CARBON COATING ON THIN ANODIC ALUMINUM OXIDE FILM MAKES INTERFERENCE COLOR BRILLIANT

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Abstract

When a thin anodic aluminum oxide (AAO) film on an Al substrate is uniformly coated with carbon by chemical vapor deposition, the saturation of interference color is substantially enhanced and the coated AAO film exhibits a brilliant color. Such remarkable saturation enhancement is predominantly due to the carbon deposited uniformly in nanochannels of the AAO film, which efficiently screens the reflected light from AAO-Al interface. The carbon coated AAO film is capable of absorbing light over a wide wavelength range, and the absorbance is highly dependent on AAO film thickness. The brilliant colored film is useful for weather-resistant decorative purpose and holds promise as an effective broadband optical limiter for nanosecond laser pulse.

Introduction

A thin AAO film (thickness < ~1 μm) supported on an Al substrate as shown in Fig. 1a, produces bright interference color in the visible light range due to the light reflected, refracted into and from the AAO film.[1] The refracted light, on meeting AAO–Al interface, is partly transmitted into Al, where it gets partly absorbed and mostly reflected. The reflected light, upon reaching air–AAO interface, is again partly reflected and transmitted out of the AAO film. As a result, there is an optical path difference between the reflected light on air–AAO interface and the emergent light after the refraction, which often gives rise to a visible interference color. A pristine thin AAO film supported on an Al substrate usually exhibits bright interference color but saturation is very low. To make the color brighter and high-saturation, colored substances are invariably required to be sealed into the AAO film nanochannels.[1] Here we demonstrate for the first time that, when a thin AAO film is uniformly coated with carbon by chemical vapor deposition (CVD), the coated film exhibits brilliant and tunable interference colors with much higher saturation than the pristine AAO film.

Experimental

In this study, AAO films were prepared by anodic oxidation of 0.5 mm-thick Al plates at 40 V in 3 wt% aqueous oxalic acid solution at 20 °C. The AAO film thickness can be estimated from the *i–t* curve recorded during the anodic oxidation, taking into account the charges involved in the oxidation of metallic Al into Al_2O_3. Figure 1b presents the estimated AAO film thickness as a function of anodic oxidation time with an assumption that current efficiency is 100% and the density of Al_2O_3 film is 3.98 g/cm^3. According to the estimation shown in Fig. 1b, we prepared AAO film with thicknesses ranging from hundreds of nanometers to over one micrometer through tuning the anodic oxidation times varying between 27 s to 10 min. The as-prepared AAO films were washed with deionized water, dried and subjected to atmospheric-pressure CVD for uniform carbon coating on the films at 600 °C for 2 h using acetylene (20 vol% in N_2 flow) as a carbon source[2]. A thin carbon layer (~5 nm thick) was uniformly deposited on both the external surface and the inner nanochannels of the AAO films (Fig. 1a). Since the carbon deposited in the nanochannel is tubular, it is hereafter referred to as carbon nanotubes (CNTs). Diffuse reflectance spectra of the pristine and the carbon-coated AAO films were recorded at room temperature by an UV-vis spectrometer (JASCO V–560) equipped with an integrating sphere. $BaSO_4$ was used as a reference. The incident light was projected onto the films on Al substrates with a near normal configuration.

Results and discussion

Figure 2a shows UV-vis diffuse reflectance spectra of the pristine AAO films and the carbon-coated AAO films with various anodic oxidation times indicated. Their corresponding thickness of the films can be estimated from Fig. 1b. It can be seen from Fig. 2a that the reflectance spectra are of well-resolved bands. These bands originate from the interference between the reflected light from the air–AAO interface and the emergent light after reflection on

the AAO–Al interference. There are three obvious features in these reflectance spectra over the wavelength range investigated. First, the reflectance of the pristine AAO films is similar regardless of their thicknesses while that of the carbon-coated AAO films strongly depends on the thickness. Second, the reflectance of the carbon-coated AAO films is lowered in such a way that the saturation of interference color is much enhanced, namely, the interference color become purer with carbon coating. This is evident from Figure 2(b) where photographs of the patterned AAO films before and after the carbon coating are shown. The decrease in reflectance upon the carbon coating will be discussed in detail in the following sections. Thirdly, the interference patterns shrink with decreasing wavelength. A similar shrinking phenomenon has been reported by Swanepoel and it was ascribed to interface roughness.[3] In addition, the interference bands of the carbon-coated AAO have a red shift because of the incorporation of electrically conductive carbon film.

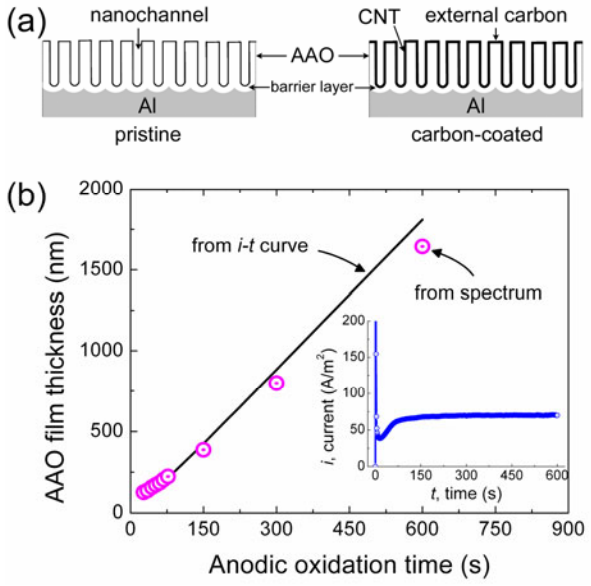

Figure 1. (a) Schematics of the pristine AAO film and the carbon-coated one. (b) AAO film thickness estimated from the *i*–*t* curve (inset) recorded during the anodic oxidation.

For thin AAO-covered Al plate, the maximum reflectance follows the equation below

$$2nd\cos\gamma = m\lambda \tag{1}$$

where n is the refractive index of the AAO film, d is the film thickness, γ is the refraction angle, m is the order of interference, and λ is the wavelength at maximum reflectance.

According to eq. 1, the number and the position of interference bands can be designed through tuning the AAO film thickness by simply adjusting the anodic oxidation time. As described above, the saturation of interference colors have been much enhanced by coating AAO film with carbon, therefore we are able to fabricate carbon-coated AAO films having desired colors with high saturation through adjusting the AAO film thickness. Figure 3 shows diffuse reflectance spectra of the carbon-coated AAO films with various thicknesses ranging from 127 nm to 224 nm. The first-order maximum interference bands shift from ~410 nm to ~790 nm for the carbon-coated AAO films when the AAO film thickness increases from 127 to 224 nm, which agrees well with the appearances varying from blue to red. The beautiful carbon-coated AAO film supported on Al substrate is useful for decorative purpose. Since the color originates from interference, the colored carbon-coated AAO film supported on Al substrate is therefore dye-free and there is no problem of fading. Obviously, the carbon-coated AAO films are of advantage with respect to light fastness or durability over the conventional dye-sealed AAO films. With carbon coating, the coated films are capable of absorbing light over the wavelength range investigated in this work. It has

been demonstrated that carbon nanomaterials including CNTs are broadband optical limiting materials.[4] The carbon-coated AAO films (CNTs embedded in AAO films) on a transparent substrate hold promise as an effective broadband optical limiter for nanosecond laser pulse. Moreover, the length, the diameter and the wall thickness of CNTs that are embedded in AAO films are tunable, allowing a precise adjustment of laser intensity.

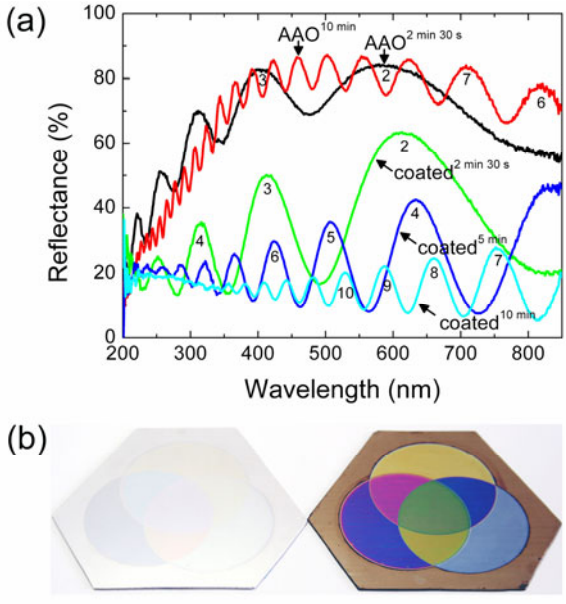

Figure 2. (a) UV-vis diffuse reflectance spectra of the pristine AAO films (the upper two patterns) and the carbon-coated AAO films which are prepared for the time indicated. The order of interference is indexed. (b) Photographs of the pristine patterned AAO films (left) and the carbon-coated one (right). The pattern consists of three partially overlapped circles. The circles were fabricated by moving stepwise an O ring that confines the area where anodic oxidation occurred for 32, 57 and 82 s, respectively.

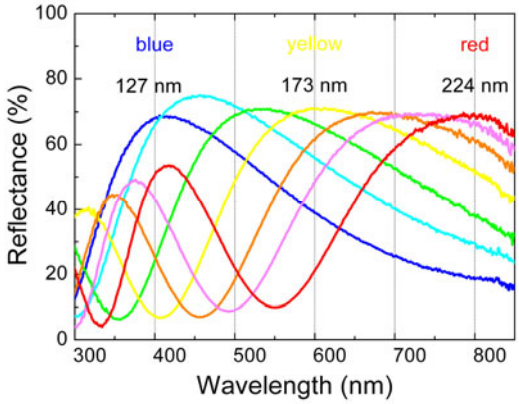

Figure 3. UV-vis diffuse reflectance spectra of the carbon-coated AAO films showing interference colors varying from blue to red. The AAO film thickness ranges from 127 nm to 224 nm.

Conclusions

In summary, carbon-coated thin AAO film (< ~1 μm) appears brilliant color because of carbon coating that screens the reflected light on AAO–Al interface. Refractive indices of pristine AAO and carbon-coated AAO films were determined from their well-resolved interference bands. Brilliant carbon-coated AAO films reported for the first time are dye-free and are useful for decorative purpose. In addition, the thickness-tunable carbon-coated AAO films on a transparent substrate also hold promise as an effective broadband optical limiter for nanosecond laser pulse.

References

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