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A study of color modulation of porous alumina processed by physical vapor deposition

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Abstract. With the development of the porous alumina (PA) fabrication technology, more and more scholars plough into the research of its properties, especially optical properties. Recently, we observed an interesting phenomenon that the PA templates processed by Physical Vapor Deposition (PVD) show color differences related to light path difference. Our work attempts to make the principle clear and to find an effective method to modulate the color of PA samples. This article describes the details of our experimental and theoretical results. We successfully prepared some PA templates with different pore-depth by controlling the time of anodization in oxalic acid solution. In order to enhance the reflectivity of air-PA interface, a layer of TiO₂ film of 18 nm is coated with PVD technique, which makes PA templates display quite distinct colors with different hole-depth. By modelling and analyzing PA samples, we make the interpretation of this optical property by taking the PA sample with 150 nm pore-depth as an example, and then put forward a way to simulate sample’s color within its hole-depth and material refraction-index. The results are in good agreement with our theoretical analysis, which proves the feasibility of our simulation mode.

1. Introduction
In recent decades, as the porous alumina (PA) gradually plays an important role in nanotechnology, a lot of researchers are interested in PA fabrication technique and its properties, including optical properties. Hideki Masuda [1][2] and Choi J [3] proposed different preparation methods of highly ordered PA membrane; B. Wang and W. J. Zheng, etc. successfully prepared PA samples with different pore-depth through controlling electrolyte temperature [4], timing in acid solution [5] and voltage of anodic oxidation [6] respectively; H. M. Chen used PA as the templates for growing of Ni...
nanowires and nanotubes in pores [7]. Worth to mention, all of them have investigated certain particular optical properties of PA and also done some work involving the interpretation to this phenomenon, but still not sufficient.

In this work, PA template is observed distinct color after physical vapor deposition (PVD) processed, which is much more intuitive phenomenon. We attempt to make the principle clear and to find an effective method to modulate the color of PA templates. This article describes the details of our experimental and theoretical results.

2. Experiment

2.1. Preparation of PA templates

PA templates were prepared using high-purity aluminum foils (99.999%). Prior to anodization, the foils were degreased in acetone and ethanol, and then annealed at 500 °C under vacuum ambient (about 2×10^{-5} torr) for 5h to remove the mechanical stress, at last electrochemically polished by a mixture of HClO4 and C2H5OH (the volume ratio is 1:9). Orderly, the process of electrochemical anodization could be divided into two steps.

In the first step, anodization lasted for 2 h under a constant anodization voltage of 40 V and electrolyte temperature of 3 °C. The specimens were then immersed in a mixture of 6.0 wt% H3PO4 and 1.8 wt% CrO3 at 60 °C for 4h to remove oxide layer on the surface.

The second step of anodization was actually the repeat of the first one. For obtaining PA templates with certain pore-depth precisely, only anodization time needs to be strictly controlled.

The morphology of PA template is characterized by a scanning electron microscopy (SEM, Carl zeiss, ULTRA55). Figure 1 shows the typical top view of the SEM image of PA template. The ordered pore arrays as seen in figure 1 have identical pore diameter of about 37.5 nm and inter-pores difference of about 100 nm, which depend on the applied voltage.

2.2. PVD processing
It is clear that PA is almost transparent in the range of visible spectrum, hence, majority of incident light reflects on the interface of PA membrane and Al base. In order to enhance the reflectivity of the interface of PA membrane and air, also make sure to avoid masking the properties of PA itself at the same time, a nano-scale layer with high reflective index needs to be coated. For this reason, TiO$_2$, this conventional colourless material, whose reflective index is about 2.4, is chosen to deposit on the PA surface with the help of PVD technique.

Figure 2 shows the SEM image of the same PA template PVD-deposited a TiO$_2$ film with the thickness round 18nm. In figure 2, surface morphology of PA template is obviously changed, which indicates that the TiO$_2$ film evenly overlays on the PA surface. Specially, some part of TiO$_2$ film above PA-pores collapses, so that the TiO$_2$ film is also pores-structure with 30nm pore-diameter and 100nm inter-pores distance, which is specified in figure 3.

**Figure 3.** Simple flowchart for illustrating the inner and outer structure of PA processed by PVD. (a) PVD procedure. (b) The layered view of PA template processed by PVD. (c) The integral view of PA template processed by PVD.

2.3. Experimental results

Figure 4(a) and (b) are the contrast photos of PA templates before and after PVD processing in irradiation of white light with 20 and 60 degree incident angle. From figure 4, the original PA template seems a little dim which looks like metallic, while the template processed by PVD strikingly displays vivid green and purple respectively.

**Figure 4.** Contrast photos of PA templates before (up) and after (below) PVD processing with (a) 20 degree and (b) 60 degree incidence angle respectively.
3. Theoretical analysis

3.1. Color Modulation

Figure 5(a) and (b) are physical models corresponding to the two samples in the figure 4(a) and (b), respectively.

As shown in figure 5(a), as PA is almost transparent in the range of visible spectra, the reflect light from Air-Al2O3 interface is much weaker compared to that from Al2O3-Al interface, which causes effective interference is not formed, consequently, PA template reveals colorless. With PVD technique, a thin TiO2 film is evenly deposited on the PA surface that balances two parts of reflect light as seen in figure 5(b).

According to Bragg reflector principle,

\[ 2nd \cos \theta = m\lambda \]  

where \( n, d, \theta, m \) and \( \lambda \) is reflective index, thickness of PA membrane, refractive angle, order number and light wavelength. These two coherent light sources will be enhanced in several certain frequencies, which depend on the unity of \( nd\cos \theta \) defined as light path difference (LPD) involved pore-depth of PA templates and incidence angle.

Actually, the LPD contains two parts, one is the original part from PA template impact, the other is affected by the TiO2 film. Hence, equation (1) may be rewritten as

\[ 2(n_{TiO2eff}d_{TiO2} \cos \theta_{TiO2} + n_{eff}d_{pore} \cos \theta_{PA}) = m\lambda \]  

where \( n_{TiO2eff}, d_{TiO2}, d_{pore}, \theta_{TiO2} \) and \( \theta_{PA} \) are effective reflective index of TiO2 film, thickness of TiO2 film, pore-depth, refractive angle in TiO2 film and refractive angle in PA membrane, respectively. It indicates that all of the wavelength fit equation (2) will be enhance mostly, but others will be weakened in different extent. As the result of that, the color according to the enhanced wavelength is observed on the PA surface.

![Figure 5. Model of light path diagram of PA template (a) before and (b) after PVD processing.](image-url)
3.2. Simulation

In order to simulate the modulated color of PA templates with certain pore-depth, it is clear that the effective reflective indexes of layers with pores-structure are necessary to obtain, as equation (2) illuminated. According to the Maxwell-Garnett theory (Garnett, 1904) [8], which is a good approximation for isolated inclusions, if we assume that

\[ \varepsilon = n^2 \]  

(3)

effective dielectric constant \( \varepsilon_{\text{eff}} \) is determined by

\[ \varepsilon_{\text{eff}} = \varepsilon_{\text{mert}} + 2f(\varepsilon_{\text{mert}} - \varepsilon_{\text{pore}}) \]

(4)

Where \( \varepsilon_{\text{mert}} \), \( \varepsilon_{\text{pore}} \) is equal to dielectric coefficient of material and air respectively, and \( f \) is the filling fraction of air, here it is equal to the porosity \( p \) [9]. The porosity \( p \) of a hexagonal structure is given by

\[ f = p = \frac{\pi}{2\sqrt{3}} \left( \frac{D}{D_{\text{int}}} \right)^2 \]

(5)

where \( D \) is diameter of the pores, \( D_{\text{int}} \) is inter-pores distance, which can be measured from SEM image. As shown in figure 2, the value of \( D \) and \( D_{\text{int}} \) before PVD processing is 37.5 nm and 100 nm, consequently, the value of \( f \) is 0.145 according to equation (5). Furthermore, put \( f \) and the value of \( n_{\text{Al}_2\text{O}_3}=1.7 \) and \( n_{\text{pore}}=1 \) into equation (4), we can calculate the effective dielectric constant of PA template is 1.52. Similarly, the effective dielectric constant of TiO₂ film is 2.32 by \( n_{\text{TiO}_2}=2.4 \).

Aiming at 150nm pore-depth PA template with 18nm thickness TiO₂ film coated by PVD in our experiment, we simulated its prospective observed color, and the specific values of various parameters are listed in Table 1. As pore-depth is defined in the scale of wavelength or sub-wavelength, in addition of concerning visible light spectra limiting, the combinations between \( m \) and \( \lambda \) sometimes are single one or two if the light path difference is a certain constant.

Table 1. The simulation of PA template of 150nm pore-depth with different incident angle.

| \( \theta (^\circ) \) | \( n_{\text{eff}} \) | \( d_{\text{pore}} (\text{nm}) \) | \( \theta_{PA} (^\circ) \) | \( n_{\text{TiO}_2}\text{eff} \) | \( d_{\text{TiO}_2} (\text{nm}) \) | \( \theta_{\text{TiO}_2} (^\circ) \) | \( m \) | \( \lambda (\text{nm}) \) | \( \text{color} \) |
|-----------------|------------------|----------------------|------------------|-------------------|----------------|----------------|---|-----------------|--------|
| 20              | 1.52             | 150                  | 13.0             | 2.32              | 18             | 8.5             | 1  | 526.9          | green  |
| 60              | 1.52             | 150                  | 34.7             | 2.32              | 18             | 21.9            | 1  | 452.4          | purple |

The “\( \lambda \)” column in Table 1 indicates corresponding wavelength to the interference frequency, concretely, that light of wavelength of 526.9 nm has enhanced mostly in 20 degree incidence angle, but 452.4 nm in 60 degree, moreover, the “color” column shows corresponding color in the chromaticity diagram, which is in good agreement with experimental results.

According to equation (3) ~ equation (5), it is clear that the effective reflective index of pores-structure layer has no relationship to pore-depth, in other words, if the pore-diameter and inter-pores difference have maintained the same, the effective reflective index is unchangeable.
Therefore, in the situation of identical PVD processing, PA templates with different pore-depth is supposed to reveal distinct colors.

Conversely, if a certain color is attempted to modulate on the surface of PA template, we could first calculate the corresponding pore-depth and then obtain such a depth by controlling anodization time strictly. The PVD technique can be finally employed to deposit a layer of TiO₂ as to acquire the modulated colors.

4. Conclusion
We have successfully prepared PA templates with different pore-depth by strictly controlling anodization time, and then processed them with PVD technique. To take the PA template with 150nm pore-depth as the given example, the according theoretical analysis has done, which has well illuminated the principle of color appearance on the surface of PA template. Furthermore, on the base of that, a method to modulate the colour of PA is proposed.

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