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Preparation of Porous Material by Replacing Microstructure of Anodic Alumina Film with Metal

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A new type of preparing method of submicron scale porous conducting materials was demonstrated. A microporous structure of anodic alumina film was replaced with metal by using a two step molding technique. The procedure and condition of the fabrication process of the porous film was described.

The films obtained by anodic oxidation of aluminum in acidic electrolytes are known to have a fine cylindrical porous structure. The micropores of the oxide film are parallel to each other and the size of the pores are of the order of submicron or less. Applications of the microporous structure of the anodic alumina film are currently being investigated.[1] However, application areas are limited to some field, because the anodic oxide films, which are composed of hydrated amorphous alumina, are chemically unstable. For this reason, we tried to replace the amorphous alumina to another stable materials, e.g. noble metals.[2] Replacement with conducting materials also contributes to the expansion of the field of application of the fine porous structure. In the present letter, the new method for preparing a submicron scale microstructure of metal films is demonstrated and the fabrication condition of the films is described.

Two step process was employed for preparing conductive porous film. In Fig. 1, the schematic diagram of the fabrication process is shown. Prior to the anodization, the mirror surface was achieved by electrolytic polish of an aluminum plate (15 mm x 60 mm x 0.5 mm) in ethanol/perchloric acid mixture solution (4:1 in volume).

A porous type alumina film was obtained by anodizing the polished aluminum plate in a 0.5 wt% oxalic acid solution under constant voltage condition of 130 V for 5 min (Fig. 1a). The dimension of porous structure obtained under this condition was ca. 400 Å in diameter, 2500 Å in cell size, and 20000 Å in pore length. En-

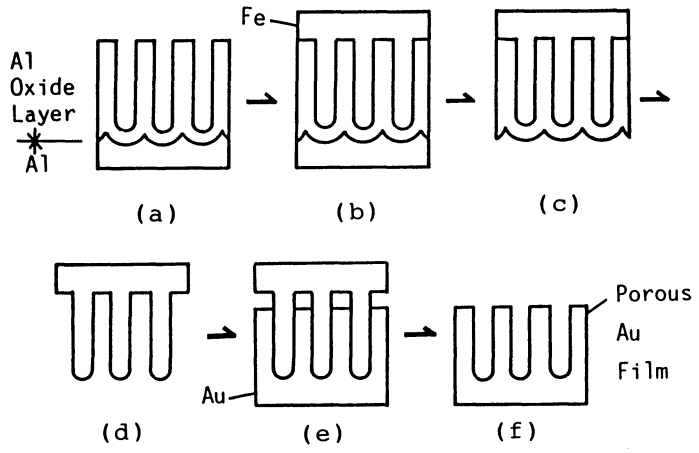

Fig. 1. Schematic diagram of fabrication process.

largement of the pore for obtaining a desired dimension was made by dipping the film in a 5 wt% phosphoric acid at 30 °C. In the case of present experiment, micropores with 700 Å in diameter were obtained after the 10 min etching treatment.

To form the negative type of the microstructure, the pores were filled with metal (Fe) by alternating current electrolysis (10 V, 50 Hz, 15 min) in a 3 x 10^{-2} M $FeSO_4 \cdot 7H_2O$ aqueous solution with 5 x 10^{-2} M H_3BO_3 (Fig. 1b). For this treatment, metal filling techniques used for electrolytic coloring or magnetic recording media preparation of anodic aluminum films can be applied.[3,4] Before the metal filling, the barrier layer at the bottoms of pores was thinned by a current recovery treatment,[1] in which anodizing voltage, at the end of anodizing, was lowered in a stepwise fashion from 100 V to 10 V at intervals of about 10 V. This was to facilitate the deposition of iron in the micropores. After the metal filling, the Fe overdeposited layer was formed on the anodic oxide film by DC constant current electrolysis (20 mA cm^{-2}). Subsequently, the composite film was removed from the Al substrate using mercury chloride solution (Fig. 1c). After that, the bottom part of the composite film was removed by argon ion etching treatment to obtain the flat surfaced cylinders. Then the cylindrical structure, which corresponds to the negative type of the microporous structure, was obtained by dissolving the anodic alumina with a 10 wt% NaOH solution at 30 °C for 24 h (Fig. 1d).

Conductive material (Au) was deposited onto the negative type structure with electrochemical plating using a $KAu(CN)_2$ electrolytic solution (Fig. 1e). Finally, the negative type structure of iron was dissolved selectively in 30 wt% H_2SO_4, and the positive type conductive porous material was obtained (Fig. 1f). Figure 2 shows the photograph of scanning electron microscopy of the Au porous sample obtained by the present method. The formation of the micropores under 1000 Å in the Au film is confirmed from this photograph. Unevenness of the surface is thought to result from the residual alumina which remained partially undissolved in the negative structure. For the Au deposition into the negative type cylindrical structure, it was found that electrochemical or electroless plating methods are preferable to other physical deposition techniques.

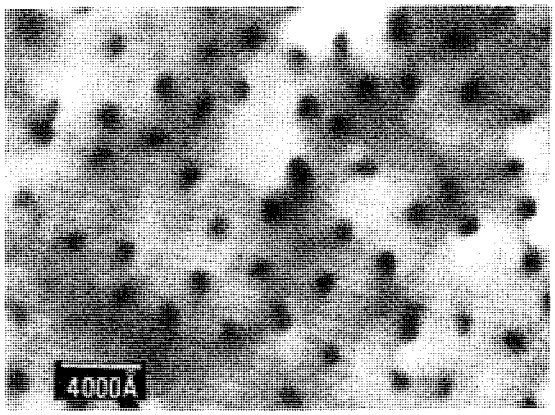

Fig. 2. Photograph of Au porous film by scanning electron microscopy.

Though the uniformity of the porous films is not sufficient at the present stage, this method will be applicable to several fields, such as, electrochemistry, catalyst, and other usages by improving the process.

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References

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