Fabrication of Anodic Aluminum Oxide Film on Large-Area Glass Substrate

Ching-Jung Yang,a Shih-Wei Liang,a Pu-Wei Wu,a,b,z Chih Chen,a and Jia-Min Shiehb

aDepartment of Materials Science and Engineering, National Chiao Tung University, Hsin-Chu 30010, Taiwan
bNational Nano Device Laboratories, Hsin-Chu 30078, Taiwan

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Recently, self-organized nanostructures and devices have received much attention because their unique properties demonstrate considerable potentials in many applications.1,2 Several techniques are reported to fabricate desirable structures including atomic layer deposition, focused ion-beam etching, and scanning probe-based nanolithography.3-5 Unfortunately, these approaches are relatively time-consuming, expensive, and in particular confined to substrates with a limited footprint. As a result, alternative methods that are simple and especially suited to large areas are being intensively pursued. One of the promising solutions is to use anodic aluminum oxide (AAO) as a template to construct the intended nanostructure. The AAO consists of a close-packed hexagonal array of nanopores. Its characteristics could be adjusted by varying process parameters such as operation voltage, temperature, as well as electrolyte type and concentration.6,7 To date, AAOs with highly ordered pore arrays are routinely prepared with tailored pore diameter and channel length.

Several studies have reported growth of AAO film by direct anodization of Al deposited on substrates such as silicon and glass.8-10 This was achieved by successive depositions of conductive underlayer and Al, and followed by typical anodization treatments. The as-synthesized AAO film was then used as the template to develop one-dimensional nanostructures in various oxides and metals.11,12 From the standpoint of device fabrication, AAO film in large area is always preferred. However, due to lab-scaled experiment, AAO film that has been prepared so far is still confined to a limited area.13,14 We believe lack of research in large area AAO formation is limiting its implementation in device fabrication of commercial scale.

Transparent glass substrate is widely used for applications in photoelectrochemistry and photocatalysis. Owing to its insulating nature, direct anodization of Al on large-area glass substrate presents a serious challenge. Previously, Chu et al. employed tin-doped indium oxide predeposited on the glass substrate as a conductive layer to facilitate complete AAO formation.15 In contrast, Miney et al. evaporated Al directly on microscope glass slide and reported successful oxidation of Al to AAO.16 In addition, they noticed a self-limiting process that gradually converted Al into AAO without breaking up necessary electrical contact. Besides, they also discovered AAO growth to be randomly initiated from perimeters instead of areas with the shortest distance to the contact point. Similar work was conducted by Das and McGinnis, whereas p-type Si was used as the substrate to support successful anodization of Al film.17 Nevertheless, the AAO films and substrates in their demonstrations were less than 10 cm². Despite promising results in small substrates, uniform AAO formation in large area is still unresolved.

In this article, we report preparation of a continuous AAO film on 4 in. glass substrate by anodization treatment using specifically designed electrode support. Our work provides an invaluable link in incorporating AAO related nanofabrication techniques with existing very large-scale integration (VLSI) technology. Successful development of AAO process on 4 in. substrate is likely to incur rapid adoption of AAO-based devices in commercial applications.

Experimental

Quartz substrate 10.0 cm in diameter (Photox Inc.) with thickness of 0.55 mm was used in our study. First, a thermal evaporation coater was employed to deposit 800 nm of Al film over the entire glass substrate. The uniformity of deposited Al was determined at 806 nm with a standard deviation of 71 nm. The Al film was then treated with a one-step anodization process at room temperature to develop nanoporous AAO structure. The anodization treatment was performed in 0.3 M oxalic acid (H₂C₂O₄) at a voltage of 40 V. The oxidation process was terminated after the current fell back to background value and stabilized for extended time.

Schematic of our specially designed electrode structure is shown in Fig. 1. A Cu cylinder 10.0 cm in diameter and 5.0 cm in height was used as the support for the working electrode. Glass substrate was positioned atop of the Cu support while four Cu tapes 1.0 cm wide and 0.05 cm thick were used to connect the Cu support to the Al film on the substrate surface. A Teflon cap was used to fasten the glass substrate with the Cu support. The effective area (41.9 cm²) exposed to electrolyte was a circle of diameter 7.3 cm. With this design, the current was directed from the electrode support to the Al layer through those Cu tapes positioned at the four corners. In addition, anodization by conventional single contact approach was carried out with an alligator clip connecting the glass substrate directly.

Figure 1. Schematic of electrode support with quadruple contacts for anodization treatment of Al on glass substrate.
with the external power source. An area of 56.4 cm² was immersed in the electrolyte. For both arrangements, Pt was used as the counter electrode. In transmittance determination, UV-visible spectra of the samples were recorded by a spectrometer (U-3500, Hitachi).

Results and Discussion

Motivated by results from Miney et al., we initiated our work to carry out direct anodization of Al on 4 in. glass substrate with similar setup in single contact arrangement. In our case we did not use an insulating tape to protect the area near the electrolyte-air interface. Unlike in Ref. 16, complete anodization of Al was not achieved after several attempts. In their work, the area of the microscope slide was less than 6.25 cm². In contrast, in our experiment the area exposed to the electrolyte was 56.4 cm². Similar pattern of AAO formation was observed where initial oxidation took place on the perimeters of the substrate and progressed inward gradually. However, the starting position differed in each experiment. Unfortunately, in our case the anodization process was terminated prematurely once the newly formed AAO cut off the conducting path to the contact point, leaving unreacted Al as isolating islands. Figure 2a exhibits the glass substrate with partial transformation of AAO using single contact arrangement. The straight line indicates the electrolyte level separating Al above and AAO below. A transparent AAO strip was seen right below the electrolyte level, while the opaque area in the middle was the unreacted Al. Because the contact was located on the top edge of the substrate, the current is expected to flow in the top-down direction. Hence, the anodization process was compromised substantially once the insulating AAO was able to isolate the top area completely.

From our observation, we determined that current distribution is critical in promoting uniform oxidation across entire surface. Therefore, efforts were spent to modify electrode support for ensuring better distribution of current during anodization. Previously, Chu et al. employed conductive tin-doped indium oxide to facilitate current conduction in order to fabricate many AAO-based devices. In contrast, we intend to proceed with anodization directly without preposition of conduction layer. Our electrode design allows the substrate to receive uniform current distribution by establishing contacts between underlying Cu support and Al atop with multiple Cu taps. With contacts at the four corners, we observed the anodization to start from those current entering points and progressed inward with anodization time. Figure 2b presents the photograph of glass substrate after complete formation of AAO. In our arrangement the electrode support was immersed in the electrolyte completely and AAO formation started from current entrance points. This is markedly different from that of the typical single contact method because in the latter case the bottom part of the substrate was submerged and anodization took place from the perimeters randomly. Therefore, it is our conclusion that electrode arrangement with multiple contacts is better suited in process control for large-area AAO formation.

Figure 3 shows typical I-T curves for the anodization process with setups in single and quadruple contacts. Under anodization voltage of 40 V, the measured current densities are 1.86 and 2.51 mA/cm² for single and quadruple contacts, respectively. Once anodization was completed, the values for current density dropped considerably and remained at background levels of 0.06 and 0.40 mA/cm², respectively. In single contact mode, the current decreased to background value after 1360 s, while for quadruple contacts the current was reduced after 1120 s. The durations of anodization for both arrangements are found to be proportional to the areas of AAO growth, a behavior that is consistent with Coulomb law. The value for background current density in quadruple contacts is moderately higher than that of single contact. A possible explanation for this discrepancy was because Al under the Teflon cap was not completely sealed from contacting electrolyte and oxidation reaction still took place locally. Our I-T curves are relatively simple and thus could be used as the indicator for AAO formation. This is significantly different from what was reported by Chu et al., where substantial current fluctuation and gas evolution were observed.

The simple I-T curves suggest our electrode design is likely to render easier adaptation to the large-scale fabrication process.

Figure 4 presents the UV-visible transmittance spectra of glass substrates before and after formation of AAO. Also shown is the transmittance response of the glass substrate itself. The as-received glass substrate demonstrated a transmittance of 90% in visible range. Due to Al’s strong reflecting nature, transmittance of the glass substrate was not obtained after Al deposition. After successful AAO formation the glass substrate became transparent again and its optical property exhibited a pattern of interference fringes with transmittance fluctuating between 60 and 70%. Because there was no notable increase in the magnitude of transmittance peaks at longer wavelengths, the effect of scattering by the porous AAO structure can be ruled out. We believe that the reduction of transmittance from 90% to 60–70% is due to absorbance by the remaining Al layer, because the previous report indicated complete conversion of Al was not possible. In a thin-film estimation the appearance of interference fringes obeys a simple rule of 2nd = mλ, where n is the effective refractive index of the film material, d is the film thickness, m is
any integer, and $\lambda$ is the wavelengths at transmittance valley from the fringes. Analysis of the interference fringes arrives at a value of 1500 for $nd$. With AAO thickness estimated at 967 nm, the effective refractive index of the AAO film is 1.55. Taking 1.66 as the refractive index for bulk alumina, the estimated porosity of the AAO film becomes 17%. We admit the estimated porosity of 17% is below what was expected from a porous AAO film; the exact reason for this discrepancy is unclear. However, we would like to emphasize that the estimation of $2nd = m\lambda$ is based on ideal thin-film structure, while in our case rather disordered AAO with height variations was present.

**Conclusion**

AAO formation on 4 in. glass substrate was successfully demonstrated with specially designed electrode structure. With contacts at the four corners, current flow was spread evenly, ensuring uniform transformation from Al to AAO over the entire substrate. In conventional single contact practice, growth of AAO near the contact area inhibited further conversion of remaining Al, thus causing anodization to terminate prematurely. The glass substrate after AAO formation exhibited a transmittance between 60 and 70%. This work provides critical information for making large-area AAO templated devices in the near future.

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