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Synthesis and properties of iridescent Co-containing anodic aluminum oxide films

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ABSTRACT

A simple method of fabricating Co-containing anodic aluminum oxide films for multifunctional anti-counterfeit technology is reported. The films display highly saturated colors after being synthesized by an ac electrodeposition method. Tunable color in the films is obtained by adjusting anodization time, and can be adjusted across the entire visible range. Magnetic measurements indicate that such colored composite films show excellent magnetic properties. The resulted short (310 nm in length) and wide (50 nm in diameter) Co nanowires present only hexagonal close-packed phase, with the coercivity and squareness ratio as high as 1.2×10^5 A/m and 0.803, respectively. The magnetization reversal mechanism is in good agreement with coherent rotation model. The color and magnetic properties remain the same over a wide temperature range. The Co-containing anodic aluminum oxide films with structural color and perpendicular magnetic recording properties have friability-resistant feature and could be used in many areas including decoration, display and multifunctional anti-counterfeiting applications.

1. Introduction

Structural color in the natural world has attracted the attention of biologists and physicists [1,2]. In contrast to pigmentary colors attributed to the selective absorption of light by pigments and dyes [3–5], structural color arises mostly from the interference of light in thin-layer, multilayer, or three-dimensional periodic nanostructures with sizes on the scale of the wavelength of visible light [6–10]. The reflected light usually appears considerably brighter than that involving pigment, although it often results from completely transparent materials.

Structural color has inspired biomimetic technologies for applications in different industries related to color [11–13]. Of these, tuning the structural color has attracted considerable interest due to potential applications in displays, sensors and anti-counterfeiting technology [14,15]. Recently, Zhao et al. [16] constructed an AAO (anodic aluminum oxide) film embedded with carbon nanotubes on an Al substrate and found that infusion with water resulted in a significant color change. Such films might be used as water sensors. Wang et al. [17] also reported that brilliant carbon-coated AAO thin films on an Al substrate were useful not only for weather-resistant decorative purposes, but also showed promise as effective broadband optical limiters for nanosecond laser pulses.

At present, much attention is also being focused on the optical properties of the above AAO films due to their potential applications in anti-counterfeiting technology. Due to the spread of imitative commodities, in which a counterfeit version of an object or device is marketed in a deceptive manner, it is necessary to develop better anti-counterfeiting technology. It is presumed that multifunctional anti-counterfeit technologies or materials combining more than one authentication modality (such as optical and magnetic) will be harder to circumvent.

In order to expand the range of potential applications of colored AAO films, materials with other functional properties (e.g. ferromagnetic [18], ferroelectric [19], semiconductor [20]) have already been introduced into the pores of colored AAO templates. Among them, it is worth to mention that Yoon et al. [21] synthesized the semiconductor/ferromagnetic metal nanowire (CdS/Co) arrays in the pores of AAO templates by ac electrodeposition, but the obtained nanocomposite films did not display structural color. Since magnetic recording has been widely used for security, it is of interest to consider additional advanced materials with combined optical and magnetic properties that can be produced in a cost effective manner. Considering that Co has single axis magnetic

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anisotropy, and already has wide applications in magnetic recording, we have chosen to attempt fabrication of porous anodic alumina films with Co deposited in the pores, hereafter referred to as Co-containing anodic aluminum oxide nanocomposite films, with the anticipation that this material will exhibit magnetic properties suitable for authentication (e.g. high quality coercivity and squareness ratio) combined with color that is tunable for a specific application. Such films increase the mechanical strength, compared to our previous free-standing AAO films which are extremely friable and also exhibit highly saturated colors [22]. In this paper, we report the fabrication of such films. The microstructures of the films have been characterized as reported below, and the optical and magnetic characteristics are discussed.

2. Experiments

For the synthesis of a porous alumina membrane, high-purity aluminum sheets (99.999%) were degreased in acetone and then annealed at 400 °C for 2 h in an argon atmosphere. The Al foils were electropolished in a mixture of C_2H_5OH and $HClO_4$ (ratio by volume 4:1) for 5 min to smooth the surface. After a first anodization, carried out at a constant dc voltage of 45 V in 0.3 M oxalic acid at 5 °C for 6 h, the alumina film produced was chemically removed by immersing the foil in a mixture of phosphoric acid (6 wt%) and chromic acid (4 wt%) at 40 °C for 8 h. Subsequently, a second anodization was conducted using an anodizing voltage that decreased in steps [23]. The specific procedures were as follows: The cell voltage was first kept at a constant voltage of 45 V for t_1 seconds ($t_1 = 40$, 50, 60, 80, respectively), and was then decreased in steps from 45 V to 15 V over a period of 10 min, with the voltage decreasing by 3 V every minute. In this way, we obtained porous alumina templates of different thicknesses on Al substrates. Afterward, Co was deposited in the pores of the templates by ac electrodeposition in an electrolyte (pH = 3) consisting of 60 g/L $CoSO_4 \cdot 7H_2O$, 5 g/L ascorbic acid, and 30 g/L H_3BO_3. The electrodeposition was carried out at 20 °C with an ac voltage of 15 V (50 Hz) for 2 min using a graphite plate as a counter electrode and the porous alumina on its Al substrate as a working electrode.

The morphology of an AAO thin film was observed using a scanning probe microscope (SPM, Veeco Nanoscope IV) operated in tapping mode with silicon probes. The microstructures were examined with a field-emission scanning electron microscope (SEM, Hitachi S-4800) operated at 20 kV, the cross section of the nanocomposite film was treated by spray-gold. The film thickness can be obtained through the cross-sectional image. The morphology of the Co which was in the form of Co nanowires was examined by transmission electron microscopy (TEM, Hitachi H-7650) after removal of the supporting AAO template by alkaline treatment. The operating voltage in the TEM measurements is 100 kV. The atomic components in the chemical composition were confirmed by x-ray energy dispersive spectroscopy (EDS). Optical images were obtained using an optical digital camera (Sony Dsc-T20). UV–Vis reflectance spectra were recorded on a Hitachi UV-3010 spectrophotometer equipped with an integrating sphere. $BaSO_4$ was used as a reference. The crystallographic structure was examined by θ–2θ geometry X-ray diffraction (XRD, Philips PANalytical – X'Pert Pro) with Cu-Kα_1 radiation (1.54056 Å). The magnetic properties were measured using a physical properties measurement system (PPMS-6700) with the magnetic field parallel and perpendicular to the Co nanowires at room temperature.

3. Results and discussion

In our previous study, we have fabricated highly ordered AAO thin films with tunable structural colors, which have been reported in Refs. [22,24], the surface and cross section images are shown in Fig. 1a and b. However, as we all known such thin films are extremely fragile, which are not benefit for practical application. Therefore, in order to increase the mechanical strength, other metal material was deposited into the pores of AAO films, so we have fabricated the colored Co-containing anodic aluminum oxide nanocomposite films with an Al substrate supported. The TEM image of a single Co nanowire obtained after removing the alumina matrix is shown in Fig. 1c. The Co nanowire surface is smooth, and the diameter is uniform. The average length and diameter of the Co nanowires are approximately 310 nm and 50 nm, respectively. The diameter of Co nanowires is consistent with the pore diameter of the AAO template. The energy dispersive spectrum (EDS) of the Co-containing anodic aluminum oxide nanocomposite film shows the presence of Co, and also establishes the absence of other elemental impurities. The Co deposition has important influence on the color of the films such as the enhancement of color saturation. The detailed explanation would be given in the following.

Photographs of the Co-containing anodic aluminum oxide nanocomposite films taken in natural light at nearly normal incidence are shown in Fig. 2. They clearly show that the color gradually changes from blue to red with increasing anodization time. Note that the color of the reflected light is highly saturated in spite of the presence of the highly reflective Al substrate behind the Co-containing anodic aluminum oxide films. It is known that the refractive index of the nanocomposite film is increased after adding magnetic element. This leads to weaken of the reflected light. Therefore, the reason that such highly saturated color is obtained is that the distinct thicknesses of the oxide layer and the increasing refractive index of Co-containing anodic aluminum oxide nanocomposite film. The detailed explanation would be given by means of calculation in the following.

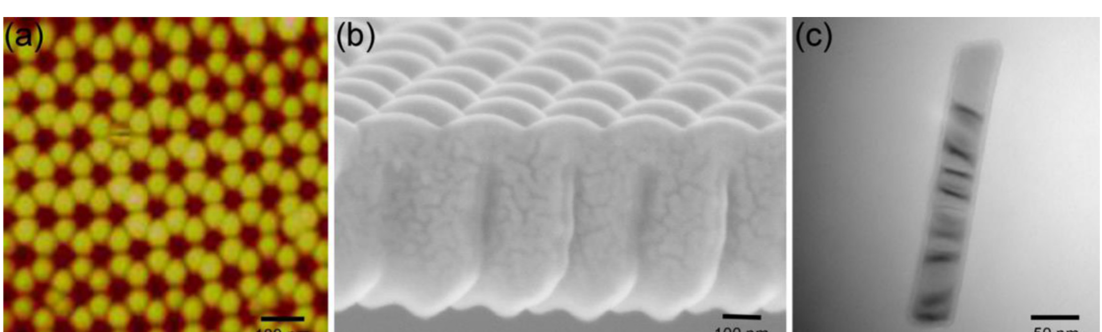

Fig. 1. SPM surface image (a) and SEM cross section image (b) of an AAO thin film. (c) TEM image of a single Co nanowire.