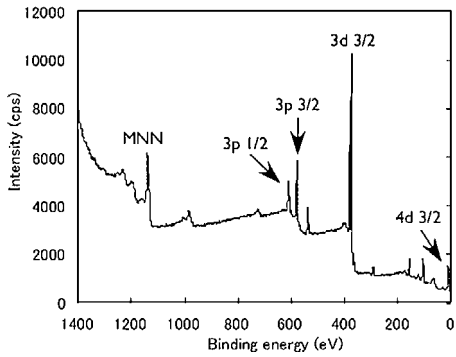

Figure 2.
XPS spectra of Ag deposited microdot arrays on Si substrate.

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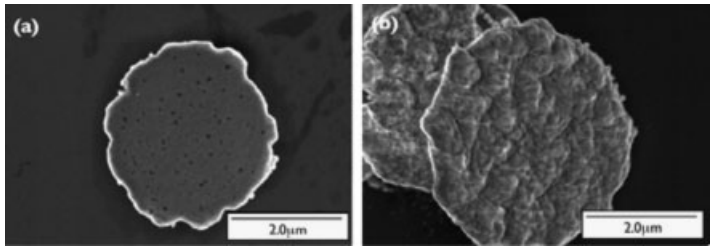

Figure 3.
FE-SEM images of two-sides of Ag micro-discs.

increased to ca.250 nm without diameter change. This result indicates the silver layer grew up perpendicularly to the dot surface. The same structure can be prepared on the glass substrate and the polymer film.

The XPS spectrum shows the formation of silver layers on the surface of a silicon substrate (Figure 2). Ag specific photoelectron is observed. Each number shown after the binding energy is attributed to the orbital of bulk Ag. The peak from MNN is originated from the Auger electron in each orbital of Ag.

Figure 1 (d) shows a FE-SEM image of metal microdiscs formed by isolation of two dimensional metal microdot arrays from the polymer substrate in chloroform. It is clearly seen that uniform sized micro-discs have been successively removed from the polymer substrate and have kept their shapes after removal and washing processes. Figure 3(a) and (b) show close-up images of two sides of the microdiscs. The one side of the microdisc was smooth; on the other hand, the surface of another side was rough. We found Pt/Pd was located on the smooth surface of microdiscs from EDX spectrum. The catalyst layer of Pt/Pd was formed on a flat polymer substrate, thus, the surface of the catalyst layer was smooth. The rough surface was formed during the deposition process of Ag.

Conclusion

We developed a simple process of preparation of metal microdot arrays on various substrates by deposition of metals and removing the honeycomb template. Microdiscs were also obtained by isolating the metal microdots from polymer substrate. The microdiscs have anisotropic shapes and asymmetric surfaces. This process is very simple and these metal microdots and microdiscs of wide variety of metal materials can be applied to electron conductive fillers, substrates for surface enhanced Raman and infrared spectroscopy (SERS and SEIRAS),[15] and left-handed meta-materials.

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