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Nanoscale Patterning of Metal nanoparticles in Polymer Thin Films

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We have developed a simple dry process to synthesize metal nanoparticles. Palladium (II) acetylacetonato (Pd(acac)$_2$) is vaporized in nitrogen atomospher and is absorbed in a polymer film. Pd(acac)$_2$ is reduced in a polymer film and converted into metal nanoparticles with a narrow size distribution less than 10 nm size. We demonstrated 2D and 3D patterning of metal nanoparticles in various polymer films using this method in self assembling block copolymer systems and by a conventional photo lithographic technique.

Key words: metal nanoparticles, nanoscale patterning, block copolymer, UV lithography

1. INTRODUCTION

The assembly and fabrication of two- or three-dimensional (2D or 3D) micro- and nanoscale structures using metal nanoparticles as building blocks are very promising techniques for the creation of next generation electronic, optoelectronic and chemical sensing devices.[1,2] The polymer/metal nanoparticle hybrid systems having well defined pattern of metal nanoparticles in 2D and 3D are expected to have variety of applications as lithographic masks[3-6], photonic band gap materials[7,8], high storage devises[9], or catalysts[10-12].

Many proposals to realize the nano-scale arrangements of metal nanoparticles within polymeric matrices have been reported. The one way is the "bottom up" approach using selfassembling systems such as block copolymers or micelles. The other way is the "top down" approach introducing conventional photo or electron beam lithography or probe techniques.

We have developed a simple dry process to synthesize metal nanoparticles within polymer films.[13,14] This process uses a one step synthesis[15]. Vapor of palladium(II) bis(acetylacetonato), (Pd(acac)$_2$) (Note: acac denotes $CH_3COCHCOCH_3$), is exposed to a polymer film in a nitrogen atmosphere at 180°C for periods up to 2 h. Pd(acac)$_2$ is sublimed at atmospheric pressure, and the vapor penetrates into a polymer film. The metal complex decomposes and is reduced into the metallic state, forming nanoparticles. Using this method, we demonstrated 2D and 3D patterning of metal nanoparticles in polymer films in wide range of scale from nanometer to micrometer.

2. EXPERIMENTS

2.1 Incorporation of metal particles into the block copolymer films.

Fig. 1 illustrates the process of our method to incorporate the metal particles into the polymer films. The bottom of a glass vessel with 10 mg of a metal complex is heated at 180°C *in vacuo* to sublime the metal complex, and then the metal complex is immediately solidified on the upper side of the glass wall within a few minutes. In the next step, a polymer film is loaded into the glass vessel, and the glass vessel is put it into the oil bath at 180°C for a defined length of time after nitrogen

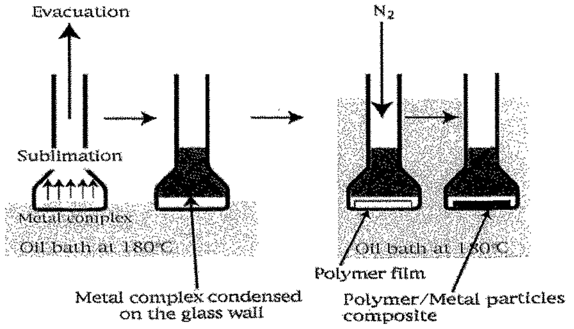

Fig. 1 A schematic illustration of the process of incorporation of metal nanoparticles in polymer films.

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replacement.

2.2 Materials

$Pd(acac)_2$ was purchased from Johnson Matthey Materials Technology and were recrystallized from acetone before use. Atactic polymethylmethacrylate (PMMA) homopolymers were purchased from Aldrich Chem., whose number-average molecular weight (Mn) is 350,000. Reprecipitation was done twice from a methylene chloride solution to methanol for purification.

A symmetric diblock copolymers of Poly(methylmethacrylate)-*block*-poly(2-hydroxyethylmethacrylate) (PMMA-*b*-PHEMA, Mn=24,300/16,700) was used as received from Polymer Source Inc..

3. RESULTS AND DISCUSSION

3.1 Nanoscale patterning of Pd nanoparticles in block copolymer films. -"Bottom Up" approach.

Fig. 2 shows TEM micrographs of a cross section of a PMMA-*b*-PHEMA free-standing film after exposure to the $Pd(acac)_2$ vapor for 30 min. The block copolymer film was prepared by casting from 2 wt% pyridine solution. The solution was dried in ambient condition overnight, then dried at 50°C on a hot plate for 1 day, and finally dried in a vacuum oven at 200°C and then 150°C. The film shows a typical lamellar micro domain structure, and Pd nanoparticles are selectively located in the PHEMA lamellae. The photographs shows the surface-induced orientation of lamellae parallel to the surface, where the component having lower surface tension is preferentially located at the air/copolymer interface. From our previous studies, it has been revealed that the polymers having alcoholic hydroxyl groups has strong reducing power against the metal complex, and that PMMA has uniquely lower the reducing power. Therefore, the Pd nanoparticles are selectively grown in the PHEMA lamellae in the PMMA-*b*-PHEMA film. The vapor of $Pd(acac)_2$ can deeply diffused into the film, thus, the constructed patter is 3D. The metal nanoparticles are arranged in patterns that reflect the underlying morphologies of the block copolymers. Therefore, the achieved patterns and the repeating distances can be tuned by the selection of the types and molecular weights of block copolymers.

2D patterning is also possible using block copolymer thin films coated on a substrate. Fig. 3 shows a pattern created in a PMMA-*b*-PHEMA thin film exposed to the $Pd(acac)_2$ vapor for 30 min. The film was prepared by dip coating from 0.5 wt% dioxane solution on a TEM grid with carbon supporting film (Fig.3a) and on a Si wafer (Fig.3b). Dioxane is a selective solvent for this block copolymer, in which the PMMA block is soluble while the PHEMA is insoluble. Thus, the block copolymer forms micelles with the PHEMA core in an as-cast film. The substrates can be coated with a micellar monolayer with a high 2D regularity by a proper coating condition. $Pd(acac)_2$ is selectively reduced in the PHEMA domains, and thus the 2D hexagonal patterns can be achieved. Fig.3a is shown as an electron energy-loss image to present the structure clearly where the contrast is inversed to a conventional TEM image [14]. The higher magnification TEM image shown in a inset of Fig.3a shows the Pd particles less than 5 nm in diameter are located in the domains.

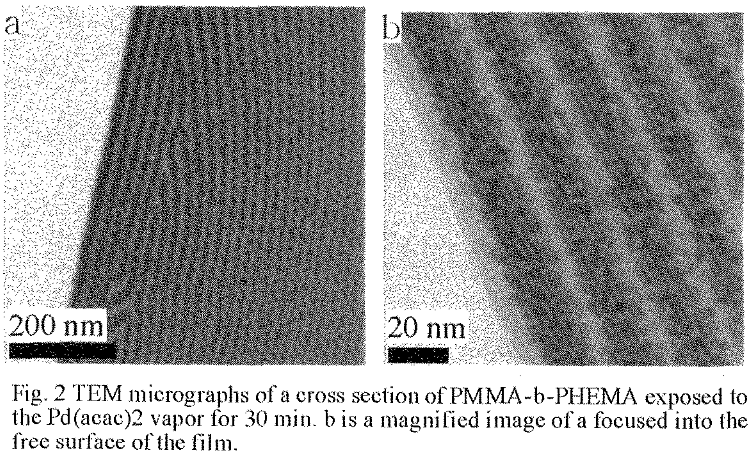

Fig. 2 TEM micrographs of a cross section of PMMA-b-PHEMA exposed to the Pd(acac)2 vapor for 30 min. b is a magnified image of a focused into the free surface of the film.

3.2 Micropatterning of Pd nanoparticles in PMMA thin films via UV lithography.-"Top Down" approach.

As reported in our previous works, PMMA showed a unique behavior with respect to the absorption and reduction of $Pd(acac)_2$.[13,14] That is, all the evaluated polymers except PMMA absorb and reduce $Pd(acac)_2$ simultaneously. On the other hand, PMMA shows an induction period between the absorption and the reduction of $Pd(acac)_2$. This means that PMMA possesses a unique character that delays the formation of metal nanoparticles.

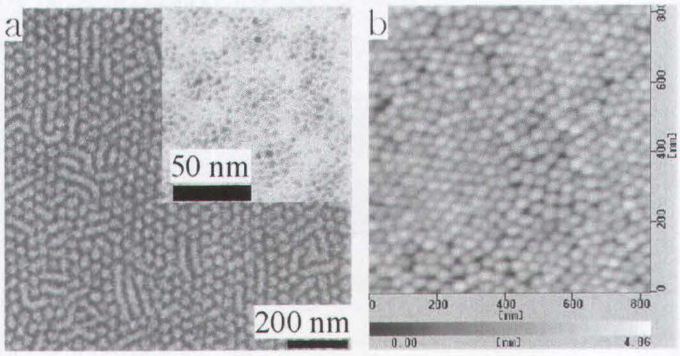

Fig.3 (a) An electron energy loss image of a PMMA-*b*-PHEMA thin film prepared by dip coating on a carbon-coated TEM grid. The inset is a magnified image by the conventional TEM mode. (b) An AFM topografic image of the film coated on a Si wafer.

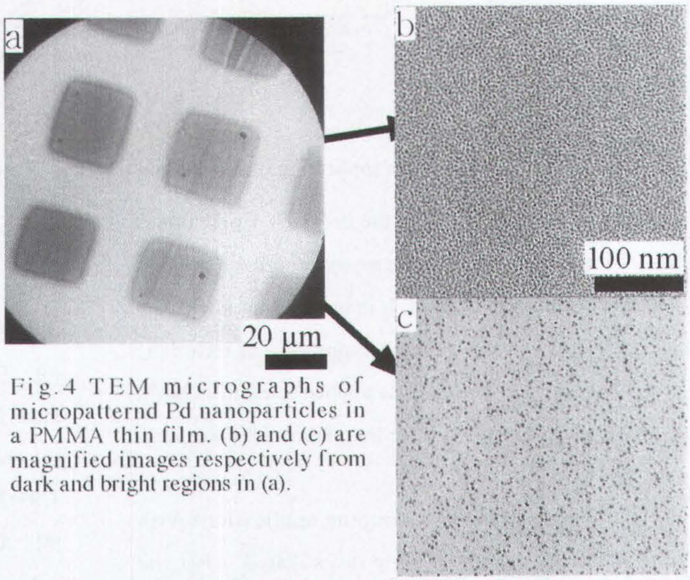

Fig.4 TEM micrographs of micropatternd Pd nanoparticles in a PMMA thin film. (b) and (c) are magnified images respectively from dark and bright regions in (a).

We found that irradiation of UV light with shorter wavelength than 300nm enhances the reducing power of PMMA.[16] By the irradiation of UV light over a photomask on a PMMA film, the aggregation of the Pd nanoparticles can be patterned. Fig. 4 shows the TEM micrograph of a pattern of the Pd particles in a PMMA thin film with the thickness of 50 nm irradiated with UV light of 7 J/cm^2 over a square metal mesh and exposed to $Pd(acac)_2$ vapor for 1 h. Magnified images from the irradiated (Fig4b) and the unirradiated (Fig.4c) regions show the state of the dispersion of Pd particles. The number of the particles is significantly different between the two regions. The differences between irradiated and unirradiated regions can be optimized by adjusting the film thickness, UV irradiation dose and exposure time to $Pd(acac)_2$ vapor.

Although the featured sizes are in the micrometer range due to the limit of wavelength of light, this artificial arrangement of metal nanoparticles can be achieved with a plane PMMA thin film with free design of patterns.

4. Summary

Fig.5 present the summary of this work. When the method of incorporating metal nanoparticles into polymer films using acetylacetonato metal complexes is applied to self-assembled block copolymer systems, metal nanoparticles can be arranged in periodic nanoscale patterns that reflect the underlying morphologies of the block copolymers. This "bottom-up" approach enables the spontaneous formation of metal nanoparticles into periodic lamellar, cylindrical or spherical manners presented as underlying nanodomain structures of used block copolymers. This approach can create with ease and elegance patterns with dimensions that are $<$ 50 nm. However, aperiodic or arbitral addressing of metal nanoparticles into a polymer film is not possible. We also show that our method can be also applied as a "top-down" approach by way of conventional photolithography. Although the featured sizes are in the micrometer range, this artificial arrangement of metal nanoparticles can be achieved with a plane PMMA thin film. Thus, our simple dry method to provide stable dispersions of metal nanoparticles in polymers can be utilized as both a "bottom-up" and a "top-down" approach. For the fabrication of functional nanostructured materials, it is essential to assemble and connect nano-objects in a controllable manner. The bottom-up approach would not fulfill these objectives. Our work presented in this paper extends our previous studies[13,14] to widen the fabrication size range and allows us free design of patterns. Moreover, the degree of the dispersion can be controlled continuously that enables to produce patterns with a gray scale gradient mask. The sizes of patterned features is limited by the

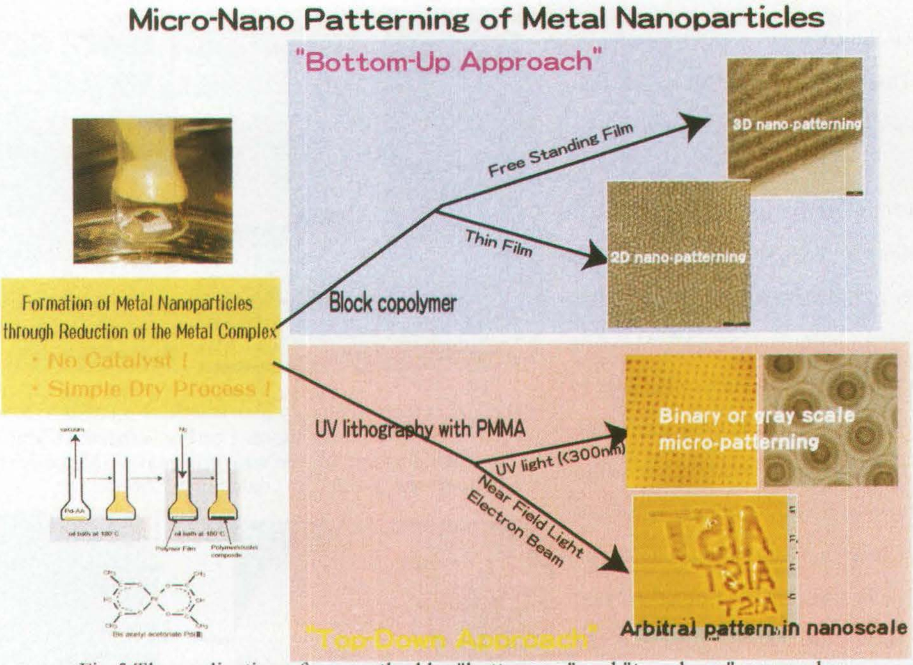

Fig.5 The application of our method by "bottom-up" and "top-down" approaches.

wavelength of light, however, the use of near field optics has a potential to create patterns with feature sizes less that the wavelength of light. It is known that PMMA is also degraded by electron beam exposure. The technique presented here is expected to be applied to electron beam lithography and could reduce the pattern size to ca. 50 nm.

The possibilities of developing applications with our system are currently being investigated. Also, the formation mechanism of metal nanoparticles through the reduction of metal ions in polymers is still unclear and is a matter to be solved.

Acknowledgment

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