



Iridescent thin films of porous anodic aluminum oxide with embedded silver nanowires



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ABSTRACT

Anodic aluminum oxide (AAO) embedded Ag with iridescent colors were fabricated by using an AC electrochemical deposition technique. It was found that by changing the oxidation time of the aluminum in a phosphoric acid electrolyte, anodic aluminum oxide composite films can be made to have different colors. Compared to the color saturation of alumina films, the color saturation of AAO/Ag composite films was dramatically increased. The mechanisms for films displaying brilliant colors were discussed, and provide experimental results for iridescent patterns that were prepared by an organics-assisted method. AAO/Ag films with structural color can be used in many areas, including display, decoration, and anti-counterfeiting technology.

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1. Introduction

In the natural world [1,2], it has been found that brilliant colors could be generated by many diverse biological structures. One of the most attractive mechanisms is called structural color [3] because of the wide range of applications such as environment-monitor, interior decoration, liquid sensors and anti-counterfeiting. The anodic aluminum oxide (AAO) [4] membranes have attracted considerable attention due to the relatively simple equipment and technology. Diggle et al. [5] reported that a thin AAO film supported on an Al substrate anodized in an oxalic acid solution could produce vivid colors. However, the color saturation they achieved was very low. In order to enhance the color saturation, Wang et al. [6] have deposited some elements such as carbon in the AAO nanopores but the preparation process was relatively complex in certain extent.

In this paper, we report a simple and efficient template-based electrochemical deposition technique [7]. The difference with this technique compared to the traditional two-step anodic oxidation [8,9] process was that our anodic oxidation process occurs in phosphoric acid [10,11] and only needs an oxidation time of about 10 to 15 min to complete. In addition, the AAO films without substrate are fragile compared to those supported by the substrate of AAO films. Deposition of Ag in the nanopore region can enhance the color saturation of the thin alumina film while still retaining the Al substrate. We obtained a variety of structural colors and production was easily controlled. This study

reports on the detailed fabrication process and optical properties of the AAO/Ag films we produced.

2. Experimental details

AAO are prepared from high-purity aluminum foils (99.99%, annealed at 673 K for 4 h in argon). In order to remove the oxide layer formed in the air condition, Al foils with a diameter of 20 mm are electro-polished with a voltage of 30 V for 5 min to smooth the surface in a polishing solution of ethanol mixed perchloric acid with a volume ratio of 1:4. Subsequently, the Al foils were rinsed with acetone and deionized water and finally dried in air.

A one-step anodization procedure was conducted using a constant direct current voltage of 30 V at 292 K for 10–15 min in 45 g/L phosphoric acid solutions. A graphite plate was used as a counter electrode and as-prepared Al foils as the working electrode. Then the AAO template was washed with deionized water in ultrasonic cleaner. The prepared AAO membranes was immersed in a 0.03 mol/L AgNO₃ solution with 30 g/L of boric acid and 5 g/L ascorbic acid. These films with aluminum substrate were mounted on another copper plate serving as the anode and a graphite plate was used as a cathode, respectively. AAO/Ag nanocomposite films were fabricated by electrodeposition at 292 K with a 50 Hz AC voltage of 15 V. The volume fraction of metal Ag can be controlled by the deposition time. According to experiment results, our team draw conclusion that the perfect color saturation could be obtained when deposition time is about 60 s. In this case, the time of deposition in the nanopore was 60 s. For comparison, we also fabricated AAO/Ag films with the same color in oxalic acid solution.

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The products were characterized using a field-emission scanning electron microscope (FE-SEM, Hitachi S-4800) and an optical digital camera (Canon IXUS 9515). A Hitachi UV-3010 spectrophotometer was used to measure the optical properties of samples, BaSO₄ was used as a reference.

3. Results and discussion

A sample of the surface morphology of the AAO/Ag nanocomposite films formed in the phosphoric acid is shown in Fig. 1a. Fig. 1c shows FE-SEM images of the AAO/Ag films formed in oxalic acid solutions. It can be seen that the pore diameter and interpore spacing of the phosphoric acid AAO/Ag film (Fig. 1a) are not as ordered as those in films (Fig. 1c) formed in oxalic acid solution. The comparison clearly shows that the distribution of the pores and the interpore spacing in the phosphoric acid is not uniform, in addition, such microstructure characteristics of the phosphoric acid AAO/Ag film (Fig. 1a) might scatter the light more effectively compared with well organized arrays (Fig. 1c) in an oxalic acid AAO/Ag film. Therefore, the film in the phosphoric acid can appear a better saturated color. We also found that there are no deposits on the surface of the film. In this case, we just roughly estimated the average pore diameter is about 50 nm, and the average interpore spacing is about 75 nm. Fig. 1b and d shows a cross-section SEM image of the sample film anodized for 15 min and 10 min in phosphoric acid solution and an electrodeposition time of 60 s. It can be seen that nanowire arrays were deposited inside the alumina channels. We roughly calculate the average length of the Ag nanowires to be approximately 50 nm.

In order to explain the influence of electrodepositing with Ag for the color saturation of the samples, Fig. 2a is a pristine AAO film which is oxidized in phosphoric acid for 11 min, Fig. 2b is a film after electrodepositing with Ag. It can be seen that the color saturation of composite film is much improved with Al substrate, which indicates the Ag layer

plays an important role in shielding the reflected light. The detailed will be given as follows.

The color mechanism of AAO membranes can be explained by the thin-film interference. When light is incident on an AAO/Ag nanocomposite films, there be constructive interference from light reflected from the interface between the air and the AAO film layer, the interface between the AAO and the AAO/Ag layers, as well as from the interface between the AAO film and the aluminum substrate as shown in Fig. 3a. The effective refractive index of two layers film in an atmospheric environment can be given by Bragg–Snell formula [12,13]:

$$2n_A d_A \cos \theta_A + 2n_B d_B \cos \theta_B = \left(m + \frac{1}{2}\right) \lambda \quad (1)$$

where n_a and n_b are the effective refractive index of two layers where the AAO film is layer A and the AAO/Ag film is layer B as shown in Fig. 3a, and dx is thickness of the each single layer film, λ is the wavelength incident the film, m is the order of interference, θ is the refraction angle. The effective refractive indices of the porous alumina layers and the AAO/Ag nanocomposite films can be calculated using effective medium approximations given by Maxwell–Garnett [14]:

$$\epsilon_{eff} = \epsilon_{Al_2O_3} \frac{2\epsilon_{Al_2O_3} + \epsilon_{void} + 2P(\epsilon_{void} - \epsilon_{Al_2O_3})}{2\epsilon_{Al_2O_3} + \epsilon_{void} - P(\epsilon_{void} - \epsilon_{Al_2O_3})} \quad (2)$$

$$\epsilon_{eff} = n_{Al_2O_3}^2 \frac{n_{Ag}^2 + n_{Al_2O_3}^2 + 2P(n_{Ag}^2 - n_{Al_2O_3}^2)}{n_{Ag}^2 + n_{Al_2O_3}^2 - P(n_{Ag}^2 - n_{Al_2O_3}^2)} \quad (3)$$

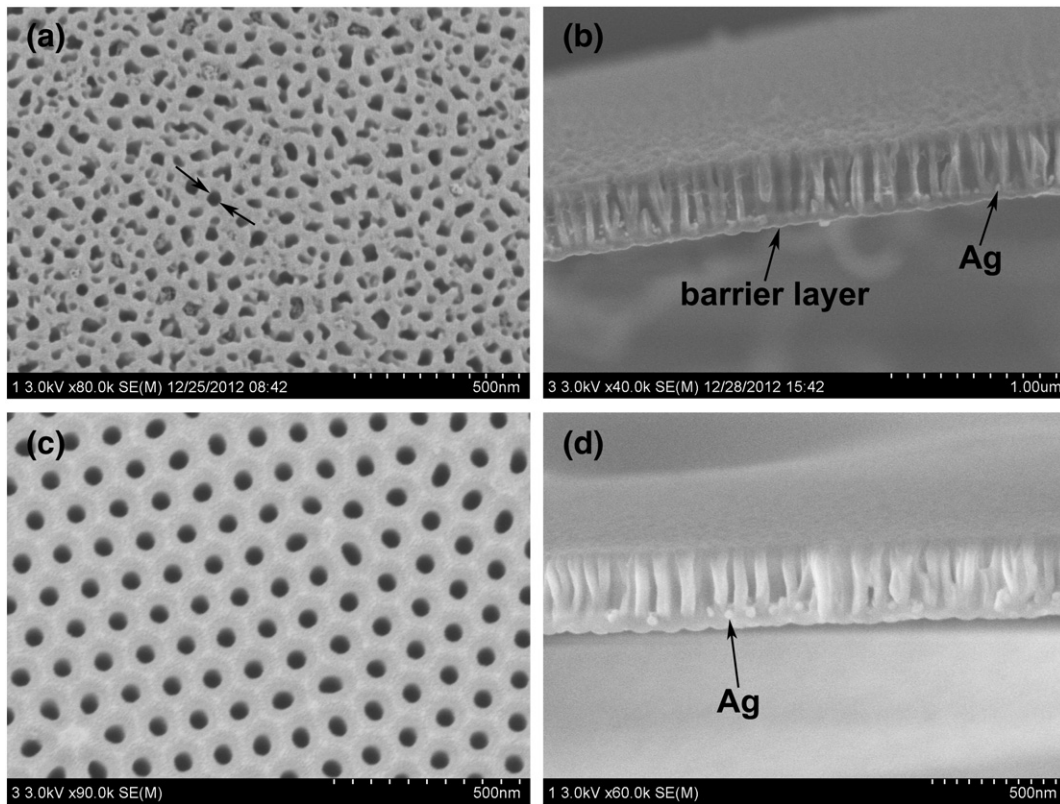


Fig. 1. Sample SEM images of an AAO/Ag nanocomposite film anodized for 15 min in the phosphoric acid and an electrodeposition time of 60 s. (a) The top view and (b) cross-section. (c) The FE-SEM image of the AAO/Ag films with same color in the oxalic acid. (d) SEM image of an AAO/Ag nanocomposite film anodized for 10 min in the phosphoric acid and an electrodeposition time of 60 s.

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