# Assembly of Metal Nanoparticles in Multiscales and Multi-Dimensions in Polymer Films

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We have developed a process to assemble metal nanoparticles in polymer films in twoand three- dimensions in multi-length scales. Polymer films are exposed to the vapor of palladium(II) bis(acetylacetonato) (Pd(acac)<sub>2</sub>) in N<sub>2</sub> atmosphere, and Pd metal nanoparticles are produced in the polymer films by the reduction of the metal complex. In the case of block copolymer (BC) films, the metal complex is selectively reduced in the phase having relatively strong reduction power and the metal nanoparticles are assembled reflecting the nanodomain structures of the BCs. The assembly patterns are three-dimensional (3D) in the case of freestanding films, and are two-dimensional (2D) in the case of ultra thin films. Also, we found that the reduction power of PMMA is enhanced by UV or electon beam (EB) irradiation, and thus the assembly patterns can be arbitrarily controlled by conventional lithography techniques. Therefore, the assembly of metal nanoparticles in wide range of scales from nano- to micrometers in periodical and arbitrary patterns can be obtained in polymer films.

Key words: metal nanoparticle, block copolymer, assembly, UV lithography, EB lithography

## 1. INTRODUCTION

Synthesis, patterning and application of metal nanoparticles have been extensively investigated because of their potential for building blocks for nano-devices.<sup>1-3</sup> The patterning of metal nanoparticles over a wide range of scales and dimensions has been recognized as a key technology for constructing nanoscale magnetic, electric and chemical systems.

We have developed a simple dry process for synthesis and assembly of metal nanoparticles in polymer films through the reduction of a metal complex used as a precursor.<sup>48</sup> Palladium(II) bis (acetylacetonato), denoted Pd(acac)<sub>2</sub>, is vaporized in ambient nitrogen at atmospheric pressure at 180 °C, and is exposed to a polymer film. The vapor can penetrate into a polymer film and is simultaneously reduced to form Pd metallic particles with diameters ranging from 2 to 10 nm with narrow size distributions.

In this paper, we report the assemblies of metal nanoparticles in polymer films in multiscales and multi-

dimensions by the two approaches. The one approach is the "bottom up" approach to use the self-assembling BCs. In this approach, the metal complex is selectively reduced in one of the phases of a BC, and produces spontaneously nanoscale periodical assemblies of metal nanoparticles. Another approach is the "top down" approach to use UV or electron beam (EB) lithography techniques, in which the reduction power of polymer films is tuned by UV or EB irradiation, and arbitrary patterns of metal nanoparticles can be produced. Additionally, using the polymer films with assembled metal nanoparticles, we attempted pattern creations by the following two methods: Using the high resistivity of metal nanoparticles against plasmas, the patterns formed by the metal nanoparticles are transferred into robust substrates located under the films by reactive ion etching (RIE) technique. And also, using the catalyst properties of metal nanoparticles, the patterns of various metals and metal oxides are created on the polymer thin films by the electroless deposition technique.

## 2. EXPERIMENTAL

The process for the incorporation of Pd nanoparticles are described in our previous papers in detail.<sup>4,5</sup> Pd(acac)<sub>2</sub> and a polymer film are loaded into a glass vessel together and is heated at  $180^{\circ}$ C in a nitrogen atomospher.

Block copolymers used in this study were purchased from Polymer Source Inc. and used as recieved.

RIE experiments were carried out using an in-house fabricated tubular reactor which generates capacitively coupled plasma excited by a 13.56 MHz RF power source. In the case of oxygen plasma, the samples were treated at 90 W for 30 min at the gas pressure of 0.5 torr. In the case of  $CF_4$  plasma, the samples were treated at 1 W for 30 min at the gas pressure of 0.08 torr.

EB lithography was carried out on a Beam Draw (Tokyo Technology Inc.) at an accelerating voltage at 20 kV.

### 3. RESULTS and DISCUSSION

3.1 2D and 3D nanoscale periodical assembly of Pd nanoparticles in block copolymer films

Due to the difference in the reduction power between the PS and the PMMA blocks,  $Pd(acac)_2$  is selectively reduced in the phase having stronger reduction power in the PS-*b*-PMMA films. In a free-standing film of a symmetric PS-*b*-PMMA (Mn=72,600/70,900), the number of the produced particles with about 4 nm in diameter increases with the exposure time of the Pd(acac)\_2 vapor, and the particles are assembled selectively in the lamellae as shown in Fig.1. We have found that PMMA has a tendency to retard the reduction of Pd(acac)\_2 although it absorbs the vapor in the same manner as the other polymers do.<sup>4</sup> Therefore, the Pd nanoparticles are assembled in the PS lamellae to form



Figure 1. TEM micrograph of a cross section of the free-standing film of PS-*b*-PMMA exposed to Pd(acac), vapor for 2 h.

periodical layers in a nanoscale. The vapor of  $Pd(acac)_2$ reaches to the inside of the film of about 100 µm in depth below the surface. Thus, in a free-standing symmetric BC film, the Pd nanoparticles can be assembled to form 3D layer structures with nanoscale repeating distances that can be tuned by the Mn of the components of BCs.

To realize the 2D regular assembly of the metal nanoparticles, BC monolayer films possessing laterally ordered nanodomains have to be prepared on substrates. The conventional spin-coating usually yields no regular patterns of nanoscopic domains in an as-cast thin film. We found that the exposure of acetone vapor is effective for the improvement of the nanodomain arrangement in a PS-b-PMMA thin film. An asymmetric PS-b-PMMA diblock copolymer (Mn=4,700/280,000) was spincasted from the 1 wt% toluene solution on a silicon wafer. As shown in the AFM image in Fig. 2a, the ascast film has no regular arrangment of the PS domain. After the exposure to acetone vapor in an ambient for 10 h, the arrangement of the PS domains can be remarkably improved as shown in Fig. 2b. The thickness of the film was estimated at 50 nm by ellipsometry, indicating that the films is a monolayer. To introduce the Pd nanoparticles into the thin film, the thin film thus prepared was exposed to the Pd(acac)<sub>2</sub> vapor for 1 h. Fig. 2c is a TEM micrograph of the PS-b-PMMA thin film showing that the Pd nanoparticles are selectively located in the PS domains. It should be noted that even though the thin film was laid at 180 °C for a long period, the arranged nano domain structure is maintained.

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Figure 2. AFM images of (a) an as-cast PS-*b*-PMMA thin film by spin-casting, and (b) the film after the exposure to acetone vapor for 10h. (c) TEM micrograph of the PS-*b*-PMIMA thin film after the exposure to Pd(acac)<sub>2</sub> vapor for 1 h.

3.2 Arbitrary nanoscales assembly of metal nanoparticles by EB lithography

We also developed the assembly of Pd nanoparticles by conventional UV lithography technique using the unique behavior of PMMA concerning the reduction of Pd(acac)<sub>2</sub>.<sup>7</sup> Although the mechanism is unknown, the irradiation of UV light with the wavelength shorter than 300 nm on PMMA causes the enhancement of the reduction power against Pd(acac)<sub>2</sub>. EB also has an effect on the enhancement of the reduction power of PMMA and enables the creation of patterns with small feature sizes. Fig. 3 shows SEM micrographs showing the pattern created by EB lithography. On a PMMA film with the thickness of 1 µm on a silicon wafer, the electron beam is scanned in a defined pattern as shown in Fig. 3a with the dose of  $120\mu$ C/cm<sup>2</sup>. Then, the film was exposed to the Pd(acac)<sub>2</sub> vapor for 30 min, followed by the thermal treatment at 500 °C under argon for the pyrolysis of PMMA. Fig. 3b is the magnified image of Fig. 3a to show the line pattern with 100 nm in width can be obtained.



Figure 3. SEM micrographs showing the assembly of Pd nanoparticles in the PMMA film created by EB lithography. (b) is a magnified image of (a) to show the line formed by the assembly of the Pd nanoparticles.

#### 3.3 Pattern transfer onto Si wafers by RIE

Self-organizing BCs have been expected for lithography masks under conventional RIE to create small features on substrates that cannot be achieved by standard lithography techniques.<sup>9-12</sup> The loading of metal species selectively into a phase in BC thin films is one of the approaches to enhance the etching selectivity against RIE. For this purpose, a poly (methyl methacrylate-*b*-2-hydroxyethyl methacrylate) (PMMA-*b*-PHEMA, Mn = 24,300/16,700) thin film was prepared on a Si wafer by dip-coating from 0.5 wt% dioxane solution. Dioxane is a selective solvent for PMMA. Therefore, micelles with the PHEMA core are formed in the solution.<sup>8</sup> Dip coating from this micellar solution gives the film in which the micelles are hexagonally arranged as shown in Fig. 4a. The thickness of this film was measured at 20 nm by ellipsometry, indicating that a monolayer film was obtained. As shown in Fig. 4b, the Pd nanoparticles can be introduced selectively into the PHEMA domains. In the first step, the O<sub>2</sub> plasma was applied to the BC thin films with the Pd nanoparticles for the selective removal of the polymer. The film thus obtained was used as a mask against RIE. Fig. 4c is the AFM image after the O2 plasma treatment, presenting that the O<sub>2</sub> plasma allows the removal of the polymer while maintaining the pattern that the BC thin film initially possesses. In the next step, the etched films was treated by CF<sub>4</sub> plasma. The region under the Pd nanoparticles on the Si-wafer is masked against the CF<sub>4</sub> plasma, thus the naked Si-wafer is etched at a higher rate and the nanodomain patterns of the BC thin films can be transferred to Si-wafers. As shown in Fig. 4d, the SEM micrograph qualitatively presents that the substrates are etched by the CF<sub>4</sub> plasma treatment. This means that the periodic patterns with the feature size of 20 nm can be produced on a Si-wafer.



Figure 4. (a) AFM image of the as-cast film of PMMA*b*-PHEMA by dip-coating. (b) TEM micrograph showing the lateral ordered assembly of Pd metal nanoparticles in the PMMA-*b*-PHEMA thin film. (c) AFM image of the film after the  $O_2$  plasma treatment. (d) SEM micrograph after the CF<sub>4</sub> plasma treatment.

3.4 Electroless deposition of ZnO nanoparticles on the surface catalyzed by Pd nanoparticles

One of the attractive properties of metal nanoparticles is the catalytic activity. We found that

the Pd nanoparticles embedded in a polymer thin film work as a strong catalyst for electroless deposition of metals and metal oxides. As one of the attempts of this technique, the electroless deposition of ZnO was investigated by the method developed by Izaki et al.13 A PMMA thin film with the thickness of 20 nm coated on a silicon wafer was irradiated by UV light through a photomask with the dose of 10 J/cm<sup>2</sup>, and then the film was exposed to the Pd(acac)<sub>2</sub> vapor for 5 min to produce the pattern of the Pd nanoparticles. Then the film was soaked in an aqueous solution of zinc nitrate  $(Zn(NO_3)_2)$ 0.05 M) and dimethylamine borane (DMAB, 0.05 M) at 50 °C for 10 min. A SEM micrograph in Fig. 5a shows the overall pattern, where the numerical numbers at the bottom of the individual patterns indicate the width of the corresponding bars in micrometer scales. The contrast between the irradiated and unirradiated regions was significantly enhanced through the deposition process, suggesting that ZnO was successfully deposited on the irradiated regions. Fig. 5b is a magnified image around the boundary, which shows that the irradiated region is covered with the deposited particles with the diameter of about 150 nm forming a dense continuous film, while very few particles are randomly distributed on the unirradiated regions.



Figure 5. SEM micrographs of the pattern formed by ZnO nanoparticles on a PMMA thin film by electroless deposition. (a) A low magnification image showing the overall pattern created by a photomask. (b) A high magnification image around the boundary region of the pattern.

#### 4. Summary

Pd nanoparticles are assembled in polymer films in multiscales and multi-dimensions by a simple dry process. Our method described here can be applied to both the "bottom up" approach using self-assembling BC systems and the "top down" approach combining the unique behavior of PMMA with regard to the reduction of the metal complex and the conventional photo- or EB lithography techniques. Using the two approaches, the obtained patterns can be extended from nanoscales to microscales, and also, the pattern features are not limited in periodical patterns and arbitrary patterns in 2D are possible. We also show that the patterns thus created can be transferred onto a substrate located under the films, and on the other hand, the patterns of various inorganics can be constructed on the films by electroless deposition. It is expected that the attainable patterns will be further extended by combining the "bottom up" and "top down" approaches.

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