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Synthesis and optical properties of alumina thin films with rainbow stripes structural colors

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Alumina thin films with rainbow striped structural colors have been fabricated by one-step electrochemical oxidation of Al foil. The relationships of the colors and density of rainbow stripes with the oxidation voltage and time in oxalic acid solution, as well as the angle of the cathode and anode are discussed. A theoretical study of the changes in colors and density of rainbow stripes is consistent with the experimental results. The test results of polarization show that reflected interference light from the top and bottom surfaces of alumina thin films are linearly polarized. These films were synthesized using a simplified process and has potential application in optical display technology, polarizers, analyzers, decorations and anti-counterfeiting.

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1. Introduction

In 1953, Keller [1] first introduced the honeycomb structure of porous alumina thin films, and pointed out that porous alumina thin films are composed of porous layers and barrier layers. In 1995, Masuda et al. [2] reported the preparation of highly ordered porous alumina thin films by applying the anodic oxidation technique for the first time. Since then, with further studies of research in this field, the preparation technique of porous alumina thin films is being constantly improved. This highly ordered porous alumina thin film has potential application in many fields, such as electronics, optics, and magnetics.

Highly ordered porous alumina thin films are widely used as a template to develop one-dimensional nanostructures, such as nanotubes and nanowires, based on its function of domain limitation. Until now, few studies exist on the optical properties of the film. Since alumina thin films are transparent within the range of visible light, Wang reported [3] that the synthesis of a massive photonic crystal of alumina thin film had been realized through a simple electrochemical method. Simultaneously, the control of the sample’s reflected wavelength was also realized by chemical etching. Great attention has been directed to this research internationally, and many research groups have developed intense interests in the optical properties of the alumina thin film. In 1969, Diggle et al. [4] reported that within the range of visible light, alumina thin films show bright color when their thickness is less than 1μm due to the interference of light. In 2007, Wang et al. [5] reported the successfully preparation of an alumina thin film with comparatively high color saturation by depositing carbon nanotubes in the alumina pores with a CVD technique. Shortly after that, in 2010, Zhao et al [6] succeeded subtle control of the colors of alumina thin films by depositing carbon nanotubes. In 2011, Sun et al. [7-9] prepared alumina thin films with iridescence, using a multiple oxidation method.

Currently, the multi-step oxidation technique is the most frequently applied method in the production of rainbow-shaped structure alumina thin films with different microstructures. This technique is complex and has high cost, and the experimental conditions are difficult to control. This paper reports a new method to produce alumina thin films with rainbow striped structural color and gradient thickness using a one-step anode oxidation technique. The paper also discusses, in theory, the relationship between the color and density of rainbow stripes and the experimental conditions. This method presents a simple production of alumina thin films with rainbow stripes and reduces its cost; more than that, the experiment process is controllable. Future research for improving this technique is significant for its implementation in numerous applied fields.

In the process of producing alumina thin films by applying the electrochemical oxidation method, a carbon rod is usually used as the cathode and high purity aluminum foil as the anode. The cathode and anode should be kept in a parallel position, and the oxidation process should be done in an electrolyte of a certain concentration. The whole process of electrolysis is divided into two stages, namely, the stable stage and the unstable stage, according to the changing current density. Patermarakis et al. [10] suggest that, to obtain the comparatively thicker Al_2O_3 barrier layer, the thickness of the film should be proportional to the product when electrolytic current is multiplied by the time of electrolysis, the thickness of the thin film is in proportion to the product when electrolytic current multiplies the time of electrolysis:

$$h = kj\mathrm{t} \tag{1}$$

Where, h is the thickness of Al_2O_3 layer; k is the electrolytic constant; j is the current density; and t is the time of electrolysis. For the super-thin alumina films, the time of electrolysis is usually very short, the reaction is taking place in the unstable area, and the change of electrolytic current is fairly considerable. Thus, the thickness of thin film is proportion to the integral of electrolytic current multiplied by the time of electrolysis:

$$h = k\int jdt \tag{2}$$

In conditions where the cathode and anode are parallel, and the integral of current density to the time of electrolysis in different positions of the boundary between electrolyte and aluminum foil are equal, the thickness of the alumina thin film is also equal. It can be inferred that if the electrolysis process is not stable, the cathode and the anode are not parallel. However, introduction of an angle, θ, between them, as shown in Fig. 1, promotes differences in current densities in different positions of the boundary. The following is the theoretical analysis.

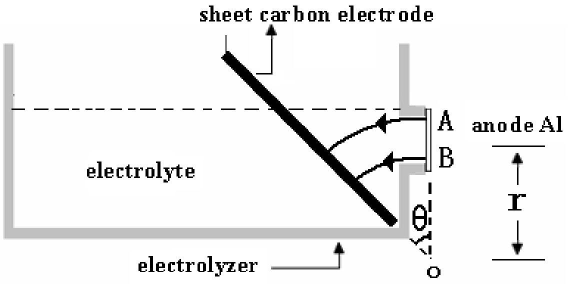

Fig. 1. The schematic diagram for electrochemical reaction of alumina thin films

At the beginning of oxidation, the barrier layer is yet to form on the surface of aluminum foil, when all of the oxidation voltage is put on the electrolyte. While the barrier layer forms on the surface of aluminum foil, the current density decreases rapidly. From this, we obtain that the current densities in the different positions of the boundary between electrolyte and aluminum foil:

$$j = \sigma \bullet E \tag{3}$$

where, σ is the conductivity; and, E is the field strength. We need to consider the certain angle between the cathode and anode, which is presented in the following equation:

$$E = \frac{U^{/}}{r \bullet \theta} = \frac{k^{/}U}{r \bullet \theta} \tag{4}$$

where, $U^{/}$ is the voltage across the electrolyte; U is the voltage across the cathode and anode, $k^{/}$ is the ration of $U^{/}$ and U; r is the distance from a random point on aluminum foil to the center of the circle O; and θ is the angle between the cathode and anode (radian), as illustrated by Fig. 1. If Equation (3) and (4) are put into (2), the following formula can be achieved:

$$h = \frac{kU\sigma}{r \bullet \theta}\int k^{/}dt \tag{5}$$

According to the electromagnetic principle, the boundary between the electrolyte and barrier layer is an equipotential surface. Thus, in an unstable oxidation process, if $\int k^{/}dt$ on the alumina thin film is equal everywhere at a certain time, and we let $\int k^{/}dt = C$, the formula for the thickness of alumina thin film in the unstable oxidation process could be achieved as:

$$h = kC\sigma\frac{U}{r \bullet \theta} \tag{6}$$

The formula above shows that, in the unstable oxidation process, when k, C, σ, U, θ keep constant, h is inversely proportional to r, that is to say, the thickness of thin film is increasing from end A to end B.

In the experiment, the stirring method was applied to maintain the uniformity of the electrolyte's temperature and ionic concentration. When k and σ are kept constant, the thickness of thin film from B to A varied with U, θ, r, and C. Theoretically speaking, the control of alumina thin film thickness from B to A could be realized by changing the oxidation voltage, U, the angle between cathode and the anode, θ, and the oxidation time. The reflected light on the top and bottom surfaces of thin film is used to produce equal thickness interference, and rainbow stripes with controllable colors and density are thus achieved. The following part presents the experimental proof of the theoretical hypothesis. This thesis discusses the relationship of the alumina thin film thickness with the changing experimental conditions at the formation stage of the micro-porous layer in the unstable electrolysis process. Fig. 2 shows the thickness of the alumina thin film at this stage of the micro-porous layer.

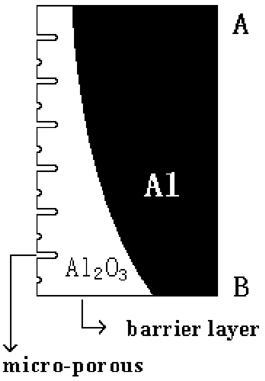

Fig. 2. The sketch diagram for thickness of alumina thin films

2. Experiments

The schematic diagram of the experimental device is shown in Fig. 1. A carbon sheet was used as the cathode and high purity Al foil as the anode, and a certain angle occurs between the two. Oxalic acid solution of 0.3mol/L is used as the electrolyte. The high purity Al foil (99.999%) was cut into round pieces with diameters of about 2 cm. After flattening, it was put into acetone solution for 30 min for ultrasonic cleaning, followed by another ultrasonic cleaning with ethanol for 30 min. Finally, the foil was washed repeatedly in deionized water. After drying in air, the foil was placed into a quartz tube furnace for a two-hour vacuum annealing at 400℃, and then cooled down to room temperature in a vacuum. After annealing, the foil was electropolished, where mixed solution of $HClO_4$ and ethanol (1:4 in volume) was used as the electropolishing solution. After polishing, the foil was placed in the electrolyzer, shown in Fig. 1 as the anode, then prepared for oxidation. A series of alumina thin films were produced, and when the oxidation voltage was varied, the angle between the cathode and anode and oxidation time.

The alumina thin films were characterized using field-emission scanning electron microscopy (FESEM, Hitachi S-4800) and by an optical digital camera (Canon-EOS 600D) with a rough black cloth as the background. All of the digital photographs were taken at viewing-angles of 20° with the normal direction of thin films. UV-Vis reflectance spectra were recorded on a Hitachi UV-3010 spectrophotometer equipped with an integrating sphere.

3. Results and discussion

Fig. 3 shows the digital photos of the alumina thin film prepared under the conditions of oxidation voltage of 50 V, cathode-anode angle of 45°, and oxidation times of 20, 25 and 30 s. In Fig. 3-(a), the color of the film changed from light green to light blue from bottom to top. It is speculated that this is caused by the thickness of the alumina film decreasing from B to A. Similar changes can be seen in Fig. 3-(b) and (c). Comparing Fig. 3-(a) and (b) with (c), it can be seen that as the oxidation time increased, the color on side B of the alumina film changed from light green to dark green and then to red, and the color on side A changed from light blue to dark blue and then yellow. It can be inferred from the above theoretical analysis that the alumina film thickened as the oxidation time increased, resulting in changes in the structural colors in the same position.

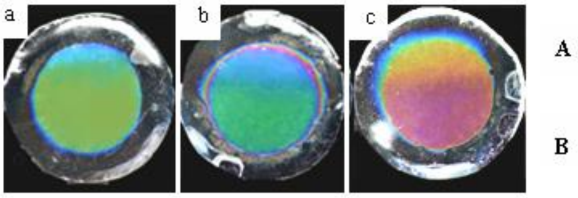

Fig. 3. The digital photographs of the alumina thin films (oxidation voltage of 50 V, the angle between the cathode and anode of 45°), oxidation time: (a) 20 s, (b) 25 s, and (c) 30 s

To prove the above speculation, Fig. 4 displays the electron micrographs of different positions of the alumina film in Fig. 3-(c). Fig. 4-(a) and (b) are the surface and cross-section pictures of side A: Fig. 4 (c) and (d) are the surface and cross-section pictures of side B, respectively. As can be seen from the micrographs, the surfaces have similar structures, and the average diameter of the micropores is about 9nm, indicating the beginning formation of pores in the oxidation process. As viewed in the cross-sectional micrographs, the test point on side A of alumina thin film is around 94 nm in thickness, and the test point on side B is around 120 nm. This corresponds to the above speculation that the thickness of the alumina film decreased from B to A. We calculated the average effective refractive index of side A and side B based on the Maxwell-Gamett theory [11], and obtained 1.65 for both sides. Table 1 shows the calculated reflected light interference wavelengths on test points of side A and side B according to Bragg’s equation (considering the half wave loss). The reflected wavelength on side B is approximately 744 nm, which belongs to the red light region, and the reflected wavelength on side A is approximately 583 nm, which belongs to the yellow light region. The results are in good agreement with what is shown in the digital photo in Fig. 3(c). This is also consistent with reflectance measurements for the film in Fig. 5, where the two reflection peaks with maximum reflectance are approximately 764 and 586 nm, which belong to the red color and the yellow color regions, respectively. The experimental result is very close to the calculated results based on Bragg’s equation. This further confirms that the thickness of the alumina film decreased from end B to end A.

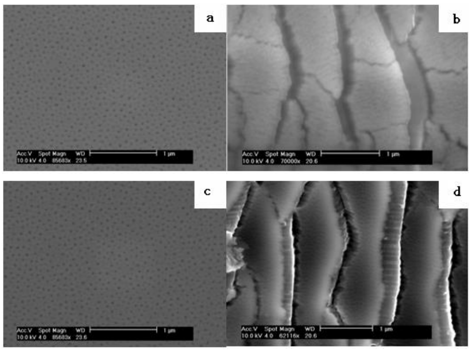

Fig. 4. The SEM images of different locations in the alumina thin films. (Oxidation voltage is 50 V; the angle between the cathode and anode is 45°; and oxidation time is 30 s)

Table 1. Calculated wavelength of the reflected interference light

Section	Index of refraction	Thickness of films	Wavelengths of the reflected light	Interference level
Side A	1.65	94 nm	583 nm	m=1
Side B	1.65	120 nm	744 nm	m=1

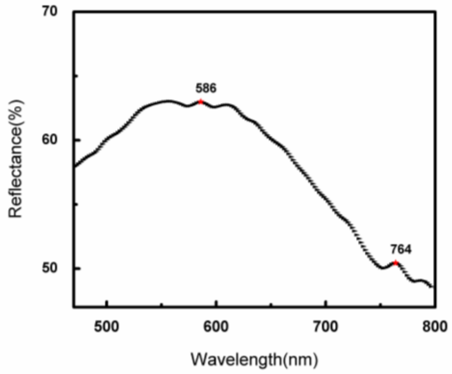

Fig. 5. UV-Vis reflectance spectra of the alumina thin films. (Oxidation voltage is 50 V; the angle between the cathode and anode is 45°; and oxidation time is 30 s)

Fig. 6 shows the photographs of the alumina thin films prepared under the conditions of oxidation voltage of 50 V, oxidation time of 30 s, and the angle between the cathode and anode being (a) 60°, (b) 45°, and (c) 30°. As displayed in the photos, more color stripes appeared on the alumina film, from a single color stripe in Fig. 6-(a) to five color stripes in Fig. 6-(c). According to the above theoretical analysis, when other experimental conditions remained constant, the average gradient of film thickness increased when the angle, θ, decrease. The difference in thickness between the top and bottom of thin film also increased, resulting in another increase in the number of color stripes due to the effect of equal thickness interference. When the angle was 60°, the difference in thickness between the top and bottom of thin film was comparatively small; only one single color was produced. When the angle was 30°, the difference in thickness between the top and bottom of thin film was comparatively big; thus, multiple color bars appeared. Conclusively, experimental results are consistent with the theoretical analysis.

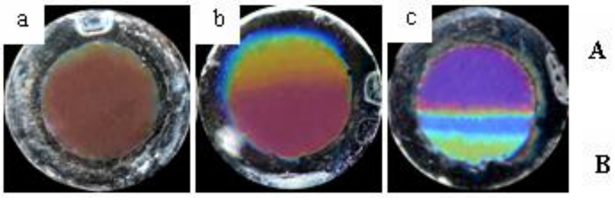

Fig. 6. The digital photographs of the alumina thin films (oxidation voltage of 50 V, oxidized for 30 s), the angles between the cathode and anode: (a) 60°, (b) 45°, and (c)30°

In order to further study the effect of oxidation voltage on structural color of films, we prepared alumina thin films under the following conditions: the angle between the cathode and anode was 60°, oxidation time was 35 s, and oxidation voltage was varied as 50, 55, and 60 V. The pictures in Fig. 7 show that, as the oxidation voltage increased, the number of color stripes also increased. The number of color stripes for the three samples were 2, 3, and 4. According to the above theoretical analysis, we know that when the oxidation voltage increases, the difference in thickness between the top and bottom of thin film increases, leading to an increase in the number of color stripes due to equal thickness interference.

There is another experimental phenomenon needs to be explained here for our results. When we compare the two pictures in Fig. 6-(a) and Fig. 7-(a), we find that Fig. 6-(a) shows a single color, while Fig. 7-(a) displays two colors. The experimental conditions for the two samples had the same oxidation voltage and angle between the cathode and anode, but the oxidation time was different. From this, we know that when the oxidation voltage and angle between the cathode and anode are the same, the gradient of the film thickness will also be the same. We also know that when the angle between the cathode and anode is comparatively large, and the oxidation time is comparatively short, the difference between the top and bottom of thin film is also small. We can deduce that is why the sample in Fig. 6-(a) has a single color. When the oxidation time was increased, the difference in the thickness between the top and bottom was comparatively large, resulting in a varying wave-length of the interference light of the top and bottom surfaces, which explains the reason that the sample in Fig. 7-(a) has two colors.

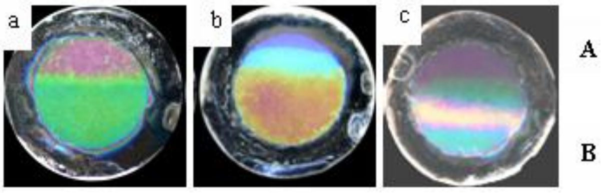

Fig. 7. The digital photographs of the alumina thin films (the angle between the cathode and anode of 60°; oxidized for 35 s); oxidation voltage: (a) 50 V, (b) 55 V, and (c) 60 V

Further, we used a polarization analyzer and digital camera to test the polarizing property of alumina thin films.

Adjusting the direction of transmissive vibration, we found that when the analyzer was at a certain position, the strength of reflected light was greatest (Fig 8). When the analyzer was rotated in one direction at angles of 30°, 60°, and 90°, the strength of reflected light decreased gradually until it reached 0, as is shown in Fig. 8 (b), (c), and (d). The same results were obtained when we tested other thin film samples; thus, this is proof that the reflected light of alumina thin films with rainbow striped structural colors is linearly polarized light. It should be noted that the study on the polarized property is still in progress.

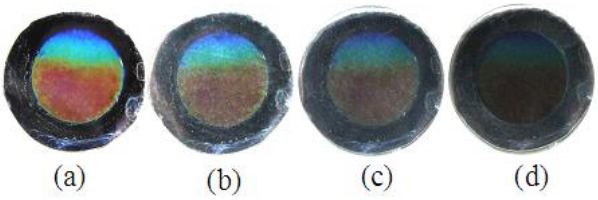

Fig. 8. The digital photographs of different angles between polarization orientation of analyzer and reflected light: (a) 0°,(b) 30°,(c) 60°, and (d) 90°

4. Conclusions

Alumina thin films with rainbow stripes were successfully fabricated using a one-step electrochemical oxidation method. FESEM shows that the alumina thin film is in the beginning of the micropores formations stage, and there is a gradient in the thickness along the radial direction of Al foil, which is why the film displays rainbow stripes. In addition, the relationships between the structural colors and their density, the anodizing voltage, the angle between the cathode and anode, and the oxidation time were discussed theoretically. We determined that the experimental results are consistent with the theoretical analysis. Moreover, the test results of polarized property show that the reflected light of alumina thin film is linearly polarized light. Conclusively, this approach simplifies traditional methods for producing alumina thin films with rainbow stripes and has a comparatively reduced cost. The results obtained in this study present significant insight for potential application of alumina thin film, such as in decorations, polarizers, analyzers, optical displays, and anti-counterfeiting.

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