Tunable structural color of anodic tantalum oxide films*

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Tantalum (Ta) oxide films with tunable structural color were fabricated easily using anodic oxidation. The structure, components, and surface valence states of the oxide films were investigated by using gazing incidence X-ray diffractometry, X-ray photoelectron microscopy, and surface analytical techniques. Their thickness and optical properties were studied by using spectroscopic ellipsometry and total reflectance spectrum. Color was accurately defined using $L^*a^*b^*$ scale. The thickness of compact Ta_2O_5 films was linearly dependent on anodizing voltage. The film color was tunable by adjusting the anodic voltage. The difference in color appearance resulted from the interference behavior between the interfaces of air–oxide and oxide–metal.

Keywords: anodic tantalum oxide, structural color, spectroscopic ellipsometry, optical interference

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1. Introduction

Structural colors are produced by interference effects rather than created from pigments. Examples of these are feathers of birds and wings of insects, which do not only offer visual aesthetics, but also provide mental entertainment. The colors of structurally colored films shift according to Bragg's law, which states that optical path length is a function of film thickness and index of refraction. Light being reflected from the air–film surface undergoes constructive and deconstructive interferences with light reflected on the underlying polymer–substrate interface. This results in selective wavelength reflection. In the past years, a number of man-made colored structures,[1−4] such as porous silicon and porous aluminum, have been investigated for potential applications in sensing and displays.

Several valve metals, including titanium, aluminum, zirconium, and niobium are known to produce colored passive layers upon undergoing anodic oxidation in a variety of acid- and salt-type electrolytes with the application of direct or alternating voltage.[5−9] Tantalum (Ta) oxide has been widely studied because of its outstanding properties, such as chemical resistance, good conductivity, high melting point, ductility, and mechanical strength.[10−12] Anodization of Ta with all kinds of structures, such as nanoporous, nanotubes, and dimples structures, has been investigated.[13−15] However, only minimal knowledge on structural color changes of uniform and compact anodic Ta oxide films is available.

In the present study, we demonstrate that uniform and compact amorphous Ta_2O_5 films created by the simple anodic oxidation of Ta sheets with varied voltages can present abundant and tunable structural colors. $L^*a^*b^*$ scale, total reflectance, and spectroscopic ellipsometry were used to investigate optical constants and thicknesses of films. Relationships between color, thickness, and applied voltage are discussed.

2. Experimental procedure

Prior to the anodic oxidation experiment, high-purity Ta metal sheets (99.99%), with a thickness of 0.25 mm, were separately degreased by sonication in acetone and alcohol. Subsequently, the sheets were rinsed with distilled water, and dried in air naturally.

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To obtain a smooth surface, the sheets were electropolished in a mixture of concentrated H_2SO_4 and 48% aqueous hydrogen fluoride (HF) solution with a 9:1 volumetric ratio for 20 min. To grow oxide films, anodic oxidation was conducted in a 1-M H_2SO_4 solution with different voltage designs for 20 min at room temperature. A large graphite plate was used as counter electrode. After anodic oxidation treatment, the specimens were thoroughly washed with distilled water and dried in an air stream.

Optical photographs of samples made with the application of different constant voltages, from 40 V to 110 V and a step width of 10 V, were taken by using a digital camera at a shooting angle of about 90°. The surface morphology of the films was investigated by using a field-emission scanning electron microscope (FE-SEM) (Sirion 200). Compositional analyses were performed using gazing incidence X-ray diffratometry (GIXRD) with X'Pert (Cu Kα, λ = 1.54059 Å, 1 Å = 0.1 nm). Surface valent states of anodic oxide films were analyzed by X-ray photoelectron microscopy (XPS), using Al Kα source. All binding energy values were calibrated using contaminated carbon (284.6 eV) as reference.

To characterize the color and the optical properties of the samples, the $L^*a^*b^*$ scale was utilized, according to the 1976 norm of the Commission Internationale d'Eclairage (CIE). The reflectance spectra in the 400 nm–700 nm range were obtained by ColorQuest@XE (HunterLab Company) using an incidence angle of 8°. Refractive index and thickness of the transparent oxide surface layers were determined by simulation with a simple model on a UVISEL ER spectroscopic ellipsometer.[16,17] A clean Ta foil was used as the standard for reference.

3. Results and discussion

We successfully produced anodic oxide films with tunable colors by anodizing Ta sheets in 1-M H_2SO_4 solution with different voltages. Figure 1(a) shows typical optical photographs of colorful films in the range of blue, indigo, Indian red, golden red, gray, grayish blue, and so on. Colors of films depend on anodic voltages and their coloration is uniform across the whole surface. This colored passive layer is considerably stable and does not fade with prolonged exposure to air for several months or years. Figure 1(b) depicts a typical SEM image for anodic Ta oxides, demonstrating that the surface morphology of the film is very flat and smooth. There are no significant changes in the morphologies of the colorful passive films prepared using 40, 50, 60, 70, 80, 90, 100, and 110 V. As shown in Fig. 1(b), the films mainly consist of numerous uniform micro-sized particles. No obvious surface defects were observed, indicating the compactness and uniformity of these films. It was only with the application of very high voltage (approximately 120 V), which caused electrical breakdown of Ta oxide films, that we observed numerous large cavities and non-uniform colors on the surface.

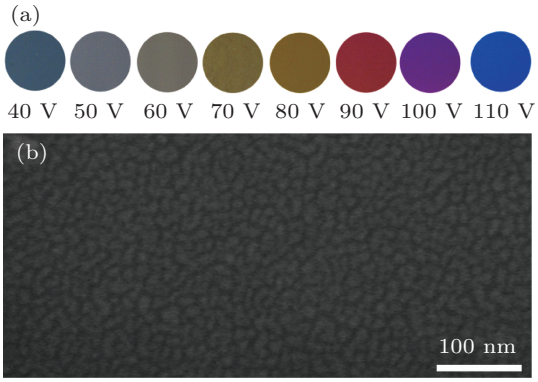


Fig. 1. (colour online) (a) Optical micrographs, viewed from an angle of about 90°, of colorful Ta-oxide films obtained by anodic oxidation of Ta sheets which were anodized for 20 min under different voltages (from 40 V to 110 V); (b) Top view of an FE-SEM image from a typical anodic oxide film.

GIXRD and XPS measurements were used to investigate the phase structure of passive oxide films. In the GIXRD spectrum, aside from metallic Ta diffraction peaks, no other peaks were observed (not shown). We conclude that the anodic film formed is predominant in an amorphous structure. In the XPS spectra of TaO_x films, as shown in Fig. 2, two Ta $4f_{7/2}$ and $4f_{5/2}$ peaks are located at binding energies of 26.04 eV and 27.84 eV. This indicates that Ta in oxide films is in a valent state of Ta^{5+}. The calculated O/Ta atomic ratio is greater than the theoretical value of 2.5. Excess oxygen could have come from absorbed pollutants during the test. The above analysis demonstrates that amorphous Ta_2O_5 compact films can be obtained using a simple anodic oxidation technique.

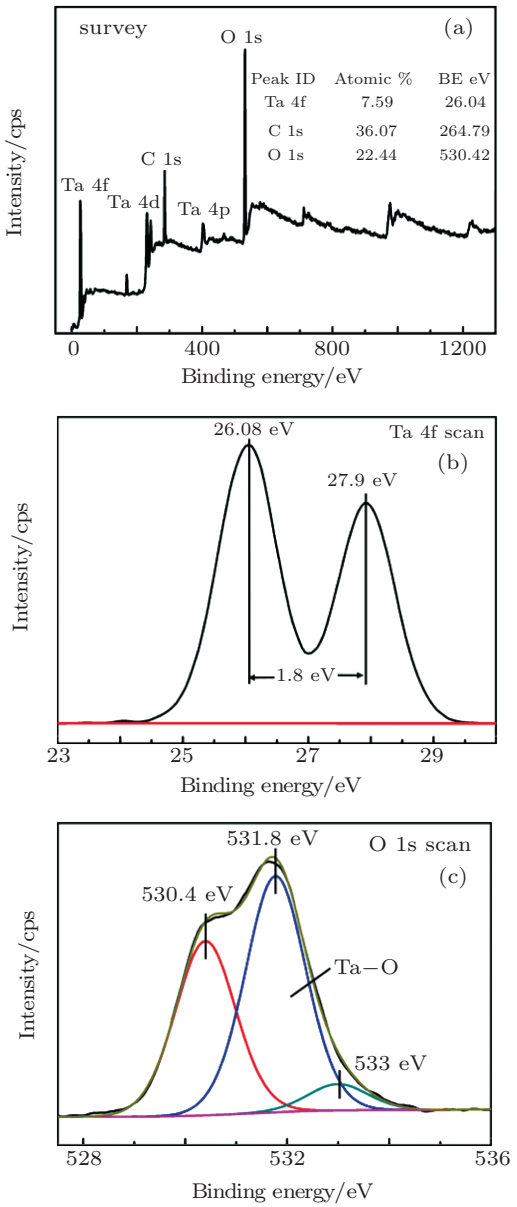


Fig. 2. (colour online) The XPS spectra of TaO_x films obtained by anodic oxidation: (a) all-survey XPS spectrum of TaO_x films; (b) valence band spectrum of Ta and high resolution XPS $4f_{7/2}$ and $4f_{5/2}$ spectra, with binding energies (BE) located at 26.04 eV and 27.84 eV; (c) valence band spectra of O after Gaussian fitting.

Table 1. $L^*a^*b^*$ values of Ta oxide film.

Anodizing voltage/V	L^*	a^*	b^*	Chromaticity
40	57.43	−5.4	−21.42	22.09
50	70.05	−2.1	−8.18	8.45
60	74.59	1.8	−21.42	22.09
70	70.08	7.8	33.09	34.87
80	65.74	17.65	63.79	66.05
90	53.15	33.98	12.04	64.54
100	35.1	31.5	−56.02	24.30
110	42.29	−35.38	−53.98	21.67

Color properties can be described accurately using the $L^*a^*b^*$ scale, and color saturation can be measured by the chromaticity $\sqrt{(a^*)^2 + (b^*)^2}$, which expresses the amount of color. Chromaticity coordinates were calculated. Results are presented in Table 1. Chromaticity is very high, with values above 8. These samples have high color saturation.

As voltage changes, surface color shows obvious changes. Thickness of the transparent oxide surface layers, which is obtained through SE measurement,[18] is directly dependent on anodic oxidation voltage. Figure 3 shows that in the measured voltage range, film thickness growth is a linear function of applied voltage and is derived by the relation $d = kV + a$. From the slope of the linear function, we can approximate film thickness growth per volt, i.e., $d = 1.91$ nm/V, which is consistent with the results of Guntherschulze.[19]

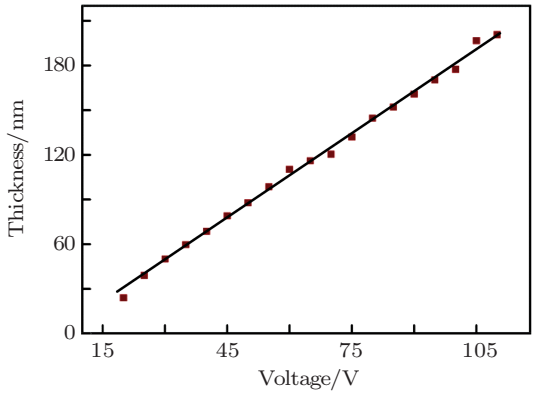


Fig. 3. (colour online) Linear relationship between thickness and anodic voltage.

In addition, different colors can be reflected by different reflectance spectra. Figures 4(a) and 4(b) show the different reflectance spectra of samples with anodizing voltages ranging from 20 V to 65 V and from 65 V to 120 V, respectively (facing air, $n = 1$). Reflectance oscillates between 0% and 60%. The variation of the reflectance spectrum with the voltage presents the typical features of the variation along with the film thickness. Samples with voltages below 65 V show a narrow undulation spread over the full spectrum. Total reflectance increased as films thickened, which displays the lightness of the films. Interference phenomena failed to explain this result probably because the films are too thin to satisfy the interferential condition. However, samples treated with voltages over 65 V show one broad valley. The corresponding wavelength value shows a regular increase with a change in film thickness. Further, the color corresponding to the wavelength is a complementary color of the visual hue of the film. This phenomenon

can be explained fully by interference behavior. In our air/oxide/metal system, when light reaches the surface of an oxide film, some of the light is reflected on the upper air/oxide film boundary, and some light travels through the oxide film and is subsequently reflected on the lower oxide/metal boundary. In general, two rays achieve a phase difference as they emerge at the upper boundary. If the two rays are in phase (the hump and the valley are together), maximum light intensity is reflected. If they are out of phase, less intensity is reflected. Intensity of the reflected light varies with film thickness. In the reflectance spectra in Fig. 4(b), the minima comply with the following formula: $nd = (m + 1/2)\lambda$, $m = 0, 1, 2, \ldots$, where n denotes the reflective index of the Ta_2O_5 thin film, as shown in Fig. 5(b), d is the thickness of the film, and λ is the wavelength corresponding to the minima in the reflectance spectra. Consequently, the thickness of the layer can be calculated. As shown in Fig. 5(a), a good accordance is observed between the theoretical values from the ellipsometry results and the experimental results. The theoretical values are slightly higher compared with the experimental ones, which mostly stem from the neglect of the transition layer and from the rough laminar between the oxide and the metal interfaces in the SE fit process.[20–22]

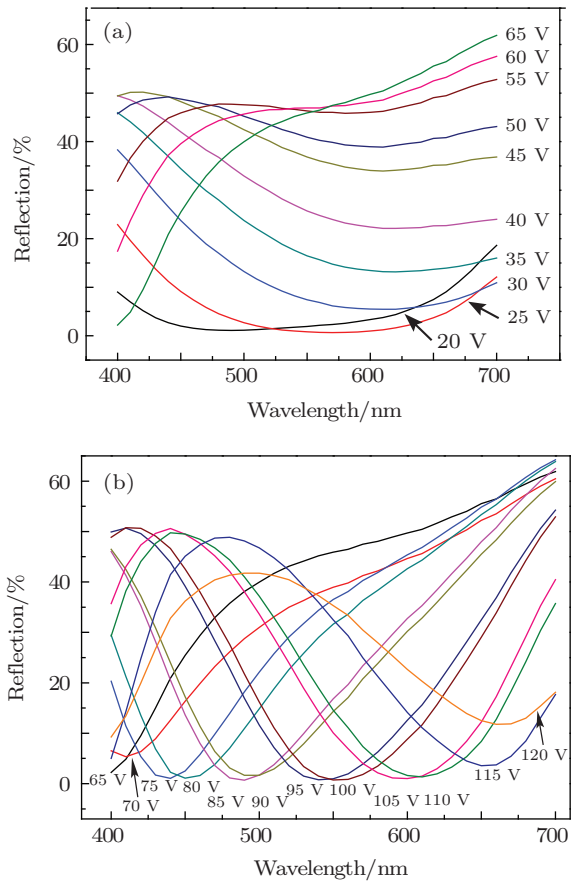


Fig. 4. (colour online) Reflectance oscillations between 0% and 60%. Samples with low voltages (a) show a narrow undulation spread over the full spectrum, whereas those with high voltages (b) can be explained by optical interference.

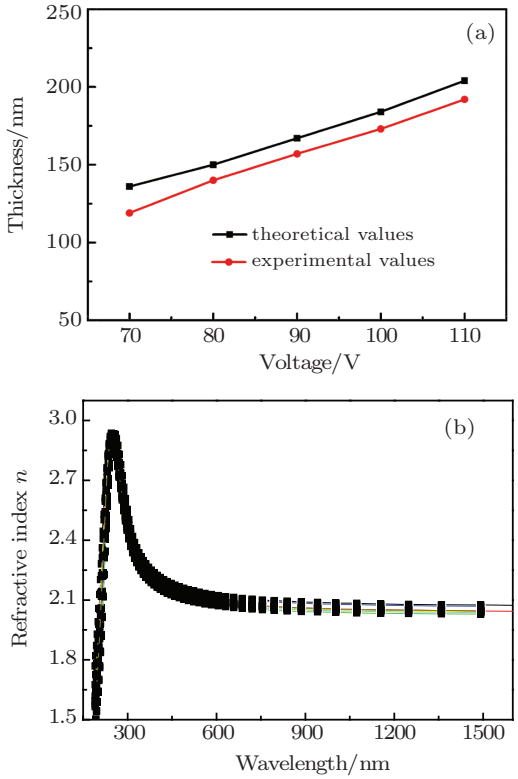


Fig. 5. (colour online) (a) The voltage thickness relationship as depicted from ellipsometry spectrum and interferential calculation data; (b) the refractive index n of the oxide films.

4. Conclusions

Amorphous Ta_2O_5 thin films with tunable structural colors were fabricated successfully by anodic electrochemical oxidation of Ta metal sheets. The structure, components, and surface valence states of the oxide films were investigated systematically by using various techniques. The optical colors and refractive index of oxides were analyzed based on optical reflectance spectra and thickness measurements. The color is directly related to the thickness of uniform, compact Ta_2O_5 films, and thickness is linearly dependent on the anodizing voltage, with a formula of $d = 1.91$ nm/V. The thickness-dependent color variation could be reasonably understood by using the optical interference phenomena. These uniform, compact Ta-oxide films with tunable structural colors are expected to find practical applications, for example, as a platform for optics-based chemical or biological

sensing.

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