Antireflection Polymer Surface Using Anodic Porous Alumina Molds with Tapered Holes

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Antireflection (AR) polymer structures composed of tapered conical pillars were fabricated using highly ordered anodic porous alumina. The shape of the holes in the anodic porous alumina was controlled by performing repeated anodization and pore-widening treatments. By replicating the structure of the anodic porous alumina with PMMA, polymer AR structures were obtained.

There has been increasing interest in the antireflection (AR) structures of polymers because of their applicability to the various types of functional optical device.[1–4] In the AR structures, tapered conical microstructures with a period shorter than the visible wavelength suppress the reflection of incident light due to the gradual change in the refractive index at the surface. AR structures have usually been prepared by EB lithography or holographic exposure, which can generate fine structures of subwavelength whose period is shorter than the visible wavelength. However, the preparation of a large-area surface is difficult by these processes. In addition, the formation of smooth tapered conical structures is difficult by these conventional lithographic techniques. In the present report, we describe, for the first time, the fabrication of AR polymer structures by replication process using highly ordered anodic porous alumina with tapered holes as a mold. The anodic porous alumina, which is formed by Al anodization in acidic solution, is a typical self-ordered material.[5] Under appropriate anodization conditions, long-range-ordered anodic porous alumina with an ideally ordered hole arrangement can be obtained. We found that the shape of the holes in the anodic porous alumina can be controlled by a process composed of a series of anodization and subsequent etching treatments.[6] By using the anodic porous alumina with shape-controlled holes as a mold for the replication, the preparation of AR structures of polymer could be achieved.

Figure 1 shows a schematic of the preparation of anodic porous alumina with tapered holes used as a mold. For the preparation of anodic porous alumina with a highly ordered hole arrangement, a previously reported two-step anodization was adopted.[7] In this process, an oxide layer, the bottom of which has an ordered hole arrangement induced by the first long-term anodization step, was removed in a solution of CrO_3 and H_3PO_4, and the second anodization step was conducted at the same anodization voltage as the first anodization. The ordered array of concaves formed on Al after the selective removal of the oxide layer acts as an initiation site for hole development and generates a highly ordered hole arrangement from the surface. Al of 99.99% purity was anodized in 0.3 M oxalic acid under a constant voltage of 40 V at 17 °C for 12 h. After the first anodization, the oxide layer was removed in a solution of chromic acid and phosphoric acid. The Al with ordered array of concaves was again anodized under the same conditions for 15 s. After the

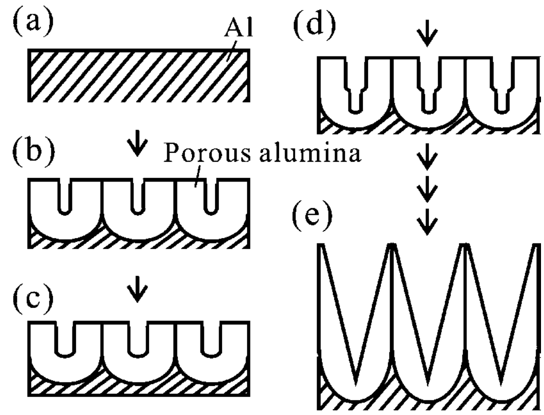

Figure 1. Schematic for preparation of anodic porous alumina mold with tapered holes. Al substrate (a), anodization (b), pore widening (c), second anodization (d), and porous alumina with tapered holes (e).

anodization, pore-widening treatment was carried out in 5 wt % phosphoric acid at 30 °C for 8 min. A series of 5 repetitions of the anodization and pore-widening treatment, and a final anodization for 15 s generated anodic porous alumina with tapered holes. In this process, the shape of the holes could be controlled arbitrarily by adjusting the number of repetitions of anodization and pore widening. An AR polymer structure was formed by the replication of the ordered structures of porous alumina onto poly(methyl methacrylate) (PMMA). A methyl methacrylate monomer, which contained 5 wt % benzoic peroxide as an initiator, was injected into the holes of the anodic porous alumina and polymerized for 12 h at 50 °C. After the polymerization, an AR PMMA structure was obtained by the selective dissolution of the anodic porous alumina in 10 wt % NaOH. The structures of the obtained samples were observed using a scanning electron microscope (SEM: JEOL JSM-6700). For a simple evaluation of the AR properties of the samples, transmission spectra were measured using a spectrophotometer (Hitachi U-3500).

Figure 2 shows a cross-sectional SEM image of the anodic porous alumina used for the mold. From Figure 2, it can be confirmed that the anodic porous alumina has controlled smooth tapered holes. The hole interval and hole size at the opening were 100 and 70 nm, respectively. The result shown in Figure 2 implies that the 5 repetitions of the anodization and pore-widening treatment are sufficient for the formation of smooth tapered holes in the anodic porous alumina.

Figure 3 shows a SEM image of the AR structure of PMMA obtained after replicating the ordered structure of anodic porous alumina onto the polymer surface. From the low-magnification SEM image shown in Figure 3a, an ideally ordered array of tapered conical pillars is confirmed over the entire view of the image. The period and height of the pillars were 100 and

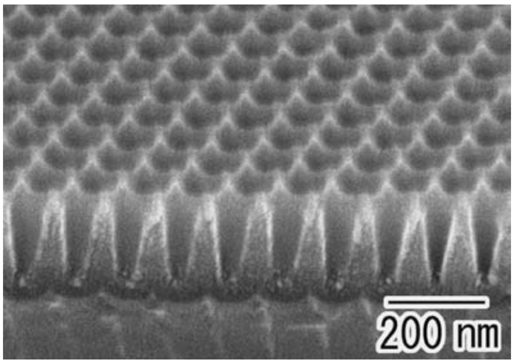

Figure 2. Cross-sectional SEM image of anodic porous alumina with tapered holes.

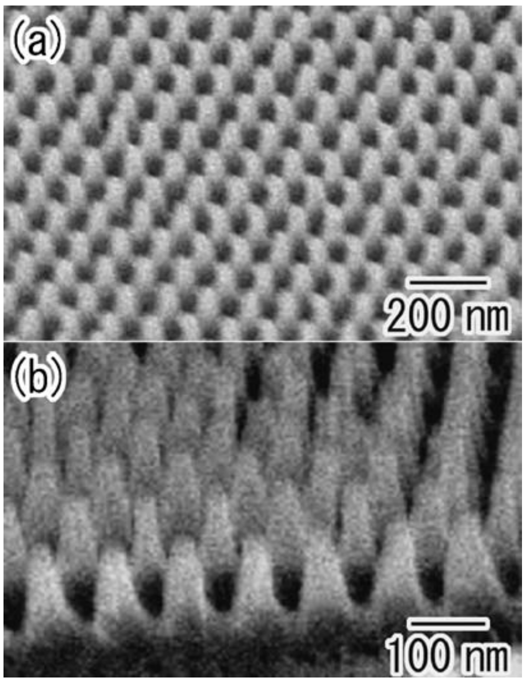

Figure 3. SEM images of AR structure of PMMA, low-magnification (a), and high-magnification (b) images.

150 nm, respectively, from the high-magnification SEM image in Figure 3b. The SEM image in Figure 3b confirms that the tapered holes in the alumina mold were precisely transferred to the AR structures of PMMA. The partially bent shape of the conical pillars in Figure 3b was due to deformation upon heating of the pillars during SEM observation.

Figure 4 shows the transmission spectra of a PMMA sample with the AR structure on both surfaces. When compared with the spectrum of the smooth PMMA, that of the PMMA with AR structures showed a higher transmission intensity at the observed wavelength. This suggests that the AR structure of PMMA effectively suppresses the reflection of incident light at the surface.

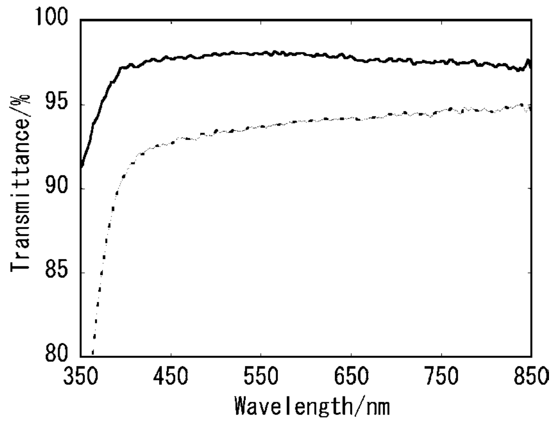

Figure 4. Transmission spectra of AR (—) and smooth (- - -) surfaces of PMMA.

The AR structures of polymers composed of smooth tapered conical structures could be fabricated using highly ordered anodic porous alumina with tapered holes, which was formed by a series of repetitions of anodization and pore-widening treatment. The obtained structures showed higher transmittance in the visible-wavelength region due to the suppression of the reflectance at the surface compared with that at the smooth surface. The process proposed in the present work allows the formation of the tapered cone structures with desired curvatures by adjusting the time of the anodization and pore widening. The effect of the change of the curvatures, and the optimization of the AR properties based on the adjustment of the curvatures are under way in our laboratory. Anodic porous alumina, or metal molds, which are prepared from the anodic porous alumina templates, can be used for the nanoimprinting of polymers.[8] The application of anodic porous alumina with tapered holes as a mold for nanoimprinting enables the high-throughput fabrication of AR structures of polymers because it can be used repeatedly. The obtained AR structures of polymers can be used in various application fields that need a large sample area, typified by flat panel displays.

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