World Journal of Nanoscience and Nanotechnology

Short Communication

Effect of Humidity on Nanoporous Anodic Alumina Oxide (AAO)

Chung CK* and Ku CA

Department of Mechanical Engineering, National Cheng Kung University, Taiwan

Abstract

The Nanoporous Anodic Aluminium Oxide (AAO) template is popularly used for fabricating 1D nanomaterial. The direct-current anodization on high-purity (99.99% or more) Aluminum (Al) foil at a low temperature (0~10°C) was applied for the traditional AAO formation. In this communication, the low-purity Al (99%) was anodized at room temperature (25°C) by hybrid pulse voltage technique using oxalic acid as the electrolyte to prepare nanoporous AAO. It is low-cost and facile method to economically form the AAO at a relatively high temperature compared to the conventional one. The humidity effect on the surface property of AAO was examined. The treated two specimens with and without pore widening treatment were placed under different humidity conditions. The relationship between the surface discoloration and humidity was observed.

Introduction

The Anodic Aluminium Oxide (AAO) can be divided into two types: barrier-type and porous-type. The former is often used for protection because its thin and tight structure, while the latter is paid more attention to the highly ordered pore structures. In recent years, more and more researchers have applied themselves to this nanoporous field. The AAO has been widely used as the template to grow 1D nanomaterial. More and more methods have emerged in order to achieve a more ordered structure or a more efficient and inexpensive process. For instance, the constant Direct-Current Anodization (DCA) method has long appeared, and followed by Pulse (PA) or Cyclic (CA) anodization. One-step or two-step [1] can be used to perform anodic oxidation process in various electrolytes of sulfuric acid [2,3], oxalic acid [3], phosphoric acid [4] and other acids. AAO has been widely used in optics, biotechnology, super capacitors [5], magnetic recording, surface enhanced Raman scattering, humidity sensors [6], catalysts, nanopattern transfer [7], nanomaterials synthesis and other fields. The conventional AAO was formed by two-step DCA on high-purity (≥ 99.99%) aluminum (Al) foil at a low temperature of 0~10°C.

In this communication, the low-purity Al was used to perform one-step AAO growth at room temperature using Hybrid Pulse Anodization (HPA) method. After fabricating the AAO template, scanning electron microscope and ImageJ software were used to analyze pore structures. Furthermore, we propose an emerging method to examine the humidity effect on the property of the nanoporous AAO. When the relative humidity exceeds a certain value, the AAO would change color, and the discoloration can be easily observed by naked eyes.

Citation: Chung CK, Ku CA. Effect of Humidity on Nanoporous Anodic Alumina Oxide (AAO). World J Nanosci Nanotech. 2018; 1(1): 1003.

Publisher Name: Medtext Publications LLC

Manuscript compiled: December 18th, 2018

***Corresponding author:** Chung CK, Department of Mechanical Engineering, National Cheng Kung University, Tainan 701, Taiwan, Tel: 886-6-2757575 ext. 62111; Fax: 886-6-2352973; E-mail: ckchung@mail.ncku.edu.tw

Experimental Procedure

The low-purity aluminum foil was used for one-step anodization. It was cut into pieces of 2.5 cm × 2.5 cm in size and then electro polished in a mixture of $HClO_4$ and ethanol (1:2 in volumetric ratio) at 20 V for 5 minutes at 0°C. The one-step anodization was performed in 0.3 M oxalic acid by HPA at 25°C for 5 minutes. The voltage of 40 V was applied in the HPA positive pulse, while the negative one was fixed at -2 V for negative pulse. The period of a hybrid pulse was 10 s (5 s: 5 s). Also, another specimen was prepared in the same manner as in the previous process. After anodization, the specimen was immersed in 5 wt% phosphoric acid at 35°C for 10 min to enlarge the pore diameter. To observe the change of surface color of AAO at different humidity, the above two specimens were coated with platinum of about 6 nm. Then place the two specimens in a chamber with controlled humidity and observe the color change at the humidity of 23%, 42%, 60%, and 72%.

Results and Discussion

Figure 1 (a) and (b) show the schematic diagram of HPA method, and the corresponding measured current-time diagram during reaction, respectively. The anodization was performed in 0.3 M oxalic acid by HPA (V_+=40 V, V_-=-2 V, t_+=5 s, t_-=5 s) at 25°C for 5 minutes.

There is negligible negative current observed in the period of small negative voltage [8,9]. The negative voltage applied to manufacture the AAO by pulse voltage can suppress the Joule's heat during the reaction, avoiding the dissolution due to excessive heat, so that the reaction temperature could raise to room temperature.

Figures 2 (a) shows the SEM micrograph after anodization. From ImageJ analyzing, the average pore Diameter (D_p) is 19 nm, the interpore Distance (D_{int}) is 72.5 nm and the porosity is 4%. Figure 2 (b) shows the histogram of the pores number per μm² area *vs.* corresponding pore diameter and the converted line graph. It is noted that the D_p of the specimen after etching is 42.6 nm, the D_{int} is 75.8 nm, and the porosity is 23%.

Figure 3 shows the discoloration of two specimens under different humidity conditions. Among them, the specimen on right side was pore widened by phosphoric acid, and the left one wasn't. In Figure 3 (a) and (b), the specimens are green and red at the humidity of 23% and 42%. When the humidity reaches 60% (Figure 3 (c)), there is a little color change, but still not obvious. When the humidity is 72% (Figure 3 (d)), the left specimen could clearly be seen the red and green colors, and the right one changed more, from the original purple to green.

When the humidity is low, the non-etched specimen has smaller pores, low porosity, and a small portion of the air, so the average refractive coefficient is high. In comparison, the pores of the etched AAO are larger, and the porosity is high. So, the air accounts for a large part, and the average refractive coefficient is low. Therefore, the scene color wavelength of the purple specimen is lower than that of the green one. The reason why the specimens would change color is because of nanoporous structure in AAO. The water vapor may enter the nanopores. The refractive coefficient of air is 1.0, and of water vapor is 1.33, which is larger than air. Therefore, when the relative humidity rises, the water vapor occupies more and more part of the air in the pores, and the average refractive coefficient becomes larger and larger, which causes the red-shift phenomenon and thus see the color change. The discoloration of the AAO is easy to observe. Such characteristics can be applied to the detection of liquid substances of different refractive coefficient, and has the prospect of developing a photochemical sensor. Also, this method can also control the color of AAO by changing the average refractive coefficient, which is helpful for future research on color-changing application.

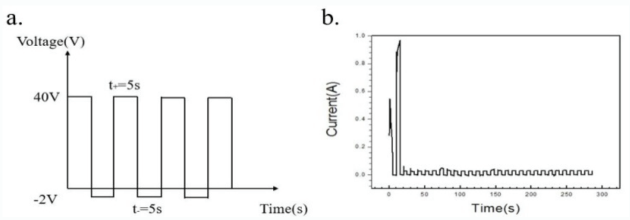

Figure 1: (a) The schematic diagram of Hybrid Pulse Anodization (HPA) method and (b) The corresponding measured current-time diagram.

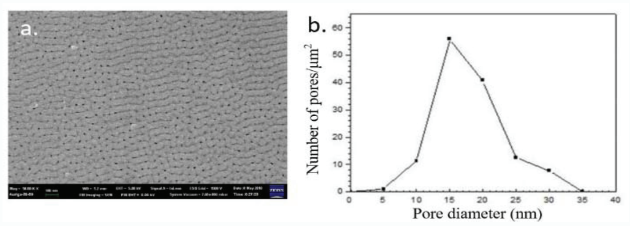

Figure 2: (a) The SEM image after anodization and (b) The histogram of the pores number per μm2 area vs. corresponding pore diameter and the converted line graph.

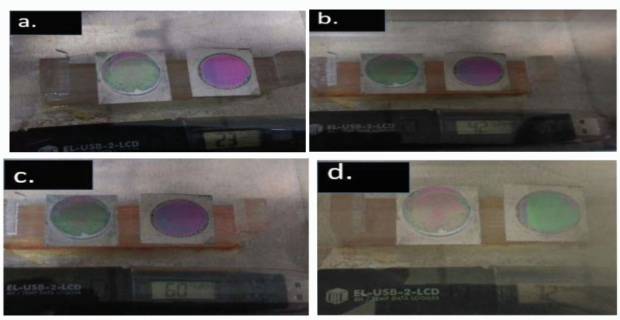

Figure 3: The specimens are at relative humidity (a) 23% (b) 42% (c) 60% (d) 72%. The discoloration from (c) (green and purple) to (d) (red and green) is obvious.

Conclusion

We have successfully demonstrated the HPA method for fabricating AAO at room temperature. The structure was analyzed and compared the difference of surface property of humidity effect on the AAO without and with the phosphoric acid etching. The discoloration of AAO by changing the environment humidity can be observed due to the refractive index change. The color will be red-shifted when the humidity is high, and the color change is clear, and visible to the naked eyes. This phenomenon can be used in the color-changing application for optical and photochemical sensors in the future AAO application.

References

1. Masuda H, Fukuda K. Ordered metal nanohole arrays made by a two-step replication of honeycomb structures of anodic alumina. Science. 1995;268:1466-8.
2. Masuda H, Hasegwa F, Ono SJ. Self-Ordering of Cell Arrangement of Anodic Porous Alumina Formed in Sulfuric Acid Solution. Electrochem Soc. 1997;144(5):L127-30.
3. Li AP, Muller F, Birner A, Nielsch K, Gosele U. Hexagonal pore arrays with a 50–420 nm interpore distance formed by self-organization in anodic alumina. J Appl Phys. 1998;84(11):6023-6.
4. Masuda H, Yada K, Osaka A. Self-Ordering of Cell Configuration of Anodic Porous Alumina with Large-Size Pores in Phosphoric Acid Solution. Jpn J Appl Phys. 1998;37(11)L1340-2.
5. Shelimov KB, Davydov DN, Moskovits M. Template-grown high-density nanocapacitor arrays. Appl Phys Lett. 2000;77:1722.
6. Nahar PK. Study of the performance degradation of thin film aluminum oxide sensor at high humidity. Sens Actuators B Chem. 2000;63(1-2):49-54.
7. Zhang Z, Shimizu T, Senz S, Gosele U. Ordered High-Density Si [100] Nanowire Arrays Epitaxially Grown by Bottom Imprint Method. Adv Mater. 2009;21(27):2824-8.
8. Chung CK, Zhou RX, Liu TY, Chang WT. Hybrid pulse anodization for the fabrication of porous anodic alumina films from commercial purity (99%) aluminum at room temperature. Nanotechnol. 2009;20:5.
9. Chung CK, Liao MW, Khor OK, Chang HC. Enhancement of pore size distribution in one-step hybrid pulse anodization of aluminum thin films sputtered on Si substrates. Thin Solid Films. 2013;544:374-9.