Fabrication of Ideally Ordered Nanohole Arrays in Anodic Porous Alumina Based on Nanoindentation Using Scanning Probe Microscope

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Ideally ordered hole array structures in anodic porous alumina were prepared by pretexturing Al using a nanoindentation apparatus equipped with a scanning probe microscope. The shallow concaves formed by the nanoindentation initiated hole development, and guided the growth of holes during the anodization. Hole arrays with hole intervals from 100 to 400 nm were fabricated by changing the intervals of concaves by nanoindentation with the scanning probe microscope.

Nanohole array structures with uniformly shaped and uniformly sized holes have been attracting increasing interest as a key material for the preparation of several types of nanodevices. Anodic porous alumina, which was formed by the anodization of Al in acidic solution, is one of the promising hole array materials due to its naturally occurring highly ordered hole array structure.[1–4] In our previous reports, we described that the pretexturing of Al prior to anodization can initiate hole development and generate an ideally ordered hole configuration over the sample.[5–7] In this process, the shallow concaves formed by the indentation process using a mold that has an ordered array of convexes initiate hole development at the initial stage of anodization and generate an ideally ordered hole configuration over the sample. In the present report, we describe the fabrication of an ideally ordered hole configuration based on the pretexturing of Al using a nanoindentation apparatus equipped with a scanning probe microscope.[8]

The indentation process by scanning probe microscopy has several advantages for the pretexturing of Al prior to anodization. In this process, it is not necessary to prepare the mold for the indentation, which requires a complicated preparation process and uses of expensive facilities. This process also has the possibility of fabricating hole arrays with high lateral resolution of hole intervals compared to the molding process. In addition, indentation by the scanning probe microscope will contribute to the quantitative analysis of the mechanical deformation of Al during the nanoindentation.

Figure 1 shows the schematic of the process for preparing the ordered hole array of anodic porous alumina using the nanoindentation process. An Al sheet (99.99% purity) was polished electrochemically using a mixture of perchloric acid and ethanol. The indentation of Al was made using the nanoindentation apparatus (Hysitron) attached to a scanning probe microscope (Shimadzu SPM 9500J2). This type of apparatus has been specially designed in such a way that a tip is attached to a force-displacement piezo column that applies force over a large range compared to the standard cantilever-type tip.[9] A three-sided pyramidal diamond tip with an angle of 142.3 degree was used as an indenter. The atomic force microscopic (AFM) image was obtained with the same tip and piezo column after the indentation. The indentation load was usually from 25 to 40 μN.

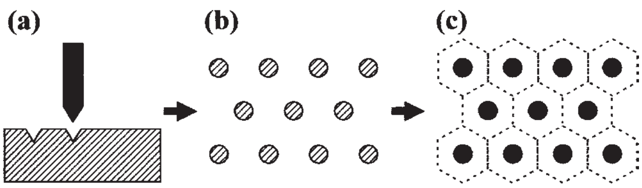

Figure 1. Schematic of the process involved in site-controlled hole development using a probe microscope: indentation of Al by tips (a), pattern of the array of concaves (b), ordered array of holes in anodic porous alumina after anodization (c).

The anodization of Al was carried out in oxalic acid or phosphoric acid solution under the constant voltage condition. The applied voltage was adjusted based on the linear relationship between the hole interval and the applied voltage (2.5 nm/V).[10] The surface of the anodized samples was observed by a scanning electron microscope (SEM: JSM6100).

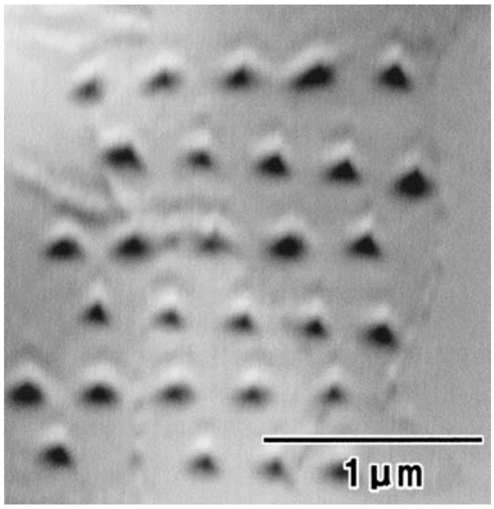

Figure 2. AFM image of Al pretextured by indentation at 400 nm intervals. The indentation load was 40 μN.

Figure 2 shows an AFM view of the surface of Al after nanoindentation with a load of 40 μN. The interval of the series of indentations is 400 nm for the sample shown in Figure 2. It was observed from Figure 2 that almost uniformly sized concaves were formed in an ordered array after the nanoindentation. The shape of the concave was inversed pyramidal, which corresponded to the tip used for the nanoindentation. The side and the depth of the pyramidal concaves were 120–200 nm and 20–30 nm, respectively.

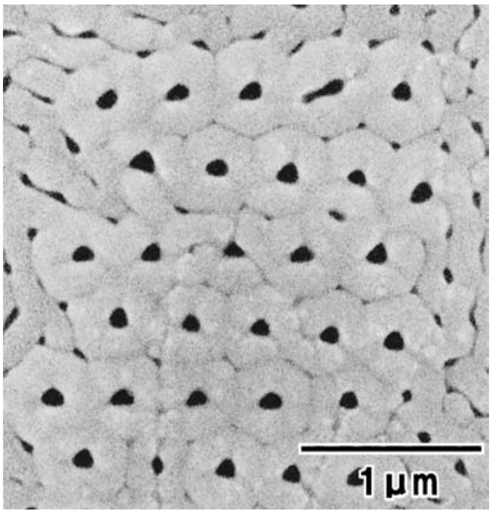

Figure 3. SEM micrograph of the anodic porous alumina: anodization was carried out in 0.2 M phosphoric acid at 2 °C under the constant voltage of 160 V for 20 min.

Figure 3 shows an SEM micrograph of the anodic porous alumina after anodization in 0.2 M phosphoric acid under a constant voltage of 160 V for 20 min. From Figure 3, it is observed that each concave initiated hole development and guided the growth of the highly ordered holes, whereas the hole arrangement in an untreated area was disordered.

Hole arrays with further reduced intervals can be achieved by indentation of Al of smaller intervals. Figure 4 shows the obtained hole array of anodic porous alumina with reduced hole intervals. These structures were formed using a series of nanoindentations at periodicities of 200 nm (Figure 4a) and 100 nm (Figure 4b). In the case of the samples shown in Fig. 4, the pore widening treatment was performed by etching the samples with 5 wt% phosphoric acid solution at 30 °C to clarify the hole arrangement. From the AFM image of the Al indented at the 200 nm interval, clear isolated concaves were observed after the indentation (Figure 4a-1). From the SEM image of the anodized surface in 0.04 M oxalic acid solution shown in Figure 4a-2, it is confirmed that these concaves could initiate hole development during the anodization. On the other hand, the concaves formed at the indentation interval of 100 nm are not isolated but overlapped, as shown in Figure 4b-1. This is because the indents formed by the tips with a relatively large angle used in the present study generated large concaves. However, even these overlapped concaves could introduce isolated holes after the anodization (Figure 4b-2). The depth of the concaves evaluated from AFM measurement of the sample with 100 nm interval is ca. 5 nm. It is noteworthy that such shallow concaves can introduce the ordered hole array during the anodization.

The fabrication of the ordered hole array was demonstrated based on the pretexturing of Al using the nanoindentation apparatus attached to the scanning probe microscope. This process is useful for the fabrication of an ordered hole array of anodic porous alumina conveniently. The use of tips with smaller angles can reduce the interval of the obtained hole array. In addition, this process will be used for the pretexturing of Al with several types of lattices, which can generate square or triangular holes in anodic porous alumina.[11]

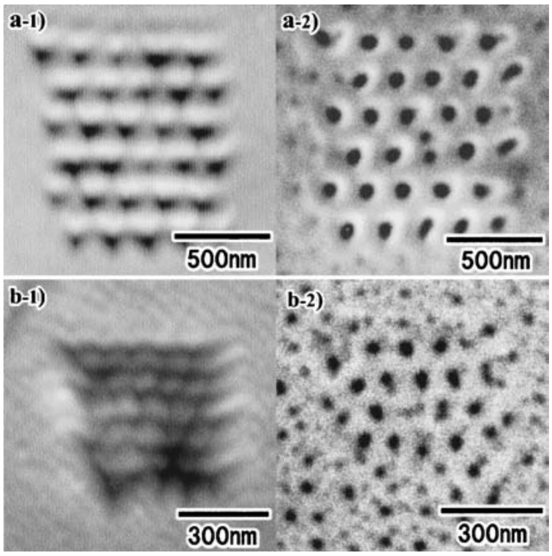

Figure 4. Images of indented and subsequently anodized samples with hole intervals of 200 nm (a), and 100 nm (b). Left figures show AFM images after indentation (a-1, and b-1), and right ones show SEM images after anodization (a-2, and b-2). Anodization was carried out in 0.04 M oxalic acid at 16 °C. The applied voltage was 80 V for (a) and 40 V for (b).

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