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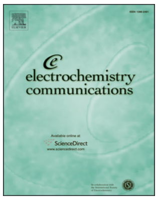

Fabrication of ideally ordered anodic porous TiO_2 by anodization of pretextured two-layered metals

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ABSTRACT

Ideally ordered anodic porous TiO_2 was fabricated by anodizing an Al/Ti layered specimen. A two-layered specimen composed of an Al top layer and a Ti underlying layer was prepared and then processed by nanoimprinting. The Al top layer was easily pretextured by nanoimprinting owing to its softness and it was straightforward to introduce an ideally ordered pore arrangement by anodization. This pore arrangement was transferred to the underlying Ti layer, resulting in ideally ordered porous structures in TiO_2. This process can be applied to the high-throughput fabrication of ideally ordered anodic porous oxides other than TiO_2 and also to other metals with high hardness.

1. Introduction

Anodic porous TiO_2, which is formed by the anodization of Ti in a F^--containing electrolyte, has attracted considerable attention owing to its high potential in various functional application fields [1–5]. The precise control of the geometrical structures of anodic porous TiO_2 is important because the performance of the obtained devices is strongly dependent on the degree of regularity of the structures. For example, in the case of photonic crystals, which are one of the promising application fields of anodic porous TiO_2, highly ordered porous structures are essential for satisfactory control of the propagation of incident light [6–8]. In our previous paper, we reported the fabrication of ideally ordered anodic porous TiO_2 by the anodization of pretextured Ti [9]. In this process, the pretextured pattern was formed by nanoimprinting the Ti surface using a metal (Ni) mold with ordered convexes, and the anodization of the pretextured Ti resulted in ideally ordered TiO_2. The shallow concaves prepared by pretexturing can act as initiation sites for pore development at the initial stage of anodization and result in ideally ordered porous structures. One of the problems to be solved in this process is the degradation of the metal mold used for nanoimprinting on hard metal substrates. In the application of this process to soft metals, such as Al, to which a pretexturing process is widely applied, the formation of pretextured patterns is easy, and this allows repeated use of the metal mold. However, unlike soft metals, the repeated use of a Ni mold on a hard metal such as Ti is difficult because of the degradation of the mold owing to the higher hardness. In the present study, we have developed a new process to overcome this problem and we achieved the high-throughput fabrication of ideally ordered porous TiO_2. In this process, a two-layered specimen composed of an Al top layer and a Ti underlying layer was prepared and then processed by imprinting using a Ni mold. The top Al layer is easily and repeatedly pretextured by nanoimprinting with the Ni mold owing to the softness of Al and the well-established procedure for introducing an ideally ordered pore arrangement by anodization. This pore arrangement can be transferred to the underlying Ti layer, resulting in ideally ordered porous structures in TiO_2. This process allows the high-throughput fabrication of highly ordered TiO_2 and will contribute to the expansion of the application fields of anodic porous TiO_2.

2. Experimental

Fig. 1 shows the fabrication scheme for ideally ordered porous anodic TiO_2 by the anodization of Al/Ti two-layered structures. First, a Ti plate (purity: 99.5%) was chemically polished by immersing it in a polishing agent (TCP-08, Ryoko Chemical Co., Ltd.) [9]. A thin Al layer was formed on the surface of the Ti using a DC sputtering apparatus (SPF-344, SEED Lab.). The purity of the sputtering target of Al was 99.99%. The thickness of the Al layer was controlled by changing the sputtering duration. For pretexturing, a Ni mold with ordered convexes was imprinted on the surface of the heated Al using an oil press apparatus (S04-50, RIKEN) equipped with a heater. The pressure was 310 MPa. The temperature of the sample during imprinting was 150 °C. The textured sample was then anodized in 0.5 M oxalic acid at 16 °C at 60 V. When the current began to decrease during anodization, the applied voltage was increased in one step from 60 to 150 V and maintained for 3 min.

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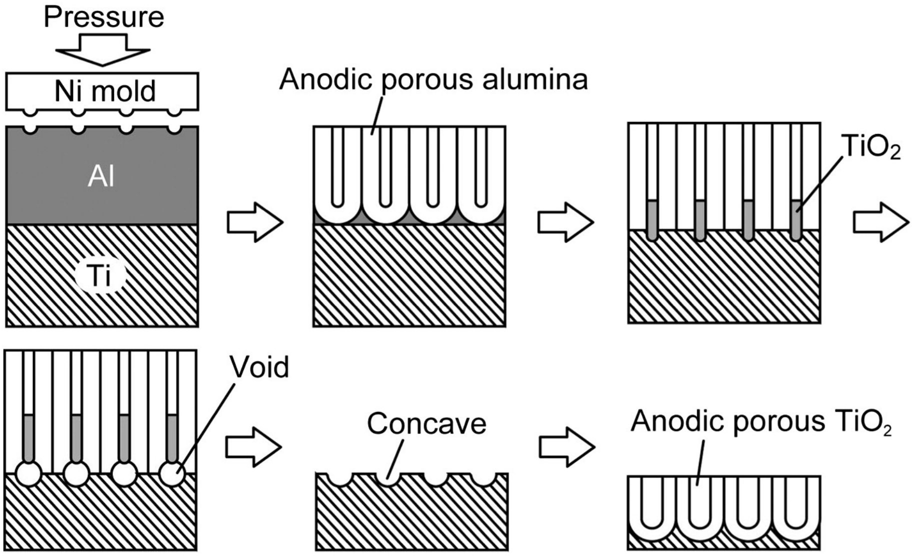

Fig. 1. Scheme of fabrication of ideally ordered TiO_2 by anodizing Al/Ti layered structure.

The anodic porous alumina layer was dissolved by immersing the sample into a mixture solution of chromic acid and phosphoric acid for 24 h. Then, the sample was anodized in 0.38 wt% NH_4F ethylene glycol solution at 20 °C by applying a voltage of 60 V for 1 h. When Ti is anodized in an electrolyte containing water as an additive, a TiO_2 nanotube array is generally formed [4]. In this study, to obtain a TiO_2 nanohole array instead of a nanotube array, water was not added to the electrolyte. The geometrical structures of the obtained samples were observed by scanning electron microscopy (SEM; JSM-6700F, JEOL).

3. Results and discussion

Fig. 2(a) shows a SEM image of a Ni mold used for pretexturing. The ordered array of convexes was confirmed in the mold. Fig. 2(b) shows a SEM image of the surface of the Al/Ti specimen after the pretexturing process. The thickness of the Al layer was 500 nm. The formation of an ordered array of concaves was observed over the specimen. When the thickness of the Al layer was less than 500 nm, concaves could not be formed over the sample area. When the thickness was over 500 nm, the Al adhered to the Ni mold, resulting in the removal of Al from the surface of Ti. The arrangement of the concaves on the Al was in good agreement with that of the convexes on the Ni mold. The interval between the concaves on the sample in Fig. 2(b) was 150 nm.

Fig. 3 shows oblique SEM images of the sample after the anodization of the top Al layer. From the low-magnification SEM image in Fig. 3(a), the formation of an ideally ordered anodic porous alumina layer was confirmed over the sample. The thickness of the porous alumina layer was 500 nm. In the high-magnification SEM image in Fig. 3(b), a characteristic structure was observed at the Al_2O_3/TiO_2 interface. That is, the formation of a TiO_2 pillar was confirmed in each pore of the porous alumina. These pillars were formed through the migration of Ti through the bottom layer of the porous alumina. Underneath these pillars, voids that reached the surface of the Ti layer were observed. The voids were generated by the evolution of oxygen gas underneath the TiO_2 nanopillars, which was caused by increasing the applying voltage from 60 to 150 V [10]. This characteristic structure was similar to that observed by other groups upon the anodization of two-layered metals such as Al/Ta, Al/Nb, and Al/Ti [10–14]. Such a structure enabled the introduction of the ordered array of concaves on the Ti surface whose arrangement corresponded to the pore arrangement in the porous alumina layer.

Fig. 4 shows SEM images of the surface of Ti after the selective removal of the anodic porous alumina layer. In the low-magnification SEM image in Fig. 4(a), the ordered array of concaves was observed over the sample area. From the high-magnification SEM image in Fig. 4(b), the interval and diameter of the concaves were found to be 150 and 75 nm, respectively. This indicates that the ideally ordered arrangement of the nanoholes of the porous alumina was transferred

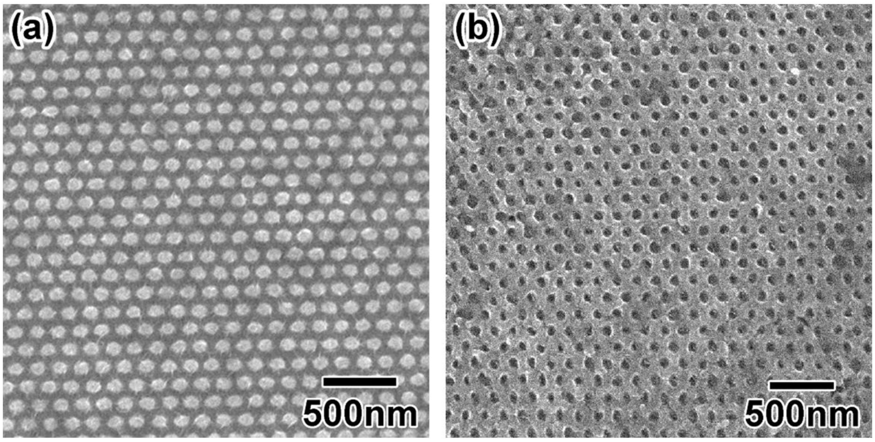

Fig. 2. SEM images of the surfaces of (a) Ni mold and (b) Al after texturing process.