Optical properties of ion assisted deposited zirconia thin films

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The nature of the dependence of refractive index, extinction coefficient, and packing density of zirconia films prepared by ion assisted deposition on the energy and current density of ions has been investigated. A broad beam Kaufman ion source has been used to generate oxygen ions in the energy range 100–700 eV and current densities up to 220 $\mu\text{A}/\text{cm}^2$. It has been found that the refractive index increases steadily up to an energy of 500 eV beyond which there is a nominal decrease. The highest index obtained was 2.21 at an energy of 500 eV and a current density of 220 $\mu\text{A}/\text{cm}^2$. Similarly, with an increase in the current density the refractive index increases initially and seems to saturate beyond a certain critical value dependent on the ion energy. The extinction coefficient was low up to an energy of 300 eV showing a marked increase thereafter. The extinction coefficient was also found to increase at high ion current densities and energies. A critical ion energy and current density beyond which the refractive index as well as the extinction coefficient of these films start deteriorating has been observed.

1. INTRODUCTION

The effect of ion bombardment on growing films has been the subject of many reviews in the recent past.¹ Ion bombardment can be used to control a variety of properties of the thin films like refractive index, absorption, scattering, stress, hardness, microstructure, structure, thermal conductivity, etc. The main motivation behind the work on optical coatings has been to prepare films with bulklike properties. The deviation of optical properties of the films from the corresponding bulk material is a consequence of the microstructure of the films. The microstructure of the films deposited by conventional physical vapor deposition (PVD) techniques is columnar which results in lower packing density and hence lower refractive index in these films. It has been found that ion bombardment of the films during deposition significantly reduces the columnar character of the films. This occurs due to the energy imparted by the ions to the adatoms increasing their mobilities, as well as reactivity in the case of reactive ion beam deposition. Some of the techniques that commonly use ions are activated reactive evaporation, ion plating, ion assisted deposition and ion beam sputtering. The latter two techniques are the most commonly used ones for producing high quality optical coatings.

Zirconia is considered a good material for optical coatings because of its fairly high refractive index (2.21 at 600 nm) and low absorption. It has been deposited by a wide range of techniques like evaporation, sputtering, ion plating, pulsed laser deposition etc. But most of these techniques result in films with either crystalline or optical inhomogeneity. Although there are some reports on the optical properties of ion assisted deposited^{14–16} and ion beam sputtered¹⁷ zirconia films, very few systematic studies of the variation in the refractive index and optical extinction coefficient with ion energy and current density have been reported to the best of the present workers knowledge.

Previous work by the present authors¹⁸ focused on the optical properties of zirconia films deposited in neutral and

low energy oxygen ions produced from a Heitmann type discharge source. This article presents a systematic study of the variation in these properties with ion energy and ion current density using a Kaufman ion source,

II. EXPERIMENTAL

The films were coated in an oil diffusion pumped chamber which could routinely give pressures of the order of 1×10^{-6} Torr. The starting material ZrO_2 (99% purity) was evaporated from a 6 kW electron beam gun (Leybold, Germany, model **ESV6**). The oxygen backfilling pressure was 2×10^{-4} Torr during deposition. Fused silica substrates were placed at a distance of 25 cm above the source on a stationary workholder. The rate of deposition was maintained at 0.2 nm/s using a home built quartz crystal monitor and films were coated to a nominal thickness of 200 nm. A 3 cm broad beam ion source (Commonwealth Scientific Corp.) was used to generate oxygen ions. The ion energy could be varied from 100 to 1500 eV and a maximum beam current of 175 mA at the source could be obtained. The discharge voltage was around 52 V. The source had a hot cathode (tungsten) filament and the ion current could be varied by varying the filament current. The maximum life in reactive gas atmosphere was 3 h. There were two collimated grids, accelerator and screen, which were made of graphite. A Faraday cup supplied by the company was used to monitor the current density at the substrate level. The ion source substrate distance was 28 cm and the angle of inclination to the substrate was $\sim 20^\circ$. The experiments in this study were not performed at energies above 700 eV due to the drastic increase in extinction coefficient at this energy. A schematic view of the experimental chamber is shown in Fig. 1.

The spectral transmittance and near normal reflectance were measured in a Hitachi (Model No. 330) spectrophotometer in the range 200–1500 nm. The refractive index and extinction coefficient were calculated from the transmittance data using the envelope technique developed by Swanpoel.¹⁹ Figure 2(a) shows a typical envelope drawn to

FIG. 1. A schematic view of the experimental chamber used in this study.

calculate the optical constants of the film represented in curve 1. In this technique the optical losses due to scattering are assumed to be negligible and hence they have not been taken into account. Packing density was calculated using the Bragg and Pippard model modified by Harris *et al.*^{21,22} as reported earlier by Martin *et al.*¹⁴ the Bragg and Pippard model gives the most reasonable values for the packing density of zirconia films and hence it has been used in the present work.

The formula for packing density (p) is

$$n_f^2 = [(1-p)n_v^4 + (1+p)n_v^2 n_s^2] / [(1+p)n_v^2 + (1-p)n_s^2],$$

where n_f = the refractive index of the film at the given wavelength, p = the packing density, n_v = the index of the voids = 1 for air = 1.33 for water vapor, n_s = bulk value of refractive index = 2.21 at 600 nm.

111. RESULTS AND DISCUSSION

The measured spectral transmittance for the films deposited at 300 eV ion energy and ion current density of 100 pA/cm² and 500 eV energy and 100 and 220 pA/cm² current density are shown in Fig. 2(a). From Fig. 2(a) it is seen that as the current densities are increased at a fixed ion energy and the energy is increased at a fixed ion current density the difference in transmittance extrema increases indicating an increase in refractive index. The absorption edge for these films is between 230 and 250 nm indicating nearly stoichiometric films. Figure 2(b) shows the deviation in transmittance of the coated substrate (T_{FIL}) from the uncoated substrate value (T_s) as calculated from the envelope drawn to determine the refractive index and extinction coefficient. It is seen from Fig. 2(b) that with increasing energy at a fixed current density of 50 pA/cm² the

FIG. 2. (a) Measured spectral transmittance curves for the films deposited at (1) 300 eV energy and 100 pA/cm² current density, (2) 500 eV energy and 100 pA/cm² current density, (3) 500 eV energy and 220 pA/cm² current density; (b) The deviation in film transmittance (T_{FIL}) from substrate transmittance ($T_{SUBSTRATE}$) for the films. The 100 eV film was deposited at 10 pA/cm² while the other films were deposited at 50 pA/cm².

deviation from substrate transmittance increases with increasing energy at any wavelength. At energies <300 eV the film transmittance approaches that of the substrate transmittance even at wavelengths less than 400 nm. This indicates lower extinction coefficient for these films.

The dispersion curves for films deposited at ion energies of 300 and 500 eV and different current densities in the range 25–220 pA/cm² are shown in Figs. 3(a) and 3(b). It is observed that at 300 eV the change in index from 1.98 at 25 pA/cm² to 2.10 at 220 pA/cm² is not as pronounced as in the case of the films deposited at an energy of 500 eV where the change was from 1.98 to 2.21 over the same range of current densities. The films deposited at a current density of 25 pA/cm² show the same index of 1.98 at a wavelength of 600 nm at both 300 and 500 eV. The divergence begins at 50 pA/cm² where the 300 eV films show an index of 2.00 while the 500 eV film shows an index of 2.14.

FIG. 3. The dispersion curves for the films (a) deposited at an energy of 300 eV and different current densities (b) deposited at an energy of 500 eV and different current densities (c) deposited at 50 pA/cm² current density and different energies. The film at 100 eV was deposited at a current density of 10 pA/cm².

The refractive index of the films deposited at 300 eV seems to saturate immediately thereafter whereas that for the 500 eV films shows a gradual increase reaching a maximum at 220 pA/cm². Figure 3(c) shows the dispersion in refractive index for the films deposited at ion energies of 300, 500, and 700 eV and a current density of 50 pA/cm² and that for the 100 eV film which was deposited at 10 pA/cm². It was observed that the value of refractive index, 1.94, at 600 nm for the film deposited at 100 eV using the Kaufman source is higher than the highest value, 1.9, at 600 nm obtained by using the Heitmann type discharge source. The index increases steadily with increase in ion energy reaching a maximum at 500 eV. At 700 eV there is a slight decrease in the refractive index value. It increases from 1.94 at 100 eV and 10 pA/cm² current density to 2.15 at 500 eV and then reduces to 2.12 at 700 eV at a current density of 50 pA/cm² and wavelength of 600 nm. The initial increase in refractive index up to an energy of 500 eV can be attributed to the increase in packing density with increasing energy and improved oxidation due to enhanced reactivity in the presence of ions.

Figures 4(a) and 4(b) show the variation in packing density as a function of current density for films deposited at ion energies of 300 and 500 eV. In the expression for the calculation of packing density, n_v is the refractive index of the voids, which can either be assumed to be saturated with water vapor or filled with air. It is observed from Figs.

4(a) and 4(b) that the former assumption leads to (1) a lower packing density for the films and (2) that as long as the packing density is less than 0.9 there is large divergence in the values obtained from the two assumptions. In the absence of *in situ* measurements of refractive index this can be taken as a good measure of the presence of moisture adsorption in the films. It can be further observed from these figures that at 300 eV the two curves start approaching each other at a current density of 100 pA/cm² whereas at 500 eV they do so at a lower current density of 50 pA/cm². This indicates that the films deposited at the higher energy adsorb less moisture. It can also be seen that the films deposited at 500 eV have a higher packing density than those deposited at 300 eV. It can thus be stated that the films deposited under the influence of ion bombardment have high packing density and therefore adsorb very little moisture.

The variation in extinction coefficient (k) of the films with wavelength is plotted in Figs. 5(a)-5(c). Figures 5(a) and 5(b) show the variation in k for the films deposited at 300 eV and current densities of 25, 50, 100, and 220 pA/cm² and 500 eV and current densities of 25, 100, 150, and 220 pA/cm², respectively. From these figures it is observed that films deposited at current densities up to 100 pA/cm² show low extinction coefficient for the 300 eV case whereas it is low up to 150 pA/cm² at 500 eV with a drastic increase in extinction thereafter in both cases. Figure 5(c) shows the films deposited at 50 pA/cm² current density and energies of 300, 500, and 700 eV. Also shown is the 100 eV film which was deposited at 10 pA/cm². It is observed that the extinction coefficient of the films deposited at energies less than 500 eV is much lower compared to the films deposited at 700 eV. At 700 eV there is drastic increase in the extinction coefficient, increasing from 0.002 at 100 eV to 0.0085 for 700 eV at a wavelength of 600 nm. These values are slightly higher than the 6.5×10^{-4} reported by Martin et al.¹⁴ but are of the same order as those

FIG. 5. The variation in extinction coefficient with wavelength for the films (a) deposited at an energy of 300 eV and different current densities (b) deposited at an energy of 500 eV and different current densities (c) deposited at 50 $\mu\text{A}/\text{cm}^2$ current density and different energies. The film at 100 eV was deposited at a current density of 10 $\mu\text{A}/\text{cm}^2$.

reported by Rujkorakarn and Sites for ion beam sputtered films.¹⁷

Figure 6(a) shows the variation in refractive index with ion current density which has also been expressed in terms

FIG. 6. (a) The variation in refractive index with current density for the films deposited at ion energies of 300, 500, and 700 eV. (b) The variation in extinction coefficient with current density at 600 nm for the films deposited at 300, 500, and 700 eV.

of the ion to (vapor) atom arrival ratio for different energies at a wavelength of 600 nm. It is seen that with increasing arrival ratio the refractive index gradually increases for arrival ratios up to 0.24 (100 $\mu\text{A}/\text{cm}^2$) remaining constant thereafter up to arrival ratios of 0.6 for 300 eV and for 500 eV the saturation is more gradual. At 700 eV the film index remains invariant up to an arrival ratio of 0.24 (100 $\mu\text{A}/\text{cm}^2$). This kind of behavior in index with increasing current density at a fixed ion energy has also been reported by Martin *et al.*¹⁴ for zirconia films deposited at 600 eV and current density up to 200 $\mu\text{A}/\text{cm}^2$.

The highest value 2.21 was obtained at an energy of 500 eV and ion current density of 220 $\mu\text{A}/\text{cm}^2$. This compares very favorably with the values of 2.19 for the ambient temperature and 2.23 for the 300 °C deposited films reported by Martin *et al.*¹⁴ for ion assisted deposited films at an energy of 600 eV and current density of 200 $\mu\text{A}/\text{cm}^2$. Values of 2.2 have also been reported for ion beam sputtered films.¹⁷ The increase in refractive index with energy in ion assisted deposition has been reported by McNally, for Ta₂O₅ films in the energy range 200–500 eV, Al₂O₃ in the range 300–1000 eV and Netterfield *et al.*²⁴ for CeO₂ films in the energy range 300–1200 eV.

Figure 6(b) shows the variation in extinction coefficient (k) at ion energies of 300, 500, and 700 eV as a function of current density at a wavelength of 600 nm. At 300 eV the k value of the films seems to be low up to 100 $\mu\text{A}/\text{cm}^2$ and increases beyond that. At 500 eV the increase in k values starts at a value of 150 $\mu\text{A}/\text{cm}^2$. At 700 eV the k value is uniformly high irrespective of the current density.

Al-Jumaily *et al.*²³ have earlier reported an increase in tungsten contamination of the films at high levels of ion bombardment in titania films and have mentioned this as a possible cause for increase in extinction coefficient at higher values of current density. McNally²³ has also reported an increase in extinction coefficient beyond 300 eV for Ta₂O₅ films and Netterfield *et al.*²⁴ have seen an increase in extinction coefficient in CeO₂ films beyond 600 eV. It should be mentioned here that Auger depth profiling done on the high extinction coefficient films in the present work did not reveal any tungsten. This eliminates the possibility of increase in k values due to film contamination by tungsten from the ion source filament and indicates that preferential sputtering of oxygen is the most probable mechanism for the increase in extinction coefficient at higher levels of bombardment.

The above discussion clearly indicates the presence of a critical value of energy at a fixed ion current density and vice versa, beyond which the refractive index and extinction coefficient behavior starts deteriorating.

The existence of a critical energy at a fixed ion current density and a critical current density at a fixed energy beyond which both the refractive index and the extinction coefficient start deteriorating has also been observed in Ta₂O₅, Al₂O₃, CeO₂, and titania films²⁶ as also in zirconia films deposited at a fixed ion energy.¹⁴ This behavior has been attributed to the degradation of film stoichiometry due to preferential sputtering or excess oxygen incorporation in the films beyond the critical value. Muller in

his models on ion assisted deposition has also referred to this process as being the cause for deterioration in optical properties at higher levels of ion bombardment.* Although, here the refractive index seems to saturate, the extinction coefficient increases by a large magnitude beyond the critical value. In a study done on ceria films by Netterfield *et al.*²⁴ at an energy of 1200 eV it was found that the stoichiometry approached the required oxygen to metal ratio, i.e., 2 up to a certain current density, while above and below this value there were large deviations in stoichiometry. This resulted in a decrease in refractive index and an increase in extinction coefficient at points away from the critical value. This would indicate that the films in the present case are most stoichiometric at the critical value. The x-ray diffraction patterns revealed that all films were x-ray amorphous. Martin *et al.*¹⁴ have reported the formation of as deposited crystalline films in their work. The possible causes for this difference in behavior could be twofold. The films in that study were deposited at a higher rate, 0.8 as against 0.2 nm/s, and to greater total thicknesses than in the present study.

IV. CONCLUSIONS

Thin films of zirconia have been deposited using ion assisted deposition. It has been found that the refractive index increases steadily with an increase in ion energy and current. There is a marked increase in packing density with increasing ion energy. The extinction coefficient of these films is lower at energies below 300 eV than at higher energies. The existence of a critical value of ion energy and current density beyond which the refractive index and extinction coefficient deteriorate has been observed.

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