Comparison of optical properties of Cu-Al_2O_3 and Ag-Al_2O_3 nano-array composite structure

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Cu-Al_2O_3 (Ag-Al_2O_3) nano-array composite structures were obtained by alternating current (AC) electrodeposition Cu (Ag) into the pores of anodic alumina. Their transmitted spectra and polarized properties were investigated in detail. Experimental results indicate that the transmittance of Cu-Al_2O_3 is superior to that of Ag-Al_2O_3 in visible and infrared wavebands, and the extinction ratio is better than that of Ag-Al_2O_3 in near infrared waveband.

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Recently, porous anodic alumina, which is characterized by fine, regular, almost cylindrical and parallel pores, has attracted an increasing interest[1−6]. Various optics devices such as micropolarizer, optical phase plate and light-emitting component can be fabricated by means of embedding different metal and semiconducting nanofilament in the pores of porous anodic alumina[7,8]. In this paper, metal-Al_2O_3 nano-array composite structures are obtained by utilizing the anodic alumina acting as a host template, embedding Cu and Ag in the pores, respectively. Their transmitted and polarized properties are systematically investigated.

The porous alumina substrates were fabricated by anodizing high purity (99.999%) aluminum foils in a sulfuric acid solution. In order to homogenize the microstructures and reduce the density of defects in the foils, the aluminum foils were annealed at 550 °C before anodizing, which contribute to the formation of high quality nanochannels over large areas in the alumina substrates. After the foils were degreased and electropolished, a high quality of flat surfaces was achieved. Anodization was performed at a constant voltage of 15 V in a 20% H_2SO_4 solution for 5 hours, thus, alumina films with thickness of 21 μm and pores in diameter of 20 nm are obtained. Then, Cu or Ag was implanted into the pores of anodic alumina by means of alternating current (AC) electrodeposition for 2 hours by using $CuSO_4$ or $AgNO_3$ solution with power frequency of 200 Hz and voltage of 10 V.

After the electroplating process, the entrance of the pores was sealed in boiling water for 30 min so that the metal columns in the pores did not be eroded in the following etching process. Then the alumina film was striped from the Al in a mixed solution of Br and methanol. Finally, the samples were eluted by de-ion water thorough to clean electrolyte adsorbing both in the surface and inner of the film, and to strengthen chemical stability of the film.

The transmitted spectra of the sample were measured by UV-3101 spectrometer (400—2500 nm) and IR-460 infrared spectrometer (> 2500 nm).

In order to measure the polarized spectrum, the sample was fixed between two right-angled glass prisms with Bromonaphthalene ($n = 1.65$[9]) acting as glue, its structure is shown in Fig. 1, and the structure angle of the prism is 45°. Two cross sections and two inclined planes of the prism were excellently polished. In order to reduce optical loss in the interface between the prism and the sample as small as possible[10], the prism was made of LaK2 glass ($n = n_G = 1.67$), whose refractive index is close to that of anodic alumina ($n_1 = 1.6$).

The refractive index of layer I depends strongly on the direction of electric field. We denote the principal refractive indices of layer I as n_H and n_V for the electric field being horizontal (H) and vertical (V) to the pores. Layer I is a composite of alumina (n_1) and metal columns ($\hat{n}_2 = n_2 - j\kappa_2$). The effective refractive index of such a composite is expressed as[11]

$$\hat{n}_i = n_1 \left[1 - f\frac{n_1^2 - \hat{n}_2^2}{(1 - L_i)\, n_1^2 + L_i \hat{n}_2^2}\right]^{1/2}, \quad (i = H \text{ or } V), \tag{1}$$

where f denotes the porosity of alumina film, and L_i denotes the depolarization factor of the columns. Depolarization factors are, for example, $L_H = 0$ and $L_V = 0.5$ for long and thin columns and $L_H = L_V = 0.33$ for spheres. For different values of n and κ in horizontal (H) and vertical (V) directions, the metal-Al_2O_3 film exhibits dichroism. This leads to the polarized property of metal-Al_2O_3 film.

Dual-path equidirectional polarization method was adopted in the process of measuring the polarized spectra of the sample in order to erase influences of polarization effect on test result[12]. As shown in Fig. 2, same type polarizers were added in dual-path of the spectrometer

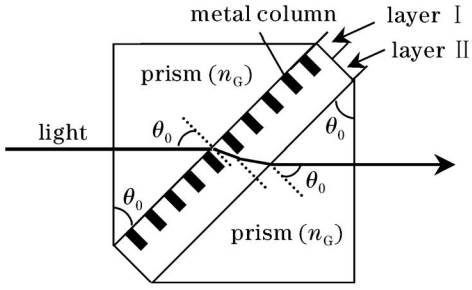

Fig. 1. Structure of testing sample.

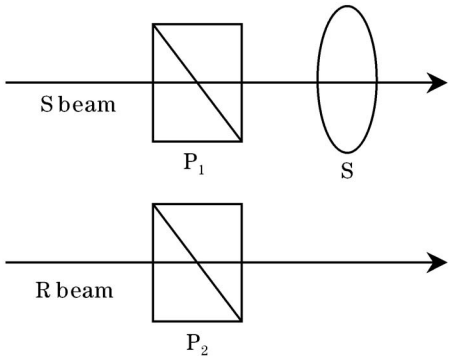

Fig. 2. Testing beam path. P_1, P_2: Glan-Tylor prisms; S: testing sample.

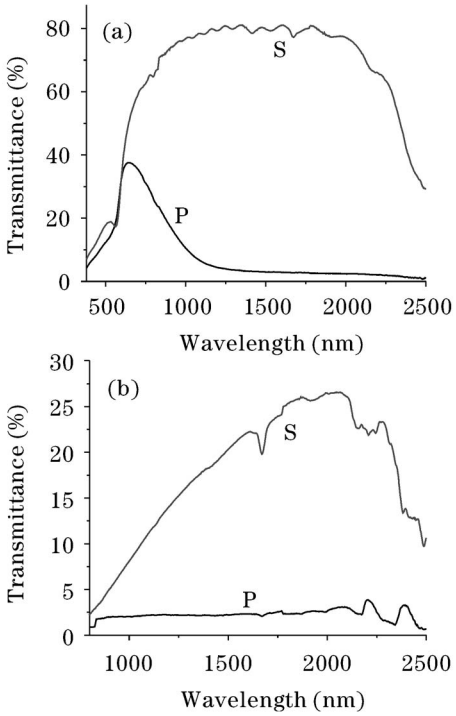

Fig. 3. Polarized spectra of anodic alumina with metal. (a) Cu-Al_2O_3, (b) Ag-Al_2O_3.

with identical polarized direction. When the sample was rotated 90° around the incident light, the transmitted curves of P and S were obtained, respectively. The extinction ratio of the anodic alumina with metal can be obtained by

$$\xi = 10 \times \log \frac{T_s}{T_p}, \tag{2}$$

where T_s and T_p denote transmittances of P and S components, respectively.

The polarized spectra of anodic alumina with metal are shown in Figs. 3(a) and (b), which correspond that of Cu-Al_2O_3 and Ag-Al_2O_3, respectively. Both Cu-Al_2O_3 and Ag-Al_2O_3 exhibited better polarization properties in near infrared waveband compared to those in visible waveband. This phenomenon may be due to the extraordinary large interval between metal column according to polarizing principle of a wire-grid polarizer[13].

Figures 4(a) and (b) show the transmitted spectra of

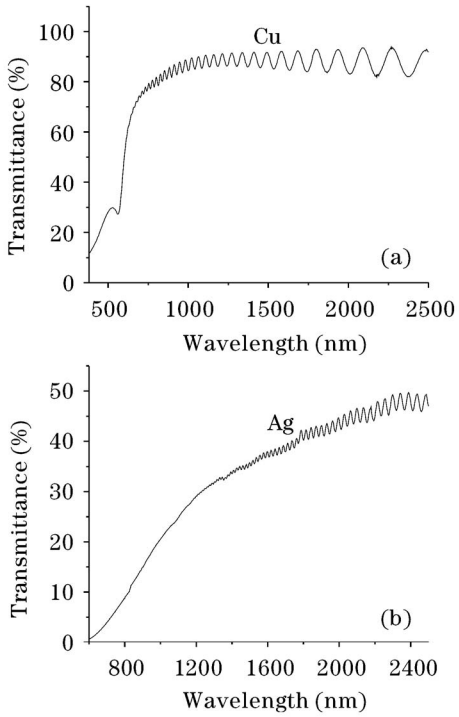

Fig. 4. Transmitted spectra of anodic alumina with metal in visible and near infrared wavebands. (a) Cu-Al_2O_3, (b) Ag-Al_2O_3.

Cu-Al_2O_3 and Ag-Al_2O_3 in visible and near infrared wavebands respectively. Both transmitted spectra of Cu-Al_2O_3 and Ag-Al_2O_3 have some vibration in near infrared waveband. It can be considered as the effect of interference inside. Though Cu-Al_2O_3 has an apparent absorption peak near 560 nm, it has good transmittance characteristic in near infrared waveband with average transmittance above 80%. Transmittance of Ag-Al_2O_3 is lower than 50% in near infrared waveband. And its transmittance is very low in visible waveband, just for this reason, its absorption peak does not show up in visible waveband.

The transmitted spectra of anodic alumina with metal in mid-infrared waveband are shown in Fig. 5. The figure shows that the transmitted spectra of anodic alumina with Cu and that with Ag both behave with the same trend in the range of 2500—8000 nm, while the transmittance of sample with Cu is superior to the sample

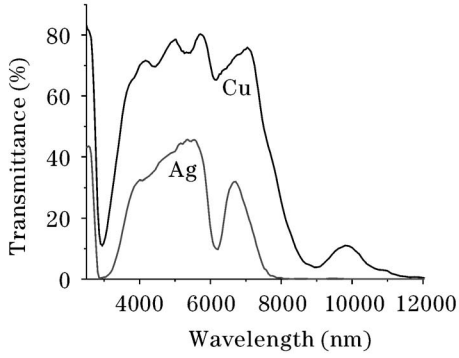

Fig. 5. Transmitted spectra of anodic alumina with metal in middle infrared waveband.

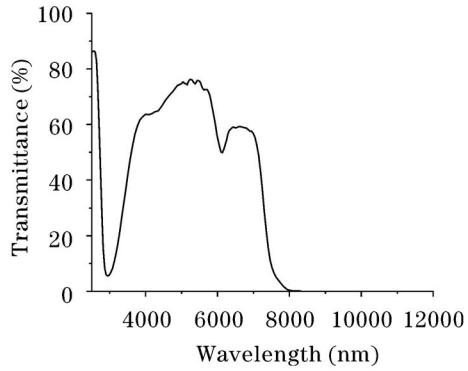

Fig. 6. Transmitted spectrum of anodic alumina in middle infrared waveband.

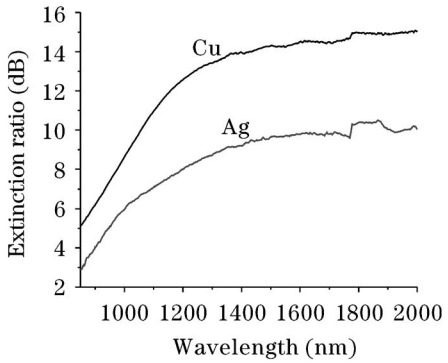

Fig. 7. Extinction ratio spectra of anodic alumina with metal.

with Ag apparently. The transmitted spectrum of anodic alumina template is shown in Fig. 6. From Figs. 5 and 6, it can be clearly seen that the nanohole metal columns do not exhibit obvious absorbing action. This phenomenon is different from that of the Refs. [14,15], in which nanohole Au columns and Cu-clusters exhibited absorbing action, and their transmitted spectral waveforms exhibited "Gauss distribution".

In order to observe the relationship between extinction ratio and wavelength, the extinction ratio spectra of Cu-Al_2O_3 and Ag-Al_2O_3 are given in Fig. 7. It can be clearly seen that the extinction ratio of Cu-Al_2O_3 is superior to that of Ag-Al_2O_3.

In this work, the metal-Al_2O_3 nano-array composite structures were obtained by AC electrodeposition Cu or Ag into the pores of anodic alumina. Their transmitted spectra and polarized spectra were investigated systematically. From the experimental result, the following conclusions can be drawn. 1) The transmittance of Cu-Al_2O_3 is larger than that of Ag-Al_2O_3. The transmittance of the former is above 80% while in the case of the latter is below 50% in the range of 700—2500 nm; the transmittance of the former is above 65% while the transmittance of the latter is about 50% in the range of 4000—7000 nm. 2) The polarization property of Cu-Al_2O_3 is superior to that of Ag-Al_2O_3; the extinction ratio of the former is above 14 dB in the range of 1200—2000 nm. So, Cu-Al_2O_3 nano-array composite structure is more suitable for fabricating micropolarizer.

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