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To cite this article: Yudong Lv 2017 *IOP Conf. Ser.: Earth Environ. Sci.* **100** 012022

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Research progress in formation mechanism of anodizing aluminum oxide

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Abstract. The self-ordering porous anodizing aluminum oxide (AAO) has attracted much attention because of its potential value of application. Valve metals (Al, Ti, Zr etc.) anodic studies have been conducted for more than 80 years, but the mechanism of the formation of hexagonal prismatic cell structure has so far been different. In this paper, the research results of AAO film formation mechanism are reviewed, and the growth models of several AAO films are summarized, including the field-assisted dissolution (FAD), the viscous flow model, the critical current density effect model, the bulk expansion stress model and the steady-state pore growth model and so on. It analyzed the principle of each model and its rationality. This paper will be of great help to reveal the nature of pore formation and self-ordering, and with the hope that through the study of AAO film formation mechanism, the specific effects of various oxidation parameters on AAO film morphology can be obtained.

1. Introduction

At the end of the 20th century, with the development of nanotechnology, the ordered porous nanostructures of anodic aluminum oxide films have attracted the attention of researchers both at home and abroad. The use of porous aluminum oxide as a template for the preparation of low-dimensional optical, electrical, magnetic nano-materials, has shown great performance and application prospects [1-3].

Anodizing aluminum oxide (AAO) template is a high purity aluminum sheet obtained by removing grease, electrochemical polishing, anodizing, secondary anodizing, stripping, and reaming. The membrane surface has hexagonal holes, with uniform distribution, coherent pore size and good orientation. The porosity is generally $(1 \sim 1.2) \times 10^{11}/\text{cm}^2$, with a pore size of 4 ~ 200 nm, and a thickness of 10 ~ 100 μm . The membrane channels are parallel to each other and perpendicular to the aluminum matrix, and the alumina film faces a clear hexagonal grid, as shown in Figure 1. The membrane parameters of the porous alumina film, such as pore size, pore pitch, film thickness, etc., can be adjusted by changing anodic oxidation process parameters and afterwards reaming process, for instance, the electrolyte type, concentration, temperature, oxidation time and voltage, so that the material can make a variety of morphological structure when utilizing the aluminum template for artificial system assembly [4,5].



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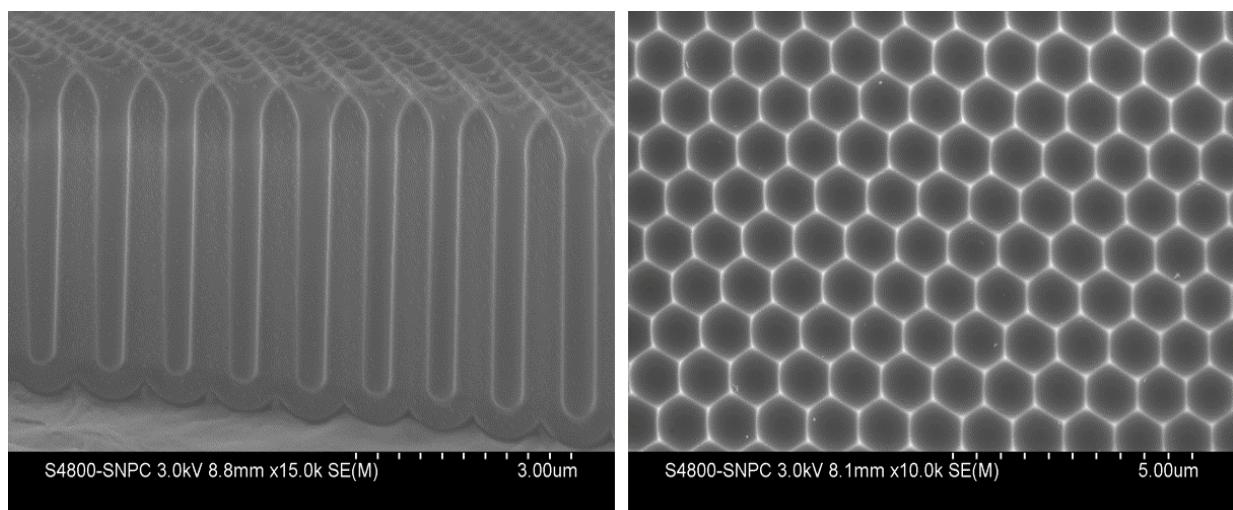
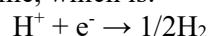


Figure 1. Side and bottom morphology of AAO

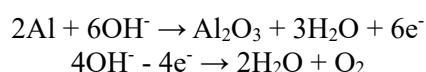
2. Principle of Anodization

Anodization is the process of forming an oxide film on the surface of the metal by electrolysis. In the case of aluminum, place high purity aluminum in a suitable electrolyte as an anode, and graphite as a cathode, with a specific operating condition and an applied voltage, the oxide film will emerge on the surface of aluminum.

After getting the power on, the reduction reaction will happen under the action of current on the cathode, releasing hydrogen at the same time, which is:



Main reactions on anode are:



The current during the formation of the oxide film includes the ionic current and the electron current. Wherein the formation of the oxide is carried out by an ion current. The ion conductances are different in strong electric field and in weak electric field. In the strong electric field, the ions play a decisive role in the direction of the electric field. In the weak electric field, the diffusion factor is enhanced, so the motion of the ion in the direction of the reverse electric field needs to be considered. When it comes to anodization, the field is a high-intensity electric field with a strength of 10^7V/cm , hence it is ion transport under strong electric field. The electric current under the strong electric field can be expressed as empirical formula [6]

$$i = A \exp(BE)$$

Where the 'i' represents the current density, 'E' refers to the electric field strength, while 'A' and 'B' are the coefficient.

3. Structure Model of AAO

As early as 1932, Setoh and Miyata [7] have pointed out that the anodic oxide film consists of two layers: a thin barrier layer directly attached to the metal and a very porous outer layer. The thickness of the barrier layer is less than 0.5-2% of the total thickness of the film. It is a thin and dense oxide with no pores and only conducts at very thin or irregular locations. While the outer layer is microporous, with a columnar structure. The pores extend through the membrane to the vicinity of the interface between the oxide and the metal, which is the barrier layer. A hole and the surrounding area form a "unit cell", which forms a tightly packed structure. The thickness of the barrier layer depends on the voltage used for the anodic oxidation as a function of voltage, approximately equal to 1.4 nm/V (referred to unit thickness or specific thickness). The structure of the membrane as a whole seems to be like honeycomb, since the pore size is as small as the size of nanometer level, while the microporous generally disorderly and

unsystematic.

In 1953, the American scholar Kelle et al. proposed the most authoritative Kelle model [8] based on the electron micrograph of alumina, which he considered to consist of many hexagonal cylindrical oxide units, and each of which has a star-shaped hole in the middle. The size of the hole is related to the type of electrolyte, yet has nothing to do with the voltage; the thickness of the barrier layer and the electrolysis voltage, and the type of electrolyte has nothing to do. The model indicates that the unit cell of the anodic oxide film is inhomogeneous, and the interior of the unit cell is composed of Al_2O_3 with high active chemical activity, while the outside is composed of a stable $\gamma\text{-Al}_2\text{O}_3$.

In the 1970s, O'Sullivan and Wood amended the Kelle model. From the view of countless observations, they found out that the holes on anodic oxide film was similar to circular and star-shaped holes rarely encountered. Based on the above understanding, they proposed a new alumina membrane structure model, which is currently dominant.

In the 1990s, Hideki, Masuda et al. proposed structural features of the self-organized arrangement of porous membranes in sulfuric acid electrolytes. At a suitable voltage, the porous membrane can achieve the ideal hexagonal pore structure after prolonged oxidation.

4. The Formation Mechanism of Several Different AAO Films

4.1. The Joule Heat Model

As early as the 1950s, Kelle et al. have discussed the growth mechanism of porous alumina. They believed that the anodic oxidation initially formed a layer of uniform distributed and dense barrier. When dissolved at a certain point, the thickness of the oxide layer would shrink, where the current reach out there to try to repair the decrease in the thickness of the oxide layer here, resulting in an increase in the local temperature, so that the dissolution rate of alumina becomes faster and eventually leads to the formation of pores. This is the original 'Joule Heat' model. In fact, the Joule heat generated during the anodic oxidation does not play a major role in the reaction, it is not difficult to understand, because any changes in the temperature conditions of the electrolyte will make the alumina parameters of the important changes. At the same time, the uncertainty of the dissolution of a certain point in the model also limits the development of this model [9].

4.2. The Field-Assisted Dissolution (FAD)

Wood et al. from University of Manchester put forward the more popular electric field assisted dissolution model combined with a variety of research methods. This model suggests that the anodic oxidation process of aluminum includes three major stages: the formation of the barrier layer, the dissolution of the barrier layer and the stable growth of the porous layer. When the voltage is applied to both ends of the electrode, the circuit resistance is very low while the current is high, a layer of solid dense amorphous alumina film is formed on the anode aluminum film, which is known as the barrier layer. Since the alumina just generated from the solution is easily dissolved in the acid solution, some of the alumina is chemically dissolved. When the barrier layer reaches to a certain critical value, the electrolyte begins to dissolve the initial pore core at the point where the surface of the barrier layer is regularly arranged. The formation of the core will cause the original uniform distribution of the electric field concentrated in the bottom of the hole area, so that the bottom of the hole at the bottom of the dissolution rate greatly enhanced. At the same time, as local electric field at the bottom of the hole enhances, the current increases, resulting in local overheating, and accelerating the dissolution process. While the solution is happening, the barrier layer and the Al film interface began to form a new barrier layer. At that time, under the action of the electric field, Al^{3+} migrates outward, and O^{2-} or OH^- migrates inward, thus forming a barrier layer, as shown in Figure 2. Finally, the dissolution rate and growth rate of the barrier layer will reach to a dynamic equilibrium and enter the stable growth stage of the porous layer.

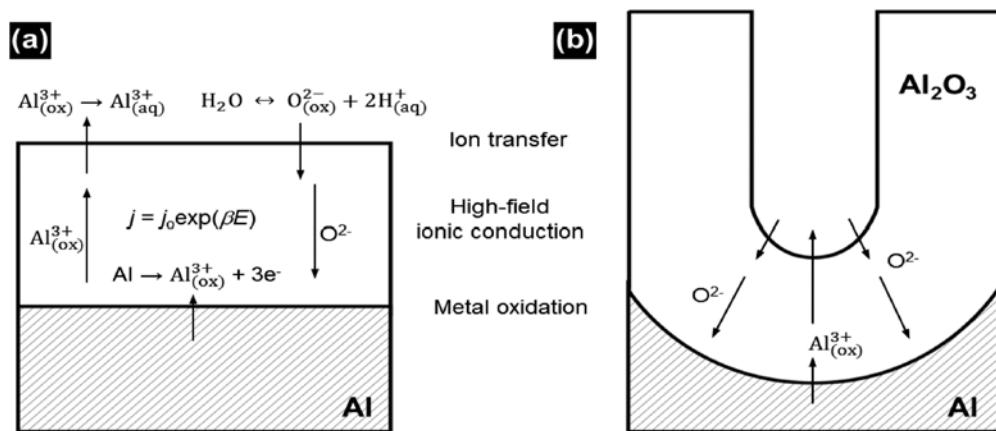


Figure 2.Schematic diagrams showing elementary interfacial reactions for (a) barrier-type and (b) porous-type anodic oxide [10]

4.3. The Viscous Flow Model

Thompson et al. labeled oxide with radioisotope W by tracing atomic techniques [11], which enabled people to see the position of radioisotope W at different times, as shown in Figure 3. The distribution of W confirms that the pore walls of AAO are formed by the viscous flow of the barrier layer toward the cell walls. The results show that the long-term constant barrier layer is caused by the flow of oxide from the bottom of the hole to the pore wall. The driving force may be the compressive stress caused by the electric field, or the volume expansion of Al_2O_3 .

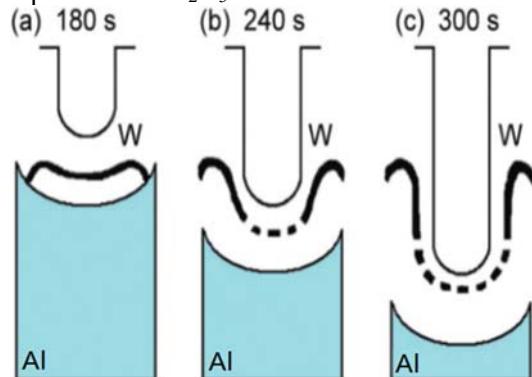


Figure 3. Viscous flow model

4.4. The Critical Current Density Effect Model

Xu Yuan et al. confirmed the leading role electric field plays on the hole development with ultra-thin slices combined with mathematical reasoning method. This model [12] suggests that the initial rise of the voltage-time curve is the initial growth period of the aluminum anodic oxide film, and its thickness is uniform. Then, due to various reasons (such as electrostress stress) on the outer surface of the oxide film began to form a small channel, the uniformity of channel generation and development of the electric field gradually disappear, penetration of the electric field between the channel is weak, yet the penetration of the electric field strength within the channel is increasing. As the penetration channel continues to extend inward, the electric field intensity is more concentrated in the channel. The electric field intensity at the front end of the penetrating channel is the largest, and so is the component of the lateral electric field at the front end of the penetrating channel, leading to the lateral expansion of the penetrating channel and the development of microporous embryos. In the process of microporous embryos to the final pore development process, it also has to go through the stages of hole developing competition, the expansion of the hole diameter, formation of the ball-shaped interface by the hole bottom membrane and the matrix and the final cavity to achieve stable development and other stages.

4.5. The Bulk Expansion Stress Model

In 1998, Muller et al. proposed a body expansion model (see Figure. 4). [13] This model is useful for explaining the ideal porous alumina film and the formation of hexagonal regular arrangement. This model suggests that, in the steady-state oxidation process, the volume of Al oxidized to Al_2O_3 is bigger than the one of equivalent Al, so that each hole in the process of each hole have a stress on the surrounding due to the volume expansion. Yet the self - organized growth of holes in hexagonal dense way make the energy of the system the lowest and the structure the most stable.

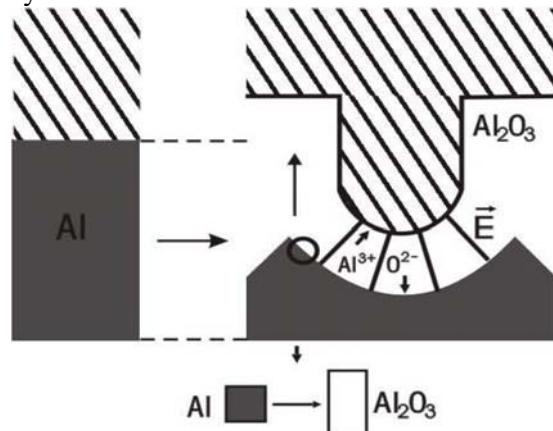


Figure 4. The cubical dilatation stress model of the self-organizing growth

4.6. The Steady-State Pore Growth Model

Parkhutik et al. proposed a steady-state pore growth mechanism model based on the observed current changes in the experiment, which suggests that the formation of pores is divided into four steps:

- (1) after the power is on, in the Al surface will form a oxide layer, whose thickness is determined by the voltage (1.4nm/V);
- (2) In some places in the oxide film, alumina dissolved, which leads to the formation of channels, so that oxygen ions can be transferred through the barrier layer and metal reaction, that is the hole nucleation process;
- (3) Some channels in the process of electrolysis will form the pore channels in the competition, which will become larger and deeper;
- (4) Steady-state pore formation.

In fact, the growth process of the pores is a process in which the oxide is formed on the metal surface and dissolved at the solution interface. The process of oxide dissolution is promoted by the electric field in the pores and the induction of hydrogen ions in the solution.

5. Conclusion

Nanomaterials have a series of new properties different from those of bulk materials, and they have wide application prospects in many fields. Anodic aluminum oxide film has a unique porous structure and stable chemical properties, which can be used as a template for the preparation of various nano-functional materials, and thus plays an important role in the preparation of nano-functional materials. In this paper, the anodic oxidation principle of porous anodic aluminum oxide film and the formation mechanism of anodic aluminum oxide film are reviewed. However, despite the large number of studies on porous anodic aluminum oxide films, there are only few touches on the intrinsic relationship between porous oxide films and compact oxide films. This is the blank spot for decades of porous membrane research. Therefore, future researchers should make a detailed perspective to explore this field, which will help to understand electrochemical reaction mechanism generated by AAO and the nature of self-ordering.

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