Double-Layered Metal Mesh Film With Limited Viewing Angle Prepared by Electroless Plating of Self-Organized Honeycomb Film

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Summary: We have reported that honeycomb-like porous polymer films, which were spontaneously formed in the casting of polymer solutions under humid conditions, were converted into honeycomb-like metal meshes by electroless plating. In this report, the unique optical properties of these meshes will be discussed. Silver-coated honeycomb mesh films were prepared by selforganization and electroless plating methods. The incident angle dependence of their transparency, and their electrical conductivity were measured. The metallized film had limited viewing angle.

Keywords: metal mesh; polymer films; self-organization

Introduction

Micro- and nano-structured metal materials are widely used in electronic and photonic devices because of their large refractive indices, high thermal and electrical conductivities, and mechanical and chemical stability. The topology and dimensions of these materials are among the most significant factors in terms of their device applications. For example, regular arrays of tiny metal spikes (smaller than 100 nm) are suited for use as electrodes in field emission displays.[1] Photonic crystals having two- or three-dimensional periodic structures have been fabricated from metal or semiconductor materials for use in novel optical circuits.[2] Recently, exotic materials having negative refractive indices, so-called "left-handed metamaterials," have been prepared from structured metal materials having periodic patterns on the sub-wavelength scale.[3] Top-down type micro-fabrication technologies, e.g., photolithography, soft lithography,[4] and nanoimprint lithography[5] are widely used to prepare micro- or nano-structures, which are formed as basal molds of metal micro- and nano-structures. Electroless plating is widely used for metallizing surfaces, and is a purely chemical process of reducing metal ions on catalysts introduced onto surfaces by chemical adsorption, sputtering, or vapor deposition.[6] A major advantage of electroless plating is its applicability to a wide variety of materials including insulating surfaces such as glass and other inorganic/organic polymers, without electrical equipment.

Recently, bottom-up type techniques including inversed opals[7] and microphase separation of block-copolymers[8] have been developed for the fabrication of metal micro- and nanostructures. Regular metal nano-structures prepared by a self-assembly or self-organization process can be used as basal molds for forming metal micro- and nano-structures. We have reported that

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honeycomb-like porous polymer films,[9] which were spontaneously formed in the casting of polymer solutions under humid conditions, were converted into honeycomb-like metal meshes by electroless plating.[10] In this report, the unique optical properties of these meshes will be discussed.

Experimental Part

Honeycomb meshes were prepared by casting a chloroform solution of 2.5 mg/mL poly-ε-caprolactone (Chart 1, PCL, Mw ~100,000 g/mol) and amphiphilic copolymer 1 (Chart 1, PCL:1 weight ratio was 9:1) in a 9 cm diameter Petri dish. After casting, moist air was applied vertically onto the solution surface. It has previously been reported that honeycomb-like porous polymer films were formed by the simple casting of polymer solutions under humid conditions.[11] During solvent evaporation, condensed water droplets were deposited on the solution surface due to evaporative cooling. The water droplets were packed regularly by lateral capillary forces among themselves.[12] After complete evaporation of the solvent and water, a porous honeycomb-like structure was formed. The film was examined by both optical microscopy and scanning electron microscopy (SEM).
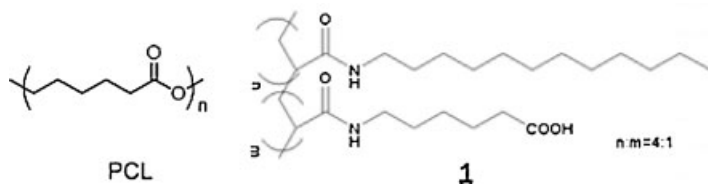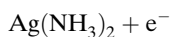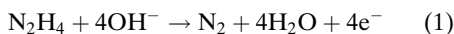
tively deposited on the Pt or Pd surface. Platinum and palladium (Pt/Pd), the catalysts for electroless plating, were simultaneously sputtered to form a catalyst layer on the surface of the honeycomb mesh film fixed on a polyethylene telephtalate (PET) substrate. The sputtering time was 50 seconds, resulting in a ca. 10 nm thick catalyst layer. After the deposition of the catalyst layer, the film was soaked in the silver plating solution, which contained 12.5 mM silver as the source of silver ion, 1.5 M ammonia, 0.36 M acetic acid to control pH, and 0.3 M hydrazine as a reducing agent, in water. After soaking for 3 minutes in the solution, the honeycomb mesh film was rinsed twice with pure water. The film was dried in air for 12 hours, and then in vacuo for 2 hours at room temperature. After silver deposition, the metallized honeycomb mesh film was transferred onto a glass slide and heated in an electric oven at 500 °C for 8 hours.

The porosity and pore size of the honeycomb mesh film were measured from an SEM image using the imaging software "Image SXM," which was freely provided by the National Institutes of Health, USA. Elemental analysis of the honeycomb mesh surface before and after electroless plating was carried out by X-ray photoelectron

Chart 1.

The honeycomb mesh films were metallized by electroless plating. Silver was deposited on a Pt/Pd catalyst surface according to the following chemical reactions[13]:

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

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

Reaction (2) proceeded only in the presence of Pd or Pt, and thus the Ag was selec-

spectroscopy (XPS) to confirm metal deposition. The X-ray source, X-ray energy and pass energy were AlKα, 1486.6 eV, and 10 eV, respectively. The surface structure and current image were simultaneously collected using a conductive atomic force microscope (cAFM). The Agcoated honeycomb mesh film was fixed on the surface of an glass substrate, and then attached to the sample holder of the cAFM. All sides of the sample were covered with carbon
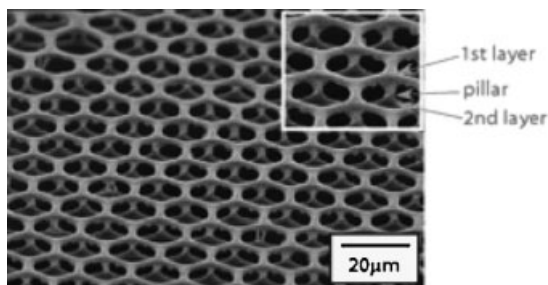
Figure 1.
SEM image of silver-coated honeycomb mesh.

adhesive tape to make an electrical contact between the film and the sample holder, which was connected to an ammeter and DC power. A gold-coated probe was used to apply a 5.00 V bias voltage between the probe and the sample.

The optical properties of these films before and after silver deposition were measured using a UV-visible-near infrared (UV-Vis-NIR) with variable angle equipment. Absorption spectra from 400 nm to 800 nm were measured at different incident angles, from 90° (normal to the surface) to 30°. As a reference experiment, the optical properties of a PCL thin film and those of a PCL film metallized by electroless plating were also measured.

Results and discussion

Figure 1 shows a typical SEM image of a metallized honeycomb mesh film. The honeycomb mesh structure remained after the deposition of silver. The close-up image shows that the mesh consisted of two porous layers supported by pillars at the vertices of the honeycomb hexagons.

The formation of a thin silver overlayer was confirmed by XPS spectra (Figure 2(a)). The surface topology and current image of the metal honeycomb-mesh film were simultaneously observed by cAFM (Figure 2(b),(c)).

The effect of incident angle on the transmittance of the honeycomb mesh film was also measured. The dashed-dotted line and dotted line in Figure 3(a) demonstrate

this incident angle dependence of the film's transmittance before and after silver deposition, respectively. When the light was irradiated normal to the mesh surface, the transmittances of the honeycomb mesh film (pore size: 10 μm) before and after silver deposition were 37% and 45%, respectively. The transmittance gradually decreased with decreasing incident angle in both cases, but the transmittance of the silver-coated film was higher than that of
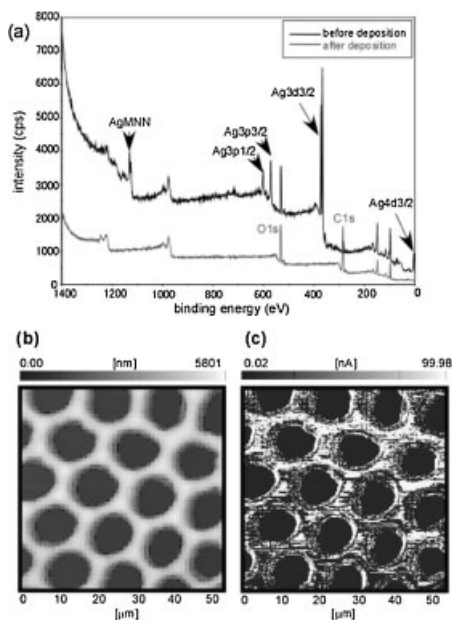

Figure 2.
XPS spectra of honeycomb-mesh before/after metal deposition (a), Topography (b) and conductivity (c) images of metallized honeycomb-mesh.
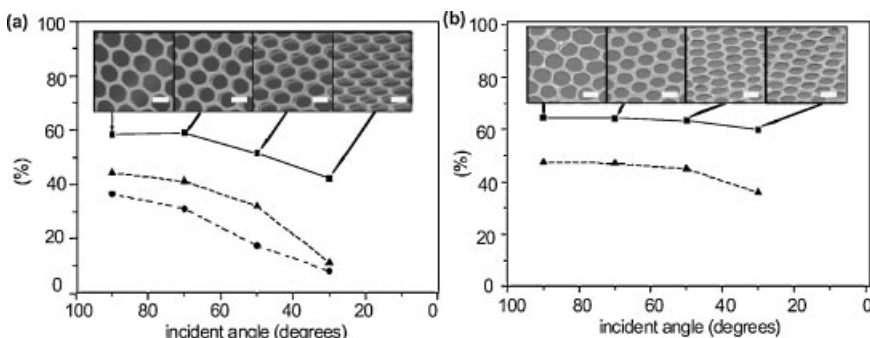
Figure 3.
(a) The incident angle dependence of optical aperture (black line), and transmittance of honeycomb mesh before (dashed-dotted line and dotted line), and after (dotted black lines) deposition of silver. (b) The incident angle dependence of optical aperture (black line), and transmittance of honeycomb mesh after sintering (dotted line and dotted line). The white bars in the SEM images indicate 10 µm.

the parent polymer honeycomb mesh film. The porosity of these films was one of the principal factors determining their optical transmittance. As shown in Figure 1, the honeycomb mesh film consisted of two porous layers supported by pillars located at the vertices of the honeycomb hexagons. When the film surface was tilted away from the direction of incident light, the optical aperture was decreased by the two porous layers overlapping. The black line in Figure 3(a) indicates the apparent porosities, equivalent to the optical aperture, of the silver-coated honeycomb mesh films calculated from the tilted SEM images shown. The calculated optical aperture of the film gradually decreased when the incident angle was decreased, the dotted and dashed-dotted lines. Such a strong dependence of the optical transmittance on incident angle can be used to limit the viewing angle of optical films, e.g., to prevent illegitimate gathering of private information shown on a display.

The dependence of the transmittance on incident angle was also measured after these films were sintered. It has already been reported that the double layer structure of the honeycomb mesh film collapsed to form a monolayer film upon sintering10. The optical aperture (black line) and the transmittance of the sintered metal-coated honeycomb mesh film (dotted line) are

shown in Figure 3(b). After sintering, the calculated optical aperture and measured transmittance of the film changed by less than 5% for incident angles ranging from 90° to 30°, indicating that the double-layered structure was required for the limitation of viewing angle.

Conclusions

Silver-coated honeycomb mesh films were prepared by self-organization and electroless plating methods. The incident angle dependence of their transparency, and their electrical conductivity were measured. The metallized film showed a higher transmittance than the original polymer film, and furthermore, had limited viewing angle. These films could therefore be useful as transparent conductive films with limited viewing angle.

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