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Optical constants of anodic aluminum oxide films formed in oxalic acid solution

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Abstract

The anodic aluminum oxide (AAO) films with highly ordered nanopore arrays were prepared in oxalic acid solution under different anodizing voltage and time, its surface and cross section appearances were characterized by using field emission scanning electron microscopy, the transmission spectra with the interference fringes were measured at normal incidence over the wavelength range 200 to 2500 nm. Then the modified Swanepoel method was used for the determination of the optical constants and thickness of the free standing AAO films. The results indicate that the refractive index increases with the increase of anodizing voltage and the decrease of anodizing time, which is mainly due to the content of Al_2O_3 with octahedron increases in the AAO films. The dispersion of the refractive index is discussed in terms of the single-oscillator Wemple–DiDomenico model, and the energy dependence of the absorption coefficient can be described using the direct transition model proposed by Tauc. Likewise, the optical energy gap E_g is derived from Tauc's extrapolation, and E_g increases from 4.178 to 4.256 eV with the anodizing voltage, but is weakly dependent on anodizing time. All the results are self-consistent in the paper.

Keywords: Anodic aluminum oxide films (AAO); Optical constants; Wemple–DiDomenico model; Dispersion parameters

1. Introduction

In recent years, the porous anodic aluminum oxide (AAO) films has received considerable attention in synthesizing nanostructure materials due to its several unique structure properties, such as controllable pore diameter, extremely narrow size distribution for pore diameters and their intervals, and ideally cylindrical shape of pores. The highly ordered polymer/AAO, metal/AAO, semiconductor/AAO, carbon/AAO nanoarray composites have been synthesized [1–6], optical properties were studied [7–10], and have great potential application for electro-optical devices. Furthermore the AAO films with highly ordered arrays have been applied as two-dimensional photonic crystals [11]. Consequently, for further studying the interesting properties appearing for the nanocomposites and designing more excellent photonic crystals related to AAO films, a complete understanding of the self-properties of the AAO films and the determination of the optical constants are necessary.

Many works have been done on optical properties of AAO films [12,13]. The AAO films formed in oxalic acid solution have a blue photoluminescence (PL) band [14], but the same PL band has not been observed obviously for the AAO films formed in sulfuric and phosphoric acid solution. The birefringence of AAO films has been studied in reference [15], the birefringence Δn of AAO films satisfies $\Delta n = 0$ at normal incidence. In our previous works [16], the Swanepoel method [17,18] was modified to determine the optical constants of uniform thickness and free standing AAO films formed in

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Table 1
Optical parameters characterization of AAO films as a function of process parameters such as anodizing voltage and anodizing time

Sample	*a*	*b*	*c*	*d*	*e*	*f*
Voltage (V)	30	40	45	20	20	20
Time (h)	2	2	2	3	4	5
Thickness[a] d (nm)	1986±3	3397±16	4463±8	1915±3	2151±15	3006±6
Δd (nm)	36	30	40	59	45	49
E_g (eV)	4.178	4.217	4.256	4.255	4.257	4.243
E_0 (eV)	10.85	9.43	10.66	9.43	7.98	9.16
E_d (eV)	15.11	14.47	17.34	17.29	12.41	11.96
Al^{3+} coordination number N_c	3.40	3.26	3.90	3.89	2.80	2.70
$n(0)$	1.547	1.592	1.621	1.683	1.599	1.519

[a] Here the error in thickness is the standard deviation of thickness calculation.

sulfuric solution, the calculated thicknesses d are agreed with the measured very well. However, no reports are available on the determination of AAO films formed in oxalic acid solution and the modulation on the optical constants by the process parameters. Hence in the paper, the transmission spectra of AAO films at normal incidence was measured over the wavelength range 200 to 2500 nm. Based on the measured transmission, the modified Swanepoel technique [16,19] was used to accurately determine the optical parameters of non-uniform thickness and free standing AAO films formed in oxalic acid solution, and investigate the dependence of optical constants of AAO films on the process parameters, namely, anodizing voltage and anodizing time, so that the optical properties of AAO film can be modulated conveniently for various needs by the process parameters.

2. Experiment

A detailed report on porous anodic aluminum oxide (AAO) formation can be found in Refs. [10,16]. Here, we just give a brief description of the preparation of our samples. First, high purity (99.999%) aluminum foils were degreased in acetone, etched in alkaline solution and rinsed in distilled water. Subsequently, the aluminum was electropolished in a 1:4 volume mixture of $HClO_4$ and C_2H_5OH to achieve a smooth surface, then rinsed in distilled water and transferred to a nitrogen environment.

Anodization was conducted under constant cell potential in 0.3 M oxalic acid solution that was used as electrolytes. The aluminum foils were mounted on a copper plate serving as the anode and exposed to the acid in a thermally isolated electrochemical cell. During anodization, the electrolyte was rigorously stirred or recycled using a pump system to keep a stable temperature (0 °C) in the electrolyte. The values of the anodizing voltage and anodizing time were listed in Table 1. After anodization, the remaining aluminum was removed in a saturated $HgCl_2$ solution.

Surface and cross section morphology of AAO membrane were characterized by using field emission scanning electron microscopy. A Perkin-Elmer UV–VIS–NIR lambda-900 spectrophotometer was employed to measure the transmission spectra at normal incidence of the AAO films over the wavelength range 200–2500 nm.

3. Theory

A simple method for accurate calculation of the main optical constants such as the refractive index n and the extinction coefficient k as a function of wavelength λ of AAO films has been achieved by using the modified Swanepoel technique [16] based on the extremes of the normal transmittance interference fringes. The samples without transparent substrate under investigation are regarded as non-uniform thin films in their thickness. It is supposed that the film thickness d varies between $d+\Delta d$ and $d-\Delta d$, where d is the average thickness and Δd refers to the actual variation in the thickness of the samples.

Based on the Newton–Raphson iteration technique, the unknown approximation values of the refractive index n and the Δd can be calculated, taking into account the transparent region (i.e. where the absorbency $x=1$) by solving the two equations [16,17]:

$$T_M = \frac{\lambda}{2\pi n \Delta d}\frac{a}{\sqrt{1-b^2}}\tan^{-1}\left[\frac{1+b}{\sqrt{1-b^2}}\tan\left(\frac{2\pi n \Delta d}{\lambda}\right)\right] \quad (1)$$

and

$$T_m = \frac{\lambda}{2\pi n \Delta d}\frac{a}{\sqrt{1-b^2}}\tan^{-1}\left(\left[\frac{1-b}{\sqrt{1-b^2}}\tan\left(\frac{2\pi n \Delta d}{\lambda}\right)\right]\right) \quad (2)$$

where T_M and T_m are the experimental envelopes of the non-uniform thickness film, $a=A/(B+D)$, $b=C/(B+D)$, $A=16n^2$, $B=(n+1)^4$, $C=2(n^2-1)^2$, $D=(n-1)^4$. Then, using the calculated value of Δd corresponding to the high wavelength, the first approximation values of the refractive index n and the absorbency x, for $0<x<1$ and absorption coefficient $\alpha>0$, can be calculated by solving the following equations:

$$T_M = \frac{\lambda}{2\pi n \Delta d}\frac{a_x}{\sqrt{1-b_x^2}}\tan^{-1}\left[\frac{1+b_x}{\sqrt{1-b_x^2}}\tan\left(\frac{2\pi n \Delta d}{\lambda}\right)\right] \quad (3)$$

and

$$T_m = \frac{\lambda}{2\pi n \Delta d}\frac{a_x}{\sqrt{1-b_x^2}}\tan^{-1}\left[\frac{1-b_x}{\sqrt{1-b_x^2}}\tan\left(\frac{2\pi n \Delta d}{\lambda}\right)\right] \quad (4)$$

where $a_x=Ax/(B+Dx^2)$, $b_x=Cx/(B+Dx^2)$.