Platinum Thin Film with a Highly Ordered Mesostructure by Contact Plating

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(Received September 8, 2004; CL-041060)

By a contact plating technique using a galvanic reaction between Al and Au in the presence of Pt complex, we have for the first time succeeded in the formation of a highly ordered mesostructured Pt film on a Au surface by reduction of Pt ions in the presence of lyotropic liquid crystals.

In 1997, Attard et al. reported the first synthesis of mesoporous metal by a chemical reduction of metal ions in the presence of lyotropic liquid crystals (LLC).[1] Since then, this liquid crystal templating strategy by electrochemical processes has been used as an approach of direct physical casting to produce mesoporous metals. Mesoporous metals with high electroconductivity, uniformly ordered pore network, and high surface areas have attracted considerate interests in a wide range of electrochemical reaction media.

The electrochemical method can be utilized to prepare not only metal films but also metal powders, depending on the operating conditions. Recently this method has been used in a wide range of the formation of micro- and nanostructures, such as functional nanoparticles and microstructure for MEMS (Micro-Electro Mechanical Systems). Electrodeposition method is a general approach for the reduction of metal ions. Metal ions are reduced on substrates by an external power supply, forming films. By applying this method to LLC systems, several mesoporous metal films with various compositions have been reported up to date.[2] The electroless deposition method, which utilizes an oxidation of reducing agent existing in a solution as the electron source to reduce metallic ion, was also performed in the presence of LLC, while only mesoporous noble metal particles (Pt[1] and Pt–Ru alloy[3]) have been reported. We have succeeded in synthesizing highly ordered mesoporous Ni[4] and mesostructured Ni–Co alloy particles[5] by an autocatalytic electroless plating using appropriately chosen reducing agents.

In this study, we extended our synthesis methods to contact plating for the preparation of mesostructured/mesoporous metal films. This plating method using a galvanic reaction between metals has been utilized at the initiation of metal deposit in the field of surface finishing.[6] Many kinds of metals can easily be deposited on conductive substrates.[7] We can avoid the formation of some defects such as holes during electroless deposition.[8] Platinum was chosen here because mesoporous Pt-group metals and alloy films (e.g. Pt,[9] Pd,[10] Pt–Ru,[11] Pt–Pd[12]), having their potentials for applications in electrochemistry and catalysis, have recently attracted much attention. Here we report the first example of the formation of highly ordered mesostructured Pt films on a Au surface by the contact plating using a galvanic couple between Al and Au in the presence of LLC including Pt ions.

Nonionic surfactant Brij 76 [$C_{18}(EO)_{10}$] was used as a former of lyotropic liquid crystals (LLC). Hydrogen hexachloroplatinate (IV) hexahydrate (1.3 g) was dissolved in distilled water (3.3 g). Brij 76 (9.0 g) was added into the solution, and the concentration of the surfactant was adjusted to 65 wt % (surfactant/water). The mixture was heated to 85 °C (higher than the melting point of Brij 76) and stirred. After the mixture was cooled to room temperature and aged, it was again heated to 80 °C and stirred. The thermal/aging procedure was repeated three times to complete homogeneous mixing. This mixture thus obtained showed a homogeneous yellow color with a hexagonal mesophase (abbreviated as H_I–Pt mixture). The formation of a liquid crystal state was confirmed by a polarizing microscope. A substrate coated with Au was prepared by deposition of titanium (1 nm) and then gold (10 nm) onto a Si substrate (1.5 × 1.5 cm) by electron beam evaporation. When the substrate in contact with an Al wire was immersed in the H_I–Pt mixture, the deposition of Pt was carried out with electrons transferred to the interface between the Au surface and the H_I–Pt mixture by dissolving the Al wire (Figure 1). The deposition was carried out for 30 min at room temperature, and then the Pt film was soaked in water and ethanol to remove the surfactants. The mesostructure and morphology of the film were examined by low-angle X-ray diffraction (XRD), transmission electron microscopy (TEM), and field emission scanning electron microscopy (FE-SEM).

The XRD profiles of the H_I–Pt mixture show two peaks in the range of low angle (Figure 2a, Profile (A)). These *d* values

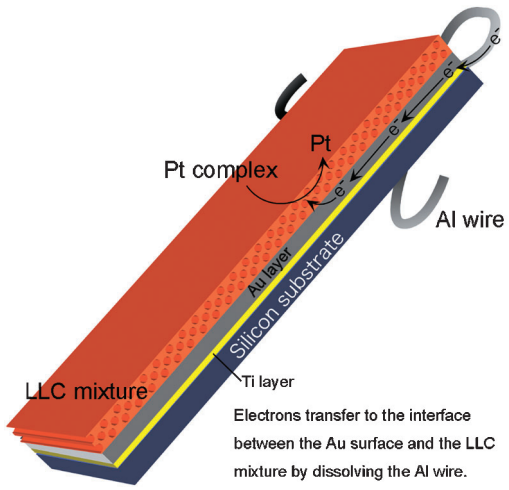

Figure 1. Schematic mechanism for the preparation of mesostructured Pt films by the contact plating using a galvanic reaction between Al and Au in the presence of lyotropic liquid crystals (LLC) including Pt ions.

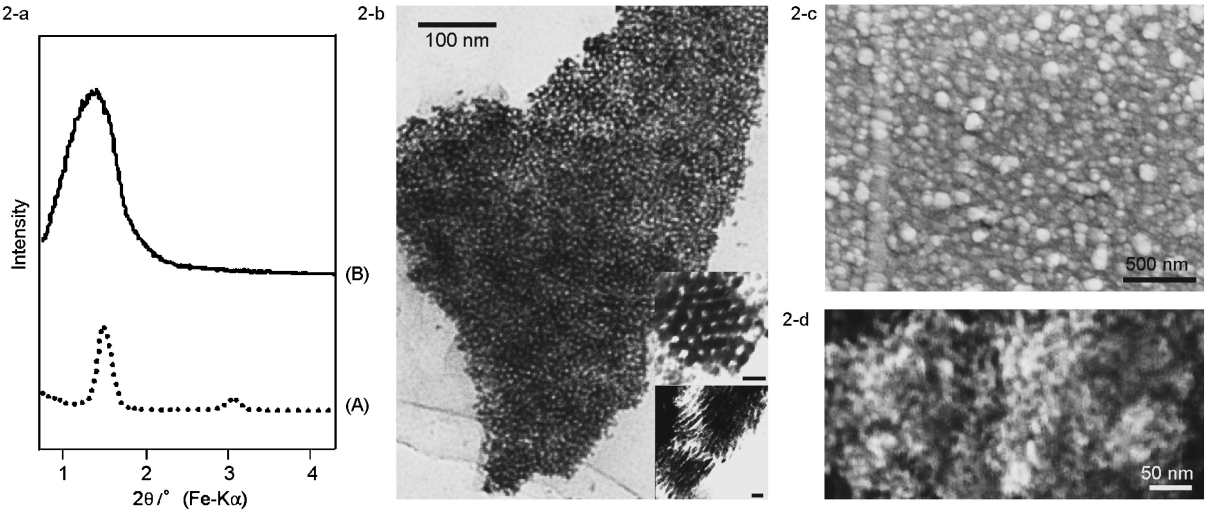

Figure 2. a); XRD profiles in the low-angle range. [(A) H_I–Pt mixture (The ternary system composed of Brij76, water, and hydrogen hexachloroplatinate (IV) hexahydrate and (B) mesostrucutured Pt thin film.] b); TEM image of mesostructured Pt film over a wide range. [Inset; Typical 2D-hexagonal arrangement and side view of mesochannels. Underbars are 10 nm.] c) and d); Top-surface SEM image of mesostructured Pt thin film at c) low and d) high magnifications.

are 7.2 and 3.6 nm, respectively, corresponding to the (100) and (200) diffraction planes. On the other hand, the film showed a single broad diffraction peak ($d_{100} = 7.3$ nm) (Profile (B)). The d spacing of this peak was almost the same as that of the H_I–Pt mixture, indicating that the mesostructure derived from the mixture was formed on the substrate.

By the TEM observations over a wide range of the film, we confirmed the formation of a porous nanostructure (Figure 2b). The clear end-on and side view images (inset) were observed, showing the presence of the 2D-hexagonal ordered mesostructure. The pore diameter and wall thickness were roughly estimated to be ca. 3.9 ± 0.3 nm and ca. 4.3 ± 0.3 nm, respectively. This observed pore size is comparable to those observed for mesoporous Pt–Ru alloy particles obtained from the hexagonal phase of Brij 76.[3] If we assume that the film has a 2D-hexagonal structure, the distance between the pores, calculated from the tentatively assigned (100) peak ($d_{100} = 7.3$ nm), is 8.4 nm ($7.3 \times 2/\sqrt{3}$), which coincides with the TEM data. In the high-angle XRD pattern (Cu Kα), a broad peak assignable to Pt (111) and (002) was observed in the range of $2\theta = 35$–55°, meaning that the pore walls are made of very minute polycrystalline Pt (fcc) (not shown).

The top-surface FE-SEM image shows that the mesostructured Pt was deposited uniformly over the entire area on the Au surface. The cross-sectional image shows that the thickness of the film was 100 nm with uniform coverage throughout the Au surface and that the film was strongly adhered to the substrate (not shown). The top-surface FE-SEM image at high magnification shows the 3D roughness on the surface of the mesoporous Pt film (Figure 2d). This image is the direct evidence that the structure derived from the H_I–Pt mixture was indeed formed in all the parts including the top-surface of the film.

Another experiment showed that, as the surface area of the contacting Al wire increased, a large amount of air tended to be generated at the interface between the Au substrate and the H_I–Pt mixture during the deposition. It has already been reported that such a gas evolution by the side reaction should lead to the disruption of a mesostructure.[13]

In conclusion, we have for the first time succeeded in preparing Pt thin films with a highly ordered mesostructure by the contact plating. This approach will be used for a very large scaled up reaction cell (in m^2 order), without controlling current densities and plating bath conditions. This method will be considerably important as a practical and technical approach for one-step synthesis of mesoporous metal thin films with uniform thickness and various compositions.

This work is supported in part by a Grant-in-Aid for Center of Excellence (COE) Research "Molecular Nano-Engineering", and the 21st Century COE Program "Practical Nano-Chemistry" and Encouraging Development Strategic Research Centers Program "Establishment of Consolidated Research Institute for Advanced Science and Medical Care" from the Ministry of Education, Culture, Sports, Science and Technology.

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Published on the web (Advance View) November 13, 2004; DOI 10.1246/cl.2004.1576