

An insight into the mechanism of ordered holes formation in porous alumina template

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Several theories have been postulated to describe the mechanism for the ordered holes array formation in electrolytic method for alumina template construction. We have proposed a new one for the same in this manuscript considering the simple coulombic forces of repulsion between the negative ions accumulated on to the initially formed barrier layer resulted in their minimal energy arrangement in circles and then in the hexagons which pulling out the Al ion through the initially formed barrier layer from Al foil due to the resultant electric field at their center. The pulled Al ion forms the alumina on the circumference of the hexagons disturbing its resulting electric field direction to facilitates the pulling of the Al ion from its displaced pointed place. The reason for the particular depth of holes has also been simulated theoretically.

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1. Introduction

Numerous methods have been developed for the synthesis of nanosized materials. Among them, template synthetic method, using a highly ordered porous alumina membrane, has attracted a good deal of research interest. The structure of porous alumina membrane has been known as early as 1932 [1]. At present, ordered porous alumina membrane is widely used to prepare nanosized materials [2-12] due to its remarkable hardness, uniform pore size, high pore density together with its potentially low cost and relative ease of their preparation. Nowadays, porous alumina membrane is a key material for the fabrication of devices in nanoscale, such as electronic and photoelectronic devices, materials science, magnetics, optics and for its applications to micro and ultrafiltration.

Since a procedure to produce highly ordered nanohole arrays was established by Masuda and Fukuda [13], many researchers have tried to explain its mechanism. And also the kinetics of the growth of porous oxide on aluminum under anodic bias in various electrolytes has been studied extensively over the last five decades [14, 15]. Many models have been presented to describe the self regulating pore geometry. O' Sullivan and Wood [16] presented a model based on the electric field distribution at the pore tip. This model is able to explain why pore grow at all and why there size distribution is quite narrow. There are also other models [17, 18, 19] which gives microscopic explanation for the dependence of pore diameter and pore distance on applied voltage and electrolyte composition.

The models based only on field distribution [16] was also proposed but it can not easily explain this behavior that highly regular polycrystalline pore structures occur only for a quite small processing window, whereas an amorphous pore structure can be obtained for a very wide

range of parameters without substantial change in morphology. Another approach for self-organized arrangement of neighboring pores in hexagonal arrays is based upon repulsive interaction between the pores [20].

The dependence of the structural properties on the anodization conditions have been investigated to gain more insight into the formation conditions of ordered pore arrays and to find a microscopic explanation of the repulsive forces [20].

The anodizing process of Al is independent of the restriction of the orientation of the crystal, because the main driving force in the formation of the channel in the anodic alumina is the electric field rather than the crystal direction. This allows the fabrication of the initiation point by a mechanical deformation process and continuous growth of the ordered channels without being affected by crystal orientation [21].

Here we propose a model to describe the nucleation of self regulating pore growth for the formation of hexagonal arrangement of the porous alumina when an optimal anodizing voltage is applied.

2. Discussion

This model is based upon the minimum potential energy of the arrangement of the same type of charges over a plane surface. The proposed model also includes the concepts of the models based on electric field distribution at the tip of the pore [16] and the repulsive interaction between the pores in the hexagonal pattern [20].

Initially when the anodization starts, an aluminum oxide layer is formed on the surface of the aluminum foil and then porous alumina over this initially formed barrier layer nucleates. Thus the structure consists of a thin (also

called the barrier layer), inner oxide layer adjacent to the substrate metal and a thick porous outer oxide layer. The continuing anodization reaction takes place from the aluminum substrate surface, i.e. from the aluminum-barrier layer interface.

Because the structure consists of dual phase aluminum oxide of a thin, oxide layer (also called the barrier layer) adjacent to the substrate metal and a thick porous outer oxide layer, the proposed model for self regulating nanoporous alumina film formation process, has three points of interest:

- (1) Initially a monolayer of same thickness which is referred as "native oxide" or a barrier layer over the surface of the aluminum is produced.
- (2) Over the electrolyte/barrier layer interface negative charge ions accumulate, which come from the electrolyte and rearrange themselves in the circles and then deform to hexagons to meet the closed packed structure.
- (3) Hexagonally arrangement of negative charge ions over electrolyte/barrier layer interface. They attractively interact with the positive charge ions of the substrate i.e. Al ions beneath the barrier layer. The Al ions, which are in attractive interaction with the hexagons of negative charge above barrier layer are pulled up to the same planes as that of the negatively charged hexagons. They recombine to the negative charge ions and hexagonal walls grow.

As it is well documented that the nature of the anodizing process is based upon the electrochemical principle, i.e. when a current is passed through an electrolyte in which aluminum is employed, the anions from the electrolyte migrate to the anode. The anion is then discharged with the loss of one or more electrons at the anode. In an aqueous solution the anion consists in part of oxygen, which is absorbed by the aluminum surface. By absorption via chemisorptions proceeds, the surface is reconstructed, forming a contiguous film as Al_2O_3 . Thus a monolayer (barrier layer) of aluminum oxide is formed. The formation of the barrier layer structure is schematically shown in Fig. 1.

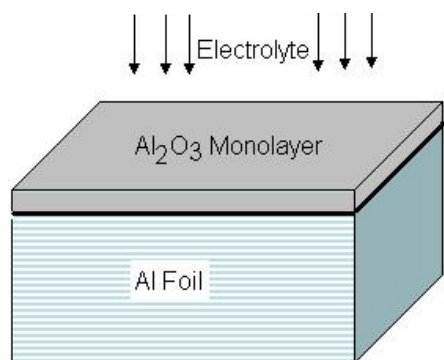


Fig. 1. General view of Al substrate with formed barrier layer over it.

After the formation of monolayer or barrier layer of alumina, the negative ions which come from the electrolyte strike to the surface of barrier layer towards the electrolyte, since in anodization process a voltage difference is applied between the aluminum substrate and the cathode. The voltage causes motion to the negative charges in the electrolyte, and the negative ions move towards the anode but as the barrier layer is already created over the anode, this barrier layer prevents the motion of these negative charges at barrier layer/electrolyte interface and the negative charges accumulate over it. The barrier layer works as a dielectric between the aluminum anode and the electrolyte. There is no transition of the ions through the barrier layer; only the accumulation of the negative charges from the electrolyte, over barrier layer/ electrolyte interface takes place.

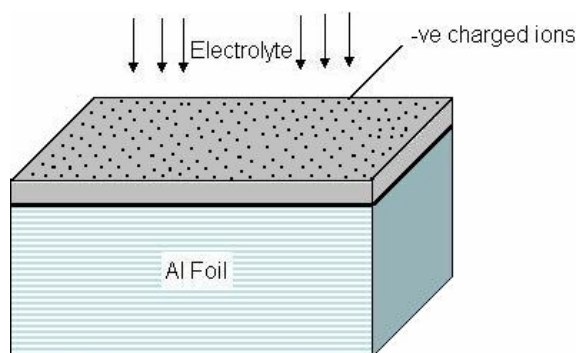


Fig. 2. Random arrangement of negative charge ions on the barrier layer /electrolyte interface when their density is low.

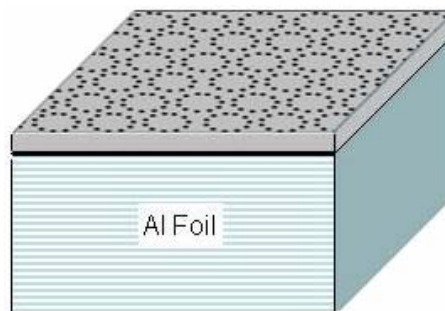


Fig. 3. Circular arrangement of negative charge ions on the barrier layer /electrolyte interface when their density increases.

Solution side surface (electrolyte/ barrier layer interface) of the barrier layer continuously receives negative ions from the solution. Initially these negative ions accumulate on this surface at random and distant positions. Since a constant voltage difference is applied between cathode and aluminum electrode, the density of the negative charge ions on the electrolyte/ barrier layer interface goes on increasing with the time as in Fig. 2. And during the increase of their density, their mutual separation this surface goes on decreasing with the time. But as all

the ions accumulating on the same surface are of same type i.e. negatively charged they start repelling to each other, because of the Coulombs repulsion between them, and their separation increases to the equilibrium separation. More precisely we can say that after formation of the barrier layer over the aluminum substrate, initially the density of the negatively charged ions on the electrolyte/ barrier layer interface remains small but with the passage of the time their density increases and their separation decreases, but the already existing ions on the surface does not allow the coming ion from the electrolyte to sit very close with themselves, because of Coulombs repulsion becomes effective for short distances and the ions arranges themselves in a manner so that the net force at each of the ion is minimum. With the passage of time the density of the negatively charged ions on the barrier layer/ electrolyte interface increases in an arranged manner. These negative ions arrange themselves in the form of circles Fig. 3 as the force experienced by each of the ion in this arrangement is found to be minimum.

The magnitude of force on a point charge on the circumference of the circle due to rest part of the circle is given by the relation

$$F = \frac{1}{4\pi\epsilon_0} \int_{\theta_1}^{\theta_2} \frac{q\rho dl}{s^2} \quad (1)$$

where q is a point charge on the circumference of the circle Fig.4 on which the force is to be calculated, $\rho = Q/2\pi r$ is charge density on the circumference of the circle assuming radius r and total charge Q .

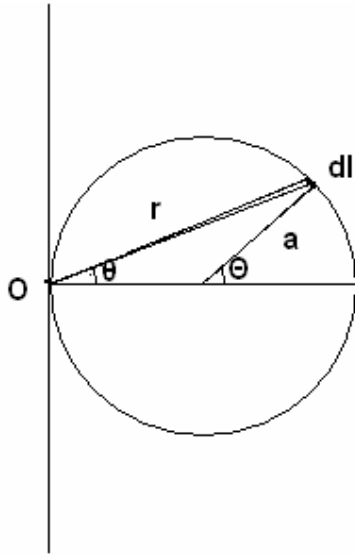


Fig. 4. Negative charges are configured as circles.

The general equation of the circle shown in Fig. 4 is given as

$$r = 2a\cos\theta$$

where r is distance of point charge at situated at O , from the elemental length dl of the charge distribution. From geometry $\Theta = 2\theta$, hence $l = 2a\theta$ or

$$dl = 2ad\theta$$

The above equation after simplification can be written as

$$F = k \int_0^{\pi} \frac{dl}{\cos^2\theta} \quad (2)$$

Where

$$k = \frac{q_1 Q}{32\pi^2 \epsilon_0 a^3} \quad (3)$$

From the equation (2) the value of force F comes out to be zero which shows that the resultant force on each point charge from the rest of the charges on the circumference of the circle is zero.

The circles of the negative charge ions formed due to Coulombs repulsion between the ions have their resultant force a vector perpendicular to the plane of the circles and passing through their centers. These circles further repel to each other to arrange themselves in the hexagonal form. And because of this the circular forms itself changes to hexagonal closed packed arrangement, which is most stable and minimum energy arrangement of the negatively charged ions Fig. 5.

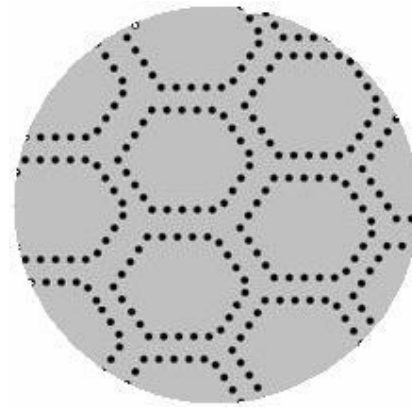


Fig. 5. Circle deformation to form hexagon due to coulomb's repulsion between similar charged ions of two different circles in neighborhood.

After the hexagonal arrangement of the negative ions on the electrolyte/ barrier layer interface the resultant vector of force, of these arrangements acts normally downwards through the barrier layer, towards the aluminum substrate because a positive voltage is applied to the aluminum substrate. So a net force acts on the Al ion in aluminum in the upward direction. Initially (instant of nucleation) this force is assumed to act on those Al ions which are normally down to the centers of the negative charge arrangements Fig. 6.

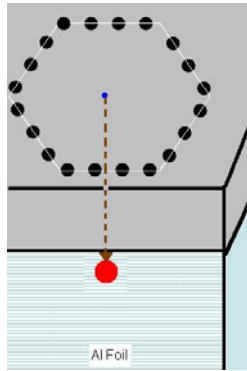


Fig. 6. Arrow from centre of hexagon to Al ion indicates the direction of resultant force vector of hexagon.

The situation can be considered as, similar to an attraction force which acts between the aluminum ion in the substrate and the centre of negative charge hexagons. Because of this force, the aluminum ions from the substrate are attracted towards the centers of the hexagons. Thus an aluminum ion from the substrate comes up to the barrier layer and reaches at the centre of the hexagonal arrangements at electrolyte/ barrier layer interface Fig. 7.

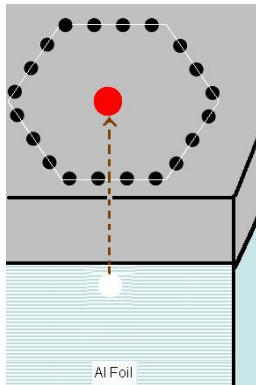


Fig. 7. Transport of Al ion from Al substrate to center of negatively charged hexagon.

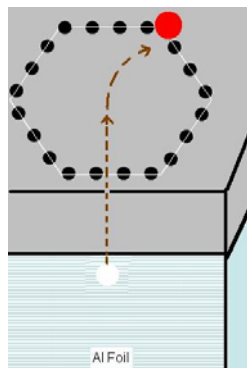


Fig. 8. Alumina formation at the circumference of the hexagon.

Because of this, deformation of the arrangement of the negative charges takes place, and now the negative ion coming from the electrolyte will occupy a different position. Also the direction of the resultant force vector of negative charges changes Fig. 9, in this situation the resultant force of the negative ions arrangement acts at the different position of the aluminum ion in the substrate, and pulls up the aluminum ion from the different position.

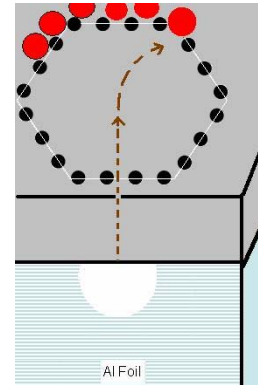


Fig. 9. Electric field direction changes and Al ions from different places transport to the hexagons and form the Alumina.

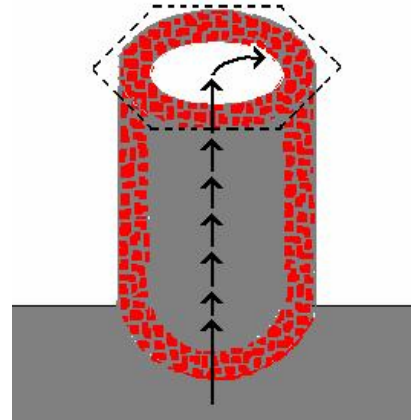


Fig. 10. Alumina hole formation due to the continuous pulling of aluminum ions from aluminum foil.

This pulled up ion of aluminum again recombines to the negative charge ion at the circumference in the negative charge arrangements. This procedure goes on and a wall of the alumina is formed as shown in Fig. 10.

3. Conclusions

Based on simple columbic repulsion forces between similarly charged particles, authors have tried to unravel the mechanism of ordered pore formation on alumina template formation in this paper, which is very important to fabricate with orderly arranged nano sized rods and wires by electrochemical method. Not only the reason why

the hexagonal pore array forms but also its growth was discussed.

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