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Preparation of Microporous Gold Films by Two-Step Replicating Process Using Anodic Alumina as Template

Hideki MASUDA,* Hideki TANAKA, and Nobuyoshi BABA
Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University,
1-1 Minamiosawa, Hachioji, Tokyo 192-03

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A new method to prepare microporous Au films was demonstrated. Microporous Au films were fabricated by using a two-step replicating process in which an anodic porous alumina film was used as a template for replication. The Au films had straight micropores, and the distribution of their diameters was very sharp. In addition, the dimensions of the microstructure of the Au films could be controlled by changing the anodizing condition of the porous alumina. The surface morphologies of the porous films examined by scanning electron microscopy and the detailed condition of the fabrication are shown.

Anodic alumina films obtained by the anodic oxidation of aluminum in acidic electrolytes have attracted much interest owing to their unique microporous structure. The structure of the porous film has been characterized in detail by Keller, Hunter, and Robinson.[1)] According to their report, the porous layer comprises an array of columnar hexagonal cells. The micropores, centered in the hexagonal cells, are parallel to each other and perpendicular to the surface. The pore size is very fine and the size distribution is extremely narrow. The dimensions of the porous layer depend on the formation condition, that is, the electrolytic solutions, temperature, time, and applied voltage. By adjusting these conditions, one can obtain porous structures of the desired dimensions.

Porous anodic alumina films have been used in several fields, such as, filters,[2)] catalysts,[3)] magnetic recording media,[4,5)] and electrodes.[6—8)] However, the application of porous anodic alumina has been restricted to specific uses because of the insufficiency of stability in aqueous solutions. The anodic porous film, which comprises amorphous alumina, swelled readily by hydration, and pore plugging occurs in an aqueous environment.

In order to overcome this disadvantage we have tried to replace unstable alumina by other stable materials, and to form chemically stable porous films by using a two-step replicating process.[9,10)] In this process, the microporous structure was replicated by using a two-step process, which consists of the formation of a duplicated negative of metal cylinders and the fabrication of positive-type microporous metals. No work has so far been reported concerning the two-step fabrication of porous films having an identical geometrical structure as that of anodic alumina.

In a previous preliminary report[10)] we described the preparation process of microporous Au films by using a metal negative type prepared by electrochemical deposition into the micropores, and a subsequent elimination of the dendritic port of the metal by Ar-ion etching. However, the uniformity of the negative type was not satisfactory over a large area because of the nonuniformity of the ion-etching rate. Here, we report on an improved process using pore filling with two kinds of metals, as well as subsequent selective dissolution to prepare and array of metal cylinders arranged according to the same height. This process contributes to an improvement of the uniformity of the porous Au film over a large area.

Experimental

The replication of a microporous structure was achieved by using the process shown in Fig. 1. In this process, the negative-type porous structure comprising an array of metal cylinders was first fabricated, the positive type of porous structure was then reproduced. For the negative-type formation, the metal filling techniques used for the electrochemical coloring of anodic alumina,[11—13)] or the preparation of magnetic recording media,[5,6)] can be applied. The details concerining the experimental procedure was as follows.

An aluminum plate (50×10×0.2 mm, 99.99%) was degreased in acetone, and polished electrochemically in a mixture of $HClO_4$ and C_2H_5OH (1 : 4 in volume) solution under a constant-current condition of 170 mA cm^{-2}. A porous anodic alumina film was formed under the constant-voltage condition (130 V) in a 4×10^{-2} M (1 M=1 mol dm^{-3}) oxalic acid solution at 27°C for 3 min.

After anodic oxidation the barrier layer was thinned by a current recovery treatment,[14,15)] in which the anodizing voltage was lowered stepwise from 130 to 10 V at intervals of 10 V, in order to deposit the metal easily into the pore by electrolysis. Without this treatment, no uniform deposition of the metal could be achieved. This current-recovery treatment by a stepwise change of the applied voltage resulted in dendritic pores in the bottom of the porous structure. Since this dendritic part is not for the fabrication of a positive type with Au, this part must be removed to obtain a straight cylinder. One of the methods used to remove these parts was a plasma etching treatment, in which the bottom part of the porous structure was eliminated by Ar-ion etching. However, it is difficult to obtain a uniform sample over a large area using by this method. We thus adopted another technique to remove the dendritic pore and to form the straight cylinders. By using the selective dissolution of two kinds of metals deposited in the pore, one in the bottom part and the other in the upper part, the dendritic part of the cylinder was eliminated, and straight cylinders could be obtained.

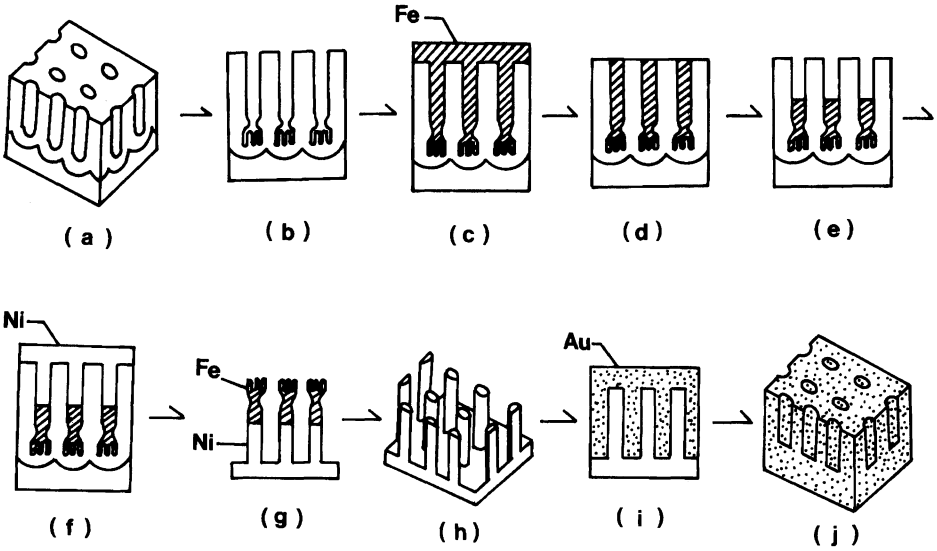

Fig. 1. Schematic diagram of the fabrication process; anodic porous alumina [mother template] (a), thinning of barrier layer by current recovery treatment (b), electrodeposition of Fe (c), peeling off of an overdeposited layer (d), etching of Fe with HCl (e), electroless deposition of Ni (f), dissolution of anodic alumina (g), selective dissolution of Fe [replicated negative type] (h), electrodeposition of Au (i), selective dissolution of Ni [Au porous film] (j).

After a pore-widening treatment in a 0.4 M phosphoric acid solution of 30°C for 10 min to obtain the desired dimensions, Fe was deposited into the pores by AC electrodeposition (10 V, 50 Hz) in a 0.1 M $FeSO_4 \cdot 7H_2O$ solution with 5×10^{-2} M H_3BO_3. After the pore-filling, and the formation of an overdeposited layer with Fe, the overdeposited layer was peeled off mechanically. The Fe was then etched with 1 M HCl at 20°C. As a result, a micropore of uniform depth was reproduced in the anodic film. Ni was deposited into the micropores with electroless plating in 0.1 M $NiSO_4 \cdot 6H_2O$ with 0.24 M $NaH_2PO_2 \cdot H_2O$ and 0.1 M $Na_4P_2O_7 \cdot 10H_2O$ of 60°C, in which the Fe at the bottom part acted as a catalyst for the electroless deposition of Ni. An Al layer was removed in a methanol solution saturated with I_2, and the alumina layer was dissolved with 2.5 M NaOH. An array of straight cylinders was obtained by removing Fe, which filled the dendritic part of the pore, with selective anodic dissolution in a saturated $(CH_3COO)_2Ni$ electrolyte.[16]

A positive type of microporous Au was fabricated by depositing Au into the cylindrical structure electrochemically under a constant-current condition. Table 1 summarizes the electrolytic condition of Au. A microporous Au film was obtained by removing the Ni cylinder in 3 M HNO_3 at 60°C.

Specimens obtained in the fabrication process were observed by scanning electron microscopy (JEOL T-100 and JS-2000).

Results and Discussion

Figure 2 shows SEM photographs of the replicated negative, which comprised a cylindrical structure of Ni. In Fig. 2 the upper part of the cylinder corresponds to the bottom part of the pore. From Fig. 2 it is observed that the Ni cylinders are aligned at almost equal distances and that the heights of the cylinders are nearly uniform. These cylinders are held upright on the surface of the overdeposited Ni layer.

Table 1. Condition of Au Electrodeposition

Composition of plating solution	0.02 M $KAu(CN)_2$ 0.32 M KCN 0.25 M KOH
Temperature	60°C
Current density	1–5 mA cm^{-2}
pH	11–13
Deposition time	15 min

The height of the cylinders depended on the time of dissolution of Fe with HCl. On the other hand, the diameter of the cylinder was determined by the time of pore widening of the anodic alumina films in phosphoric acid. The aspect ratio of the height to the diameter of the cylinder was ca. 5 in the specimen shown in Fig. 2. In the case where the aspect ratio was over 10, it became difficult to obtain a structure of upright cylinders, since the cylinders were standing close to each other.

Figure 3 shows photographs of the surface of the microporous Au films. Micropores are observed over the entire part of the sample (Fig. 3a), and the interval of the micropores is almost equal (Fig. 3b). From a photograph of low magnification, it was found that the porous film contained some defective points. These defects resulted from dropping the cylinder from the sample surface during the course of the fabrication process.

Figure 4 shows the typical distribution of the pore diameters. This result was obtained by measuring the pore diameters in the SEM photograph. The measured points of the photograph were 500. The pore diameters are distributed over a range of 500—1500 Å, with a mean value of 1000 Å. From the result shown in Fig. 4, it can be confirmed that the distribution of the pore

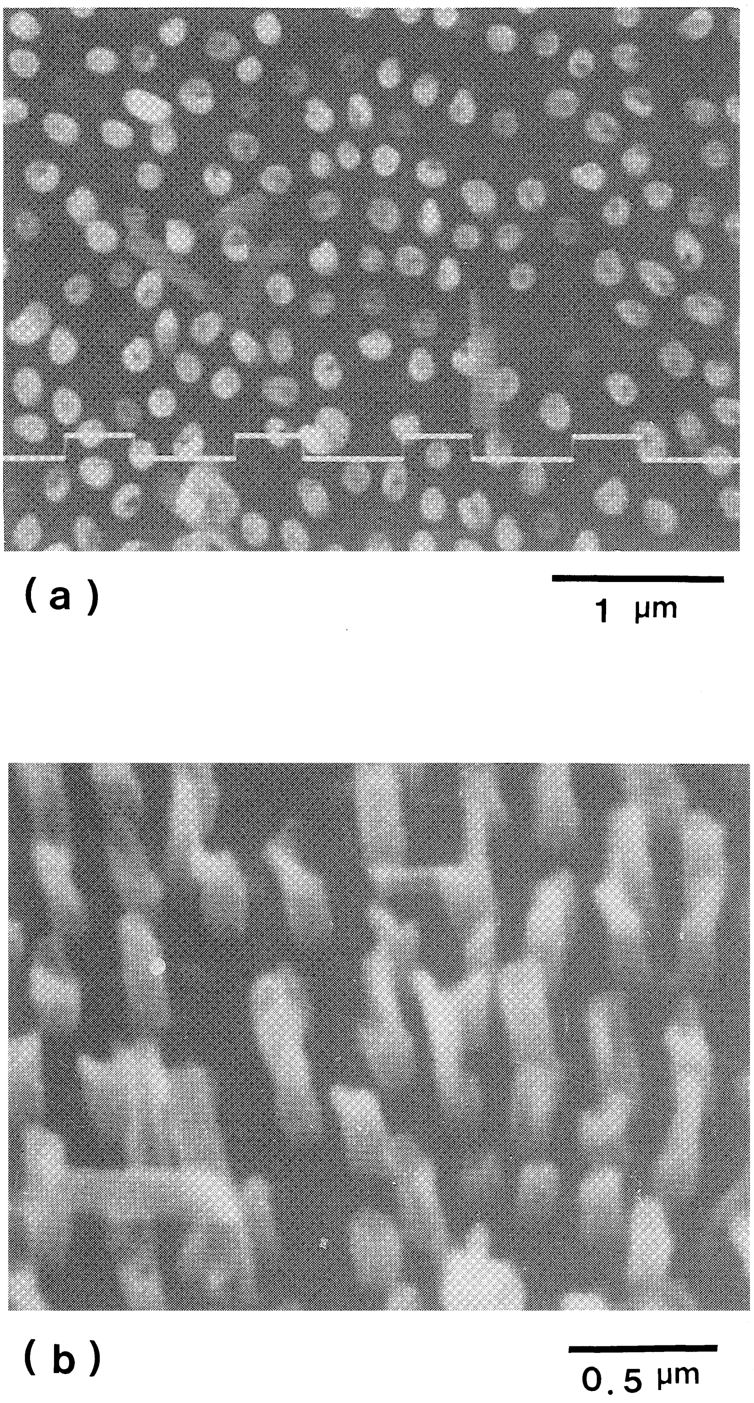

Fig. 2. Scanning electron micrographs of a Ni cylindrical structure (replicated negative type), surface (a) and diagonal view (b).

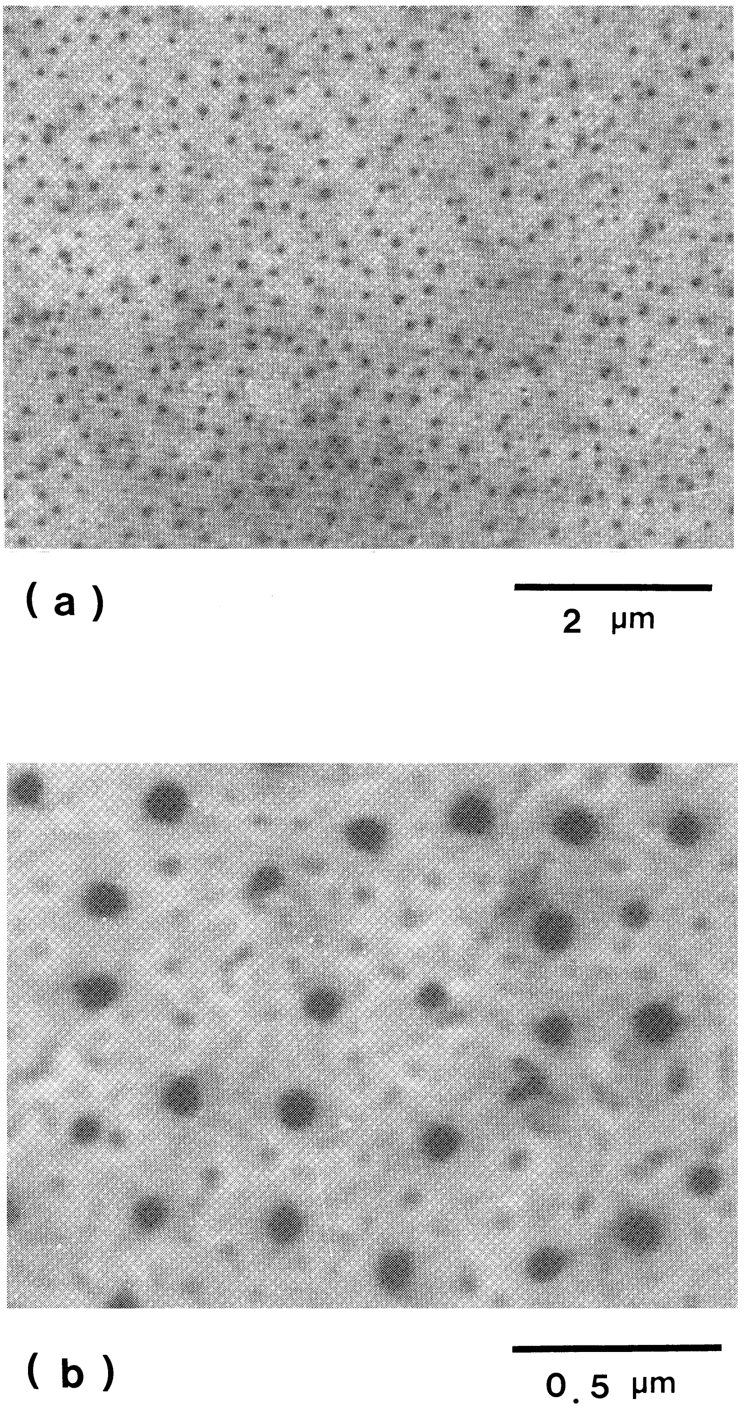

Fig. 3. Scanning electron micrographs of the surface of an Au porous film; low magnification (a), higher magnification (b).

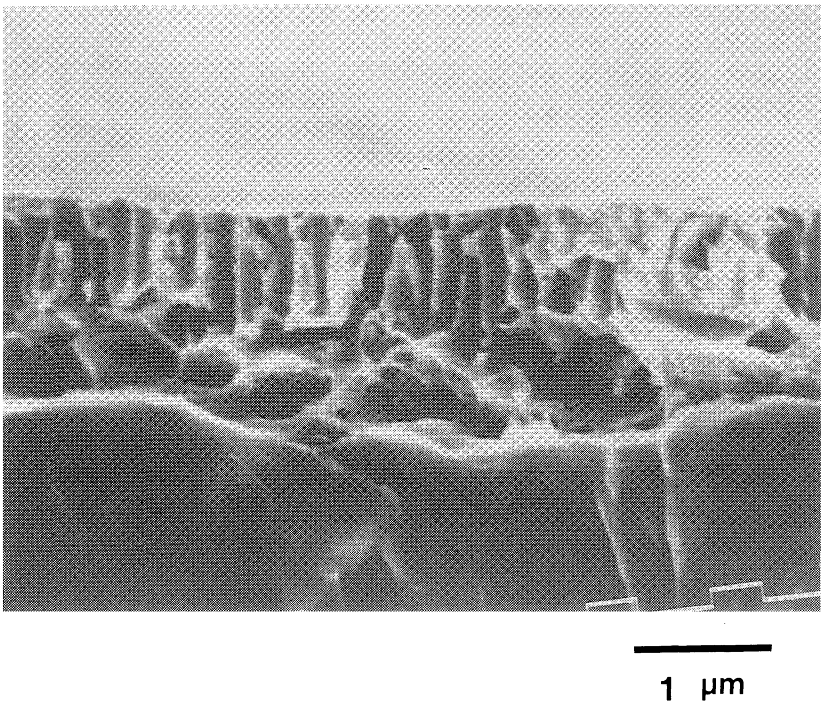

Fig. 5. Cross-sectional photograph of an Au porous film by SEM.

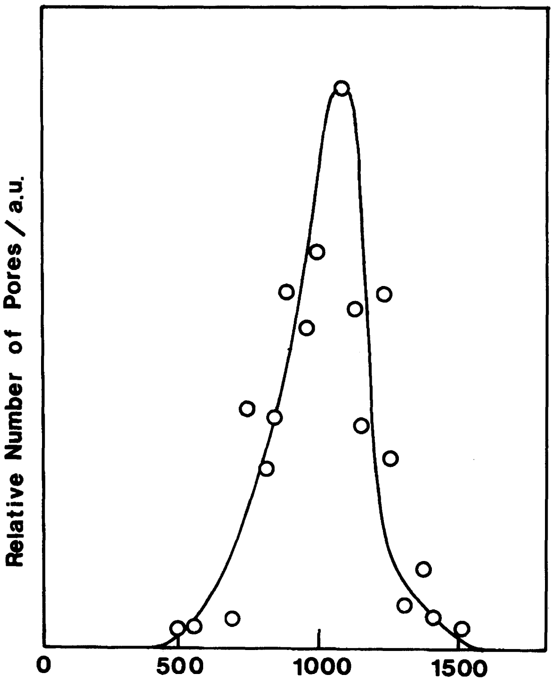

Fig. 4. Distribution of the pore diameter of an Au porous film.

diameters of the Au porous films is very narrow.

Figure 5 shows the cross section of the Au porous film. It is observed that straight micropores are formed parallel to each other and perpendicular to the surface. The depth of the pore was in good agreement with the height of the Ni cylinder. In Fig. 5, it is shown that the Au film has some imperfections, which were not filled up minutely with Au. This stacking fault arises from an insufficiency of Au-ion supply into the narrow gap in the cylindrical structure.

The uniformity and flatness of the surface of the microporous Au films depended on the condition of the electrodeposition of the Au, especially on the current density. Figures 6a, 6b, and 6c show photographs of the surface of the Au films obtained under the constant-current condition at various current densities. As shown in Figs. 6a, 6b, and 6c, a uniform film was obtained at a high current density, while the film has some defects at a low current density. The difference in the morphology of the Au surface results from the rate of nuclear generation. The rate of the nucleus generation of Au is higher under a high current density than under a low current density. The higher nucleation rate results in a depression of the growth of large crystals and contributes to the formation of a minute matrix.

It was confirmed that microporous Au films can be obtained by using a two-step replicating process of the microstructure of the anodic alumina films. By employing this method, porous films of the desired dimension can be obtained by changing the fabrication parameters.

This method will be applicable to several fields, such as electrochemistry, catalyst, chemical sensors, optical devices, and other usage, in which a textured surface of controlled periodicity is required.

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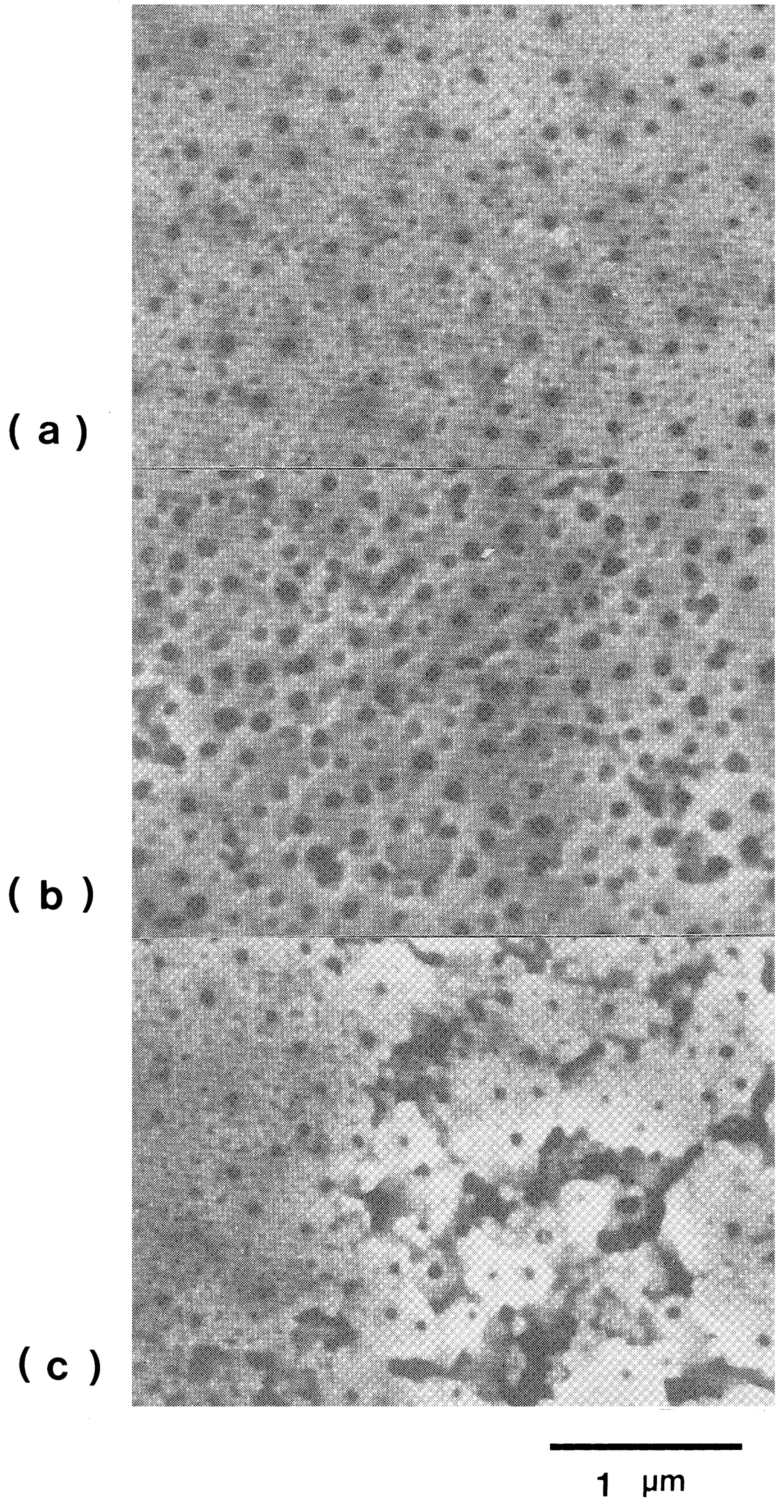

Fig. 6. Scanning electron micrographs of Au porous films obtained at different current densities; (a) 10 mA cm^{-2}, (b) 5 mA cm^{-2}, (c) 1 mA cm^{-2}.

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