

## Brilliant and tunable color of carbon-coated thin anodic aluminum oxide films

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(Received 18 May 2007; accepted 13 June 2007; published online 6 July 2007)

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, as a result, the coated AAO film exhibits a brilliant color. Such remarkable saturation enhancement is predominantly due to the carbon deposited on the inner walls of nanochannels of the AAO film, which efficiently screens the reflected light from AAO–Al interface. The brilliant carbon-coated AAO film is useful for weather-resistant decorative purposes and holds promise as an effective broadband optical limiter for nanosecond laser pulse. © 2007 American Institute of Physics. [DOI: 10.1063/1.2754649]

A thin anodic aluminum oxide (AAO) film (thickness  $< \sim 1 \mu\text{m}$ ) supported on an Al substrate, as shown in Fig. 1(a), produces a bright color in the visible light range due to the interference of light.<sup>1</sup> The incident light, on meeting AAO–Al interface, gets partly absorbed into Al and mostly reflected. The reflected light, upon reaching air–AAO interface, is again partly reflected, but the other is 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. The color is bright but its saturation is very low. To make the color pure and highly saturated, colored substances always have to be sealed into the AAO film nanochannels.<sup>1</sup> Here we demonstrate that, when a thin AAO film is uniformly coated with carbon by chemical vapor deposition (CVD), the carbon-coated film exhibits a brilliant and tunable interference color with much higher saturation than the pristine AAO film.

One side of an Al plate with a thickness of 0.5 mm was anodically oxidized at 40 V in 3 wt % aqueous oxalic acid solution at 20 °C. We estimated the thickness of the AAO film on the Al plate from the current-time ( $i$ - $t$ ) curve during the anodic oxidation [the inset of Fig. 1(b)], assuming that total electric charge was consumed only for the oxidation of metallic Al into  $\text{Al}_2\text{O}_3$ . Figure 1(b) presents the estimated AAO film thickness as a function of anodic oxidation time. By changing the time from 27 s to 10 min, we prepared AAO films with different thicknesses ranging from hundreds of nanometers to over  $1 \mu\text{m}$ . The channel size is about 30 nm in diameter. The as-prepared AAO films were washed with de-ionized water, dried, and subjected to atmospheric-pressure CVD for uniform carbon coating<sup>2</sup> on the films at 600 °C for 2 h using acetylene (20 vol % in  $\text{N}_2$  flow) as a carbon source. A thin carbon layer ( $\sim 5 \text{ nm}$  thick) was uniformly deposited on both the external surface and the inner nanochannels of the AAO films [Fig. 1(a)]. If the carbon part in the nanochannels is liberated by dissolving the AAO film with HF or alkali washing, the carbon can be obtained as

carbon nanotubes (CNTs).<sup>2</sup> Therefore it is hereafter referred to as 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.  $\text{BaSO}_4$  was used as a reference. The incident light was projected onto a sample film with a near normal configuration.

UV-vis diffuse reflectance spectra of the pristine and carbon-coated AAO films with various anodic oxidation times are shown in Fig. 2(a), where their corresponding film thicknesses estimated from the plot in Fig. 1(b) are indicated. These reflectance spectra are characterized by well-resolved bands originating 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 the reflectance spectra over the wavelength range investigated. First, the reflectance of the pristine AAO films looks similar regardless of their thicknesses, while that of the carbon-coated AAO films strongly depends on the

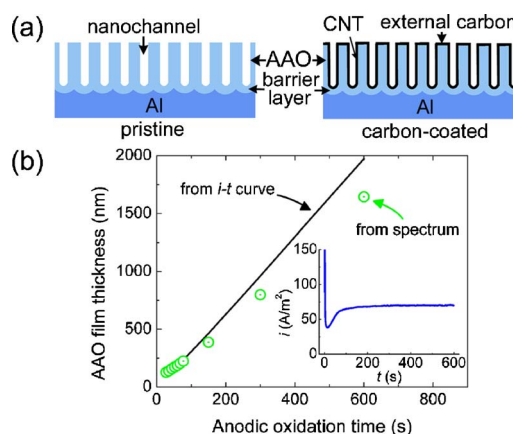


FIG. 1. (Color online) (a) Schematic of the pristine AAO film and the carbon-coated one. (b) AAO film thickness estimated from the  $i$ - $t$  curve (inset) recorded during the anodic oxidation as a function of time. Alternatively, the thickness can be calculated from the interference spectra and the refractive indices in Fig. 4(b) according to Eq. (1). The calculated values are plotted together with the result from the  $i$ - $t$  curve, indicating a good agreement between these two different calculation methods.

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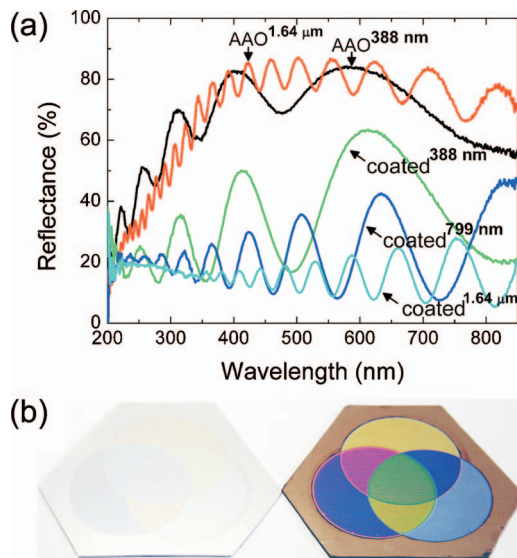


FIG. 2. (Color) (a) UV-vis diffuse reflectance spectra of the pristine AAO films (the upper two patterns) and the carbon-coated AAO films. The film thickness of each sample is indicated. (b) A photograph of the pristine patterned AAO film (left) and its carbon-coated one (right). The pattern consists of three partly overlapped circles. The surface of each circle was separately subjected to the anodic oxidation for a different period (32, 57, or 82 s) so that the part where the three circles are overlapped has the longest oxidation period (171 s = 32 + 57 + 82).

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 becomes purer with the carbon coating. This is evident from Fig. 2(b) where a photograph of patterned AAO films before and after the carbon coating is shown (note that the colors in the films change with different viewing angles, because they are derived from the interference). 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 was reported by Swanepoel and it was ascribed to interface roughness.<sup>3</sup> In addition, the interference bands of the carbon-coated AAO films have a redshift because of the incorporation of electrically conductive carbon film.

For a pristine AAO film, the maximum reflectance of each interference band follows the following equation:

$$2nd \cos \gamma = m\lambda, \quad (1)$$

where  $n$  is the refractive index of the AAO film at a wavelength of  $\lambda$ ,  $d$  is the film thickness,  $\gamma$  is the refraction angle,  $m$  is the order of interference, and  $\lambda$  is the wavelength at maximum reflectance. In order to confirm that the behavior of carbon-coated AAO films also obeys this equation, we prepared the coated films with seven different thicknesses from 127 to 224 nm. Note that this thickness range was selected to have the first-order interference bands appear in the wavelength range measurable by the UV-vis spectrometer. Figure 3 shows the resulting diffuse reflectance spectra of these films. With increasing the thickness from 127 to 224 nm, the first-order bands shift from  $\sim 410$  to  $\sim 790$  nm, which agrees well with the change in color from blue to red when we observed the films perpendicular to their carbon-coated surface. Moreover, the thickness is directly proportional to the wavelength at maximum reflectance in each first-order band, as Eq. (1) predicts.

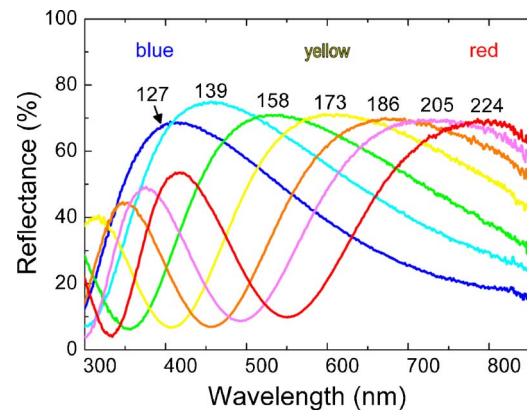


FIG. 3. (Color online) UV-vis diffuse reflectance spectra of the carbon-coated AAO films with seven different thicknesses. The films show interference colors varying from blue to red. The AAO film thickness varies from 127 to 224 nm.

As shown in Fig. 1(a), the deposited carbon on the AAO film consists of two distinct parts, i.e., the carbon layer on the external surface of the film and the inner CNTs embedded in the nanochannels. To understand exactly the contribution of these two carbon parts to the enhanced saturation of the interference colors, the coated films were subjected to oxygen plasma to remove the carbon from the outside inward in a time-controlled oxygen plasma reactor. After the controlled removal of the carbon by exposing to oxygen plasma, the films were examined with the UV-vis spectrometer.

Figure 4(a) shows UV-vis diffuse reflectance spectra of the original carbon-coated AAO film (anodic oxidation period: 10 min) and those subjected to the oxygen plasma treatment

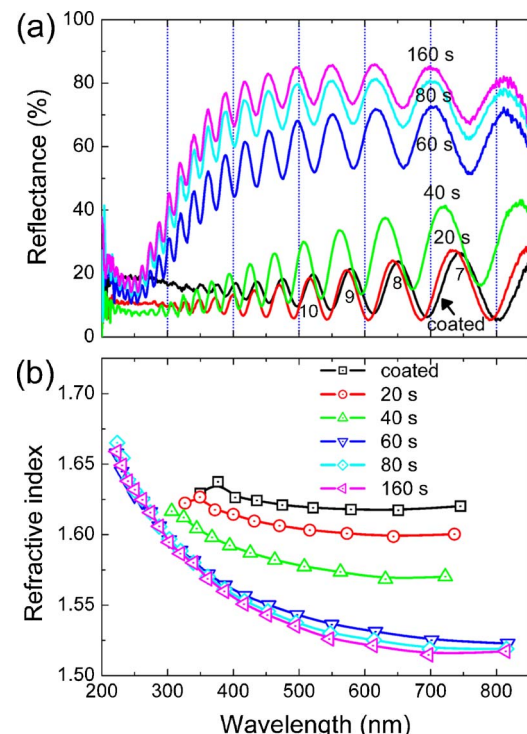


FIG. 4. (Color online) (a) UV-vis diffuse reflectance spectra of the carbon-coated AAO film (the anodic oxidation: 10 min) and those subjected to the oxygen plasma treatment for various accumulated times (20–160 s). The indicated number corresponds to the order of interference. (b) Dependence of the refractive index on wavelength for the original carbon-coated AAO film and the oxygen plasma-treated ones.

ment for different times. For the original film, the reflectance over the wavelength range investigated is below 30% which is much smaller than that for the bare AAO film, indicating that the deposited carbon helps AAO film absorb most of light. When the carbon-coated AAO film was treated for 20 s, the reflectance almost remains unchanged and the color was kept. Careful observation on the remaining carbon by transmission electron microscopy (TEM) after liberating the carbon from the AAO film indicates that only the external carbon was removed but the CNT part was not altered. However, as the treatment time was elongated to over 20 s, for example, 40 or 60 s, the reflectance is remarkably increased and the color became paler and paler. Accordingly, we have found that, when we observed the CNTs taken from these carbon-coated films with TEM, the CNT length was decreased from the original value ( $1570\pm 45$  nm) to  $1100\pm 260$  nm with the treatment for 40 s and to  $840\pm 70$  nm with the treatment for 60 s. These results clearly indicate that the inner CNTs are predominantly responsible for the enhanced saturation of interference color. Besides the increase in reflectance with elongating the treatment time, blueshift of the interference bands is significant. The reflectance and interference band position are changed until the oxygen plasma treatment time reaches 160 s, indicating that the carbon was completely removed with the treatment for 160 s or longer. The spectrum of the 160 s-treated film is very similar to that of the pristine AAO film [Fig. 2(a)] and, as a matter of fact, the former film has the same appearance as the latter one.

As stated above, the length of the original CNTs embedded in the AAO film used in Fig. 4(a) is  $1570\pm 45$  nm. Considering the contribution of the barrier layer in the AAO film, we estimated the total thickness of this AAO film to be  $1610\pm 45$  nm (this value is a little smaller than the thickness determined from the  $i$ - $t$  curve, probably because the current efficiency is less than 100% when the thickness becomes as large as above  $1\ \mu\text{m}$ ). Using the value of the thickness and the well-resolved interference bands in Fig. 4(a), we can deduce refractive indices of the films according to Eq. (1). Figure 4(b) shows the wavelength dependence of the refractive indices of the films. It can be seen that the refractive indices strongly depend on the oxygen plasma treatment time, i.e., the CNT length or the carbon content in the films. The shorter the treatment time is, the more the content of electri-

cally conductive carbon and the larger the refractive index.

According to Eq. (1), the number and the position of interference bands can be designed through the tuning of the AAO film thickness by simply adjusting the anodic oxidation time. Since the saturation of interference color of an AAO film has been much enhanced by the carbon coating, we are able to fabricate a carbon-coated AAO film having a desired color with high saturation through adjusting the AAO film thickness. Such beautiful carbon-coated AAO films supported on an Al substrate are useful for decorative purposes. Since the color originates from interference, the colored carbon-coated AAO films are therefore dye-free and there is no problem of fading. Obviously, the carbon-coated AAO films are of advantage with respect to light fastness and durability over the conventional dye-sealed AAO films. Very recently, Chin *et al.* have demonstrated that carbon nanomaterials including CNTs are broadband optical limiting materials.<sup>4</sup> The present carbon-coated AAO films (CNTs embedded in AAO films) on a transparent substrate also hold promise as an effective broadband optical limiter for nanosecond laser pulse, because, with the carbon coating, the AAO films are capable of absorbing light over a wide wavelength range, as demonstrated in the present study. Moreover, the length, the diameter, and the wall thickness of CNTs that are embedded in an AAO film are tunable,<sup>2</sup> which allows a precise adjustment of laser intensity.

In summary, the carbon-coated thin AAO films ( $< \sim 1\ \mu\text{m}$ ) have a brilliant color with high saturation because the carbon layer screens the reflected light on AAO-Al interface. Refractive indices of the pristine AAO and carbon-coated AAO films were determined from their well-resolved interference bands. Brilliant carbon-coated AAO films reported in the present study are dye-free and are useful for decorative purposes. In addition, the carbon-coated thickness-tunable AAO films on a transparent substrate also hold promise as an effective broadband optical limiter for nanosecond laser pulse.

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