

Self-Ordering of Anodic Porous Alumina Induced by High Electric Field Strength

Sachiko Ono, Nobuyuki Kato, Makiko Saito, and Hidetaka Asoh

Department of Applied Chemistry, Kogakuin University, 1-24-2 Nishi-shinjuku, Shinjuku-ku, Tokyo 163-8677, Japan

Anodic porous alumina film, a typical self-ordered nanohole material formed by anodizing aluminum in an appropriate acidic solution, is a promising candidate for starting materials of nanofabrication of various devices. Except for the pretexturing methods for an aluminum substrate such as an imprinting process, highly ordered self-organizing porous alumina could be obtained only in three types of electrolyte at individually specified self-ordering voltages, i.e., sulfuric acid at 25V, oxalic acid at 40V and phosphoric acid at 195V, giving 63nm, 100nm and 500nm pore intervals. To widen the applications of anodic porous alumina, the fabrication of ordered porous alumina with an arbitrary pore interval is required.

Therefore, we have investigated self-ordering behavior of anodic porous alumina formed in sulfuric acid, oxalic acid and phosphoric acid solutions with focusing on the effect of pore diameter to cell diameter ratio, which is controlled by the electric field strength at the film growth [1]. The homogeneity of cell size was improved with increasing formation voltage accompanied by the exponential increase in current density. The maximum anodizing voltage for proceeding uniform oxide growth while avoiding extremely high current accompanied by gas evolution was identical with the previously established self-ordering voltage. With the increase in formation voltage up to the self-ordering voltage, the ratio of pore diameter to cell diameter $d_{\text{pore}}/d_{\text{cell}}$ lowered and converged to approximately 0.3 regardless of the electrolyte type. Moreover, domains of highly self-ordered pore arrays were found in the film formed during burning, where extremely high current was locally concentrated. This suggests that the condition inducing film growth under high current density, i.e., high electric field strength is the key controlling factor of self-ordering.

To confirm this mechanism, the film formed by burning in 0.2 mol dm⁻³ phosphoric acid solution at 0°C-5°C was examined. Figure 3(a) shows an SEM image of a burnt area indicating the protrusion of thickened anodic film. The protrusion is divided into three regions: (A) center, (B) intermediate and (C) the outer. Because the current density seems to be higher at the center, the regularity of cell arrangement could be further improved. In addition, barrier layer thickness as well as cell size of the center of the burnt film is significantly thinner than that of the standard film. Thus, it is verified that the high electric field strength E at the barrier layer is a strong controlling factor of the self-ordering. The cells of the film grown under the high field must be pressed each other, so that self-ordering could be attained (Fig.2).

Based on the above mechanism, new self-ordering films formed in malonic acid and citric acid could be obtained [2]. Further, variation of self-ordering voltage in phosphoric acid was attempted. The relations between final current density after 60min anodizing and formation voltage with the change in concentration of phosphoric acid electrolyte were shown in Fig.3. As described above, self-ordering occurs at the highest current density anodizing just under the burning voltage. The critical

voltage for self-ordering could reduce by increasing the electrolyte concentration. The ordering indexes, namely, the fraction of regular hexagonal cells which are neighboring to six cells, of the films formed at 160V and 177V were the similar level to that of well established condition of 0.2 mol dm⁻³ phosphoric acid at 195V.

Therefore, it is concluded that self-ordering of arbitrary pore intervals by using adequate electrolytes and conditions is achievable for maintaining a high current condition, i.e., high electric field on the entire specimen area, while avoiding extremely high current leading to burning or electric breakdown.

[1] S. Ono, K. Takeda, and N. Masuko, *Proc. The 2nd Int. Symp. on Aluminum Surf. Sci. and Tech.*, p.398 (2000).

[2] M. Saito, H. Muto, H. Asoh and S. Ono, 204th Meeting of the Electrochem. Soc., (Orlando, 2003) Abstracts No.30

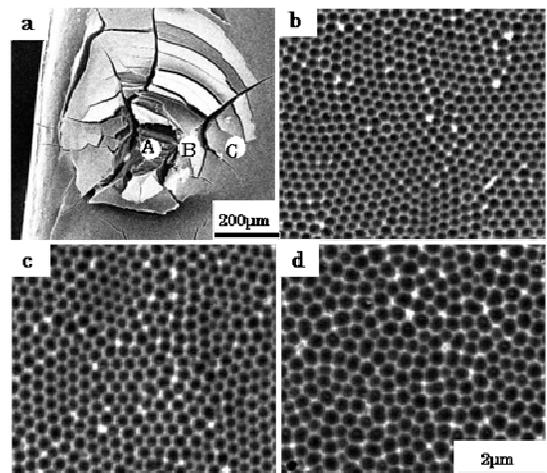


Fig.1 (a) SEM image of a burnt film. (A) center, (B) intermediate and (C) the outer regions are corresponding to Figs. b, c and d.

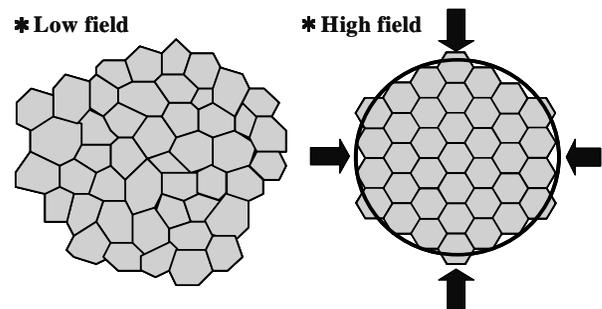


Fig.2 Schematic representation of self-ordering.

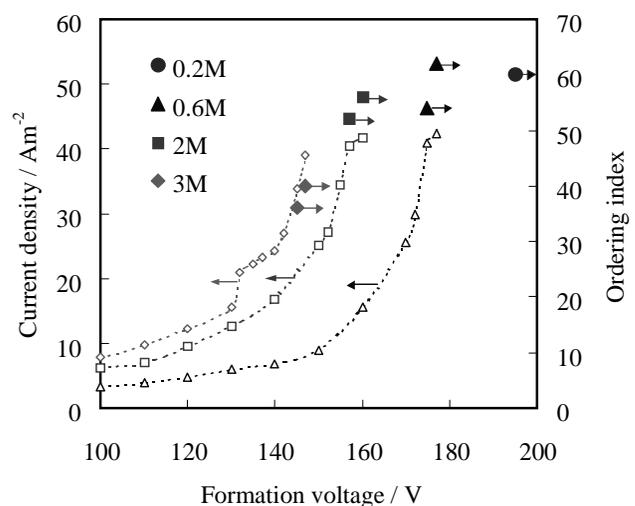


Fig.3 Variation of self-ordering voltage by changing concentration of phosphoric acid.