Optical and structural properties of Ta$_2$O$_5$–CeO$_2$ thin films

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Abstract

In this study, the sol–gel spin-coating method has been used to make Ta$_2$O$_5$–CeO$_2$ thin films. These films have been prepared in various composition ratios to observe changes in their optical and structural properties. Reflectance and transmittance spectra were collected in the spectral range of 300–1000 nm and were accurately fit using the Tauc–Lorentz model. Film thicknesses, refractive indices, absorption coefficients, and optical band gaps were extracted from the theoretical fit. The highest refractive index value was found at 5% CeO$_2$ doping. The structure of the films was characterized by X-ray diffractometry and Fourier transform infrared spectrometry, while the surface morphology was examined through atomic force microscopy.

Keywords: Sol–gel; Spin coating; Ta$_2$O$_5$–CeO$_2$ thin films; Tauc–Lorentz model

1. Introduction

Ta$_2$O$_5$ films have been widely studied due to their chemical and thermal stability, high dielectric constant and refractive index. Their applications include ion conductors for electrochromic devices [1,2], optical waveguides [3,4] and protective coatings [5]. As microelectronics moves toward the nanoscale, SiO$_2$ will reach its practical limit due to direct tunneling currents at 1–2 nm thicknesses, and high-permittivity materials like Ta$_2$O$_5$ are possible replacements for SiO$_2$ in next-generation devices such as ultra-high-density dynamic random-access memories (DRAMs) [6,7].

It is known, for certain composites of Ta$_2$O$_5$–TiO$_2$, Ta$_2$O$_5$–Al$_2$O$_3$, and Ta$_2$O$_5$–ZrO$_2$ polycrystalline ceramics [8–10], that there is a significant increase in the dielectric constant compared to pure Ta$_2$O$_5$; this has stimulated research of doped thin films of Ta$_2$O$_5$ for use in microelectronics. Gan et al. [11] investigated the change in the dielectric constant of magnetron sputtered Ta$_2$O$_5$–TiO$_2$ films as a function of the composition. Cevro deposited Ta$_2$O$_5$–SiO$_2$ thin films by ion-beam sputtering using a single ion-beam gun and determined the optical properties as a function of the composition of the films [12]. Cappellani et al. characterized sol–gel-made Ta$_2$O$_5$ and Ta$_2$O$_5$–TiO$_2$ dielectric thin films [13]. Kaliwoh et al. studied the growth of Ta$_2$O$_5$–TiO$_2$ films using excimer lamps with photo-induced CVD [14] and sol–gel methods [15]. The present work reports on the optical and structural properties of sol–gel derived Ta$_2$O$_5$–CeO$_2$ thin films for compositions of 5%, 10%, and 15% CeO$_2$ (by volume) prepared with the spin-coating method.

2. Experimental procedure

The preparation of Ta$_2$O$_5$ coating solution is described elsewhere [16], with the only difference that in our case, the initial molarity of tantalum ethoxide in ethanol was 0.13 M. Cerium oxide solution was prepared using cerium ammonium nitrate (Ce(NH$_4$)$_3$(NO$_3$)$_6$) [99.99 %, Aldrich], absolute ethyl alcohol (EtOH) [99.8%, Riedel-deHaën], nitric acid (HNO$_3$) [65%, Carlo] and diethanolamine (DEA,
We construct a simple theoretical model which can be used to extract the film refractive index $n_{\text{film}}(\lambda)$ and absorption coefficient $\alpha_{\text{film}}(\lambda)$ functions from the reflectance and transmittance spectra of the film-substrate system, adapting the approach of Ref. [17]. Fig. 1(a) shows schematically the passage of a light beam through the system. Since the thickness of the film, $d_{\text{film}} \approx 10^2 \text{ nm}$, has the same order of magnitude as the wavelength of the incident light, the multiple reflected and transmitted beams as the light is passing through the film are nearly coherent. In contrast, the thickness of the substrate is $d_{\text{sub}} \approx 10^6 \text{ nm}$, so that beams passing one or more times through the substrate are treated as incoherent. We identify three sets of reflection and transmission coefficients, shown in Figs. 1(b)–(d): $r_1$, $t_1$, for a beam passing through the film from the outside in; $r_2$, $t_2$, for a beam from within the substrate hitting its uncoated back surface; and $r_3$, $t_3$, for a beam passing through the film from the inside out. All these coefficients can be easily determined through the standard transfer matrix method [18], and expressed as functions of $d_{\text{film}}$, $n_{\text{film}}(\lambda)$, $\alpha_{\text{film}}(\lambda)$, and the substrate refractive index $n_{\text{sub}}(\lambda)$. The reflection and transmission coefficients for beams making multiple passes through the substrate are just products of the $r_i$ and $t_i$, as shown in Fig. 1(a). Additionally, we took into consideration that every time the light passes from one side of the substrate to the other, its intensity is reduced by a factor $\delta_{\text{sub}}(\lambda) = \exp(-\alpha_{\text{sub}}(\lambda)d_{\text{sub}})$, where $\alpha_{\text{sub}}(\lambda)$ is the substrate absorption coefficient. Even a relatively small increase in $\alpha_{\text{sub}}(\lambda)$, for example in the near-UV region ($\lambda \lesssim 350 \text{ nm}$), will result in a significant intensity loss because $d_{\text{sub}} \approx 10^6 \text{ nm}$. Putting

$$\alpha_{\text{film}}(\lambda) = \exp(-\alpha_{\text{sub}}(\lambda)d_{\text{sub}})$$
everything together, the total $R$ and $T$ of the film-substrate system is found by summing the coefficients of the series of beams incoherently:

$$R = |r_1|^2 + \sum_{n=0}^{\infty} \delta_{\text{sub}}^{2n+1} |r_1 r_2^{n+1} f| t_1^2 = |r_1|^2 + \frac{\delta_{\text{sub}} |r_1 r_2 t_1|^2}{1 - \delta_{\text{sub}} |r_2 t_1|^2},$$

$$T = \sum_{n=0}^{\infty} \delta_{\text{sub}}^{2n} |r_1 r_2^n f|^2 = \frac{\delta_{\text{sub}} |r_1 t_2|^2}{1 - \delta_{\text{sub}} |r_2 t_1|^2}. \tag{1}$$

To determine $n_{\text{sub}}(\lambda)$ and $\delta_{\text{sub}}(\lambda)$, the reflectance and transmittance spectra of an uncoated substrate were fitted to a version of Eqs. (1) and (2) suitably modified for a naked substrate. This gives a value for $n_{\text{sub}}(\lambda)$ and $\delta_{\text{sub}}(\lambda)$ at each measured wavelength $\lambda$, and the values were interpolated to get continuous functions over the whole wavelength range. The results are shown in Fig. 1(e) and (f).

The final element of the theoretical description is the choice of a physical model for $n_{\text{film}}(\lambda)$ and $\alpha_{\text{film}}(\lambda).$ For this purpose we employed the Tauc–Lorentz form of the dielectric function [19], which has been successfully applied to a variety of semiconductors and insulators [20], among them thin layers of TiO$_2$, Ta$_2$O$_5$, and other optical coating materials [21]. In an attempt to capture the optical response of the material both near the optical band gap and at much larger energies, the imaginary part of the Tauc–Lorentz dielectric function was taken as the product of a Tauc law and a Lorentz oscillator. In addition, the real and imaginary parts of the dielectric function were correctly related through a Kramers–Kronig transformation. As a result, the model was able to accurately reproduce experimental results over a wide spectral range, including regions both above and below the band edge. We used a modified version of the Tauc–Lorentz model which incorporates the possibility of Urbach tail absorption in the subgap region [22]. The imaginary part of the dielectric function $\alpha_2(E)$ as a function of photon energy $E$ is given by

$$\alpha_2(E) = \begin{cases} \frac{E_1}{E} \exp \left( \frac{E - E_1}{E_a} \right) & \text{for } E \leq E_1, \\ \frac{A E_0 \Gamma (E - E_2)^2}{E(E^2 - E_0^2)(E - E_0)^2 + \Gamma^2 E^2} & \text{for } E > E_1. \tag{3} \end{cases}$$

Here there are six fitting parameters with the dimension of energy, which are defined as follows: $E_1$ marks the border between the region of Urbach tail and band-to-band transitions; $E_g$ is the optical band gap; $E_a$ controls the width of the Urbach tail, since the form of $\alpha_2(E)$ for $E \leq E_1$ leads to an absorption coefficient $\alpha_{\text{film}}(E) \propto \exp(E/E_a);$ $A$, $E_0$, and $\Gamma$ are, respectively, the Lorentz oscillator amplitude, resonance energy, and oscillator width. The parameter $E_1$ is not free, but chosen so that $\alpha_2$ is continuous at $E = E_1$. In general, $E_1 \geq E_g$, and the original Tauc–Lorentz model is obtained in the limit $E_a = 0$, $E_1 = E_g$.

### 4. Results and discussion

Fig. 2 shows that the number of extrema in the $R$ and $T$ curves remains the same with increasing CeO$_2$ content for...
the given spectral region, which indicates that the film thicknesses are of the same order; this is supported by the thickness results in Table 1. For the visible region, the transmittance values are between 88–73% for the pure Ta$_2$O$_5$ film and 88–70% for the 5%, 10%, and 15% CeO$_2$-doped films. The maximum transmittance (88%) for the 100% Ta$_2$O$_5$ film is observed at the wavelength 780 nm; the 5%, 10%, and 15% CeO$_2$-doped films all have the maximum at 705 nm with values of 88%, 88% and 87%, respectively. The second-largest transmittance (87%) for the pure Ta$_2$O$_5$ film is reached at the wavelength 410 nm; the 5%, 10%, and 15% CeO$_2$-doped films have local maxima at 390, 400, 405 nm with values of 83%, 81% and 77%, respectively.

As evident from Table 1 and Fig. 3, there is a sudden increase in the refractive index when Ta$_2$O$_5$ is doped with 5% CeO$_2$. The index drops off at 10% doping (though the decrease is slight at shorter wavelengths), and again at 15%. The absorption coefficient in the near-UV region increases dramatically with CeO$_2$ doping, and the absorption edge shifts to longer wavelengths compared to the pure Ta$_2$O$_5$ film. This is reflected in the optical band gap, which shows a marked decrease from 3.85 ± 0.06 eV in the pure sample (comparable to the earlier sol–gel result of 3.75 [16]) to 2.65 ± 0.02 eV at 5% doping. The band gap remains essentially unchanged (within the uncertainty) at 10% doping, but falls to 2.5 ± 0.03 eV at 15% doping.

The XRD measurements revealed that the Ta$_2$O$_5$–CeO$_2$ films heat treated at 550°C were all amorphous. Even
though CeO$_2$ has a crystallization temperature at or above 400°C [23], because Ta$_2$O$_5$ begins to crystallize at 600°C and becomes perfectly crystallized above 700°C [24], Ta$_2$O$_5$ apparently shifted the crystallization temperature of CeO$_2$ to a higher value.

The evolution of the chemical structure of Ta$_2$O$_5$–CeO$_2$ thin films with the composition is given by the ATR-FTIR spectra in Fig. 4. In Fig. 4(a), Ta–O–Ta stretching vibrational modes can be seen between 650 and 800 cm$^{-1}$, while the 800–1000 cm$^{-1}$ absorption band indicates the presence of suboxides TaO and TaO$_2$ [25]. The small bands located at 1041 and 1123 cm$^{-1}$ belong to C–C and C–O bending modes, respectively. The band around 1356 cm$^{-1}$ can be attributed to C–H deformation, which is supported by the stretching vibrational modes of C–H bonds found at 2827 and 2883 cm$^{-1}$. Similarly, vibrations of bending modes of C–H are seen in the sharp absorption peak at 1586 cm$^{-1}$, which is located in the 1498–1702 cm$^{-1}$ band region [25,26]. The broad band around 3286 cm$^{-1}$ is related to the stretching vibration of H$_2$O content and O–H groups. When Figs. 4(a)–(d) are compared, it can be seen that the Ta–O–Ta and TaO, TaO$_2$ suboxide absorption peaks and bands become less distinct with increasing CeO$_2$ concentration, while the amplitudes of the other absorption peaks increase.

AFM images of the Ta$_2$O$_5$–CeO$_2$ films are given in Fig. 5. The surface morphology is dominated by islands whose average diameters increase with doping: 79 ± 4, 97 ± 5, 107 ± 6, and 153 ± 8 nm going from the pure to the 15% doped samples. The maximum height ranges of the AFM images vary between 9 and 17 nm, indicating that even the steepest valleys between the islands are shallow compared to the total thickness of the films (∼200 nm). Thus the islands are connected to each other, at least within the resolution of the AFM probe. The root-mean-square (RMS) roughness values of the samples are 1.3, 1.8, 1.9, and 2.5 nm for the pure, 5%, 10%, and 15% CeO$_2$-doped films, respectively. These relatively small roughness values indicate that the top surfaces of the islands are nearly coplanar, with a slight increase in roughness at larger
dopings. At all doping levels the films were found to be crack-free.

5. Conclusion

This work examined how the optical and structural properties of sol–gel spin coated Ta$_2$O$_5$–CeO$_2$ thin films heat treated at 550 °C evolved with CeO$_2$ concentration. As determined through fitting to the Tauc–Lorentz model, the most notable change in the optical properties occurred with 5% CeO$_2$ doping: a significant increase of the refractive index and a decrease of the optical band gap. Characterization of the films showed that their structure was amorphous at all doping levels, while both the chemical properties and surface morphology changed. The latter exhibited connected islands of increasing diameter with doping, while the overall surface roughness remained small.

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References