Optical properties of ion assisted deposited CeO_2 films

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Single layer films of CeO_2 have been deposited both by conventional electron beam evaporation and ion assisted deposition with oxygen and argon ions. A broad beam Kaufman ion source (3 cm diam) has been used to generate the ions. A systematic study has been made on optical properties such as refractive index, extinction coefficient and inhomogeneity of the films as a function of: (1) oxygen partial pressure in the range 1×10^{-4} to 1×10^{-5} mbar. (2) Incidence of oxygen ions with energy in the range 300–700 eV and current density in the range 50–220 $\mu A/cm^2$. (3) Incidence of mixed argon and oxygen ions of different ratios. The refractive index of the films deposited under the influence of ion bombardment showed higher indices than the conventionally evaporated films. The maximum index obtained with an oxygen ion bombardment was 2.3 at an ion energy of 600 eV and current density of 220 $\mu A/cm^2$. The bombardment of the films with a mixed argon–oxygen (25% Ar) ion beam of the same energy and current density was found to further increase the refractive index. The extinction coefficient in both cases was negligible.

1 INTRODUCTION

Cerium dioxide (CeO_2) is one of the important oxide materials used for high index films in optical devices because of its desirable properties such as high refractive index, good transmission in the visible and near infrared region, good adhesion, and high stability against mechanical abrasion, chemical attack, and high temperatures.[1,2] CeO_2 has also been used to prepare mixed films with materials such as MgF_2, CeF_3, Y, O, , TiO_2, and SiO_2, with intermediate refractive indices being produced by coevaporation and co-sputtering.[3–6]

CeO_2 films have been deposited by resistive as well as electron beam evaporation. As in the case of other oxides (ZrO_2, SiO_2, Al, O, , etc.), it is difficult to evaporate CeO_2 by resistive evaporation. Some of the problems encountered during the deposition of oxides by resistive evaporation are source reactions and frequent breaking of boats, maintenance of uniform and high deposition rates, dissociation of film material, excessive heating due to source radiation, and insufficient evaporant capacity. As a result, the film properties have been found to be difficult to reproduce. Though CeO_2 material dissociates during heating, it has been observed that reactive evaporation is not necessary because it reassociates easily.'

Hass *et al.*[1] made a comprehensive study on the optical and structural properties of CeO_2 films deposited using a heavy tungsten boat. Reproducible, high index, and durable films were obtained only when the evaporation material was thoroughly degassed prior to deposition. The refractive index of the films depended strongly on substrate temperature. The films were found to have the cubic crystal structure for all substrate temperatures measured. The increase in refractive index at elevated substrate temperature was attributed to greater film density. The refractive index of thicker films was observed to be much lower than the thinner ones. The thicker films ($t>$ 100 nm) were found to have higher scattering losses, especially in the ultraviolet (UV) region. The refractive index of the electron beam evaporated CeO_2 films ($t = 220$ nm) have been observed to be lower than those reported by Hass (1.794).[7] Coleman' sputtered CeO_2 films using an oxide target, and investigated the optical properties. The CeO_2 target dissociated during the deposition, resulting in cerium rich films which were optically absorbing. However, when the substrate temperature was raised, the films were found to be absorption free and the index was observed to be the highest (2.50 at 550 nm) reported so far. The optical band gap of thermally evaporated CeO_2 films was observed to be 3.10 eV.[9] Additionally, CeO_2 films have exhibited characteristic absorption bands in the infrared region at 575 and 280 cm^{-1} with polarized light.''

In recent years, ion assisted deposition (IAD) has been extensively used for the preparation of a variety of thin films with improved properties like packing density and stoichiometry.[11–17] The microstructure of conventionally deposited films is columnar, resulting in a lower packing density. This is the primary cause of the poor stability of the films with respect to spectral characteristics.[15] On the other hand, ion bombardment of the films during deposition has been shown to significantly reduce the columnar character of the films. The additional energy provided by ions to the condensing atoms are thought to be responsible for this behaviour. In general, films with high index, low absorption, low scattering, reduced stress, and high stability have been obtained using IAD.[16]

Recently, Netterfield *et al.*[17] investigated the properties of CeO_2 films deposited by electron beam evaporation and simultaneous oxygen ion bombardment. Moisture absorption in the films was less when the ion energy and current density were maintained at 1200 eV and 150 $\mu A/cm^2$ respectively. The packing density of the films increased from 0.55 to unity as a result of ion bombardment. For the same ion-to-molecule arrival rates, the maximum densification occurred in the ion energy range of 300–600 eV. The absorption and scattering losses increased when the ion energy was increased from 300 to 1200 eV. The crystal structure was cubic, and was stable with ion bombardment. At higher energies (1200 eV), changes in the preferred crystal orientation of the film was observed. An excess oxygen-to-cerium ratio was observed in RBS measurements on the films prepared by IAD when the current density was more than a critical level.

Surprisingly, there is not much information on the influence of ion bombardment of ceria films with a mixture of ions (i.e., Ar^+ and O^+). This combination could produce films with a higher packing density and a high refractive index, without affecting the film stoichiometry. Hence, it is of great interest to study the influence of ions with different ratios of argon and oxygen in the gas mixtures.

In this work, we report on the preparation of CeO_2 films by (i) electron beam evaporation (ii) oxygen IAD (iii) argon IAD, and (iv) IAD with an argon and oxygen mixed gas. The influence of the deposition parameters such as oxygen partial pressure, ion energy, and ion current density on the optical properties will also be reported.

II. EXPERIMENTAL

CeO_2 films were deposited in an oil diffusion pumped chamber with a base pressure of 2×10^{-6} mbar. The high purity (99.99%) gases were leaked in to the chamber during deposition using two needle valves to control the two gas flows independently. The evaporation material (CeO_2 purity 99.98%) was evaporated from a 6 KW electron beam gun (ESV6 of M/s LEYBOLD, Germany). The films were deposited on to optically polished fused silica substrates 2.5 cm in diameter and 2 mm thick. A stationary holder placed 28 cm directely above the electron beam source supported the substrates. A Kaufman 3 cm diameter broad beam ion source (M/s CommonWealth Scientific Inc. USA) was used to generate the ion flux. The ion gun was 25 cm below the substrates and the beam made an angle of 20" with the substrate normal. The films were deposited at the rate of 15–18 nm/min, with a nominal thickness of 250–350 nm. The film thickness and rate of deposition were monitored using a quartz crystal monitor built in this laboratory. A schematic view of the experimental chamber is shown in Fig. 1.

The spectral transmittance and near-normal reflectance of the films were measured using a Hitachi model 330 spectrophotometer scanning from 300 to 1500 nm. The refractive index and extinction coefficient were calculated from the transmittance data using the envelope technique developed by Swanepoel.[18] The inhomogeneity of the films was estimated using the method described by Arndt *et al.*[19] The packing density was calculated using the Bragg and Pippard[20] model which was modified by Harris *et al.*[21]

III. RESULTS AND DISCUSSION

Figure 2 shows the variation of the refractive index as a function of the oxygen partial pressure for films deposited using electron beam evaporation in a neutral oxygen atmosphere for two different rates of deposition (15 and 18 nm/min). From Fig. 2, as the pressure increased from 1×10^{-5} to 1×10^{-4} mbar, the refractive index of the film decreased from 1.99 to 1.86. Ritter[22] has observed similar behaviour for TiO_2 films. The decrease in refractive index of the films with pressure is probably due to the porous nature of the films at higher pressures.

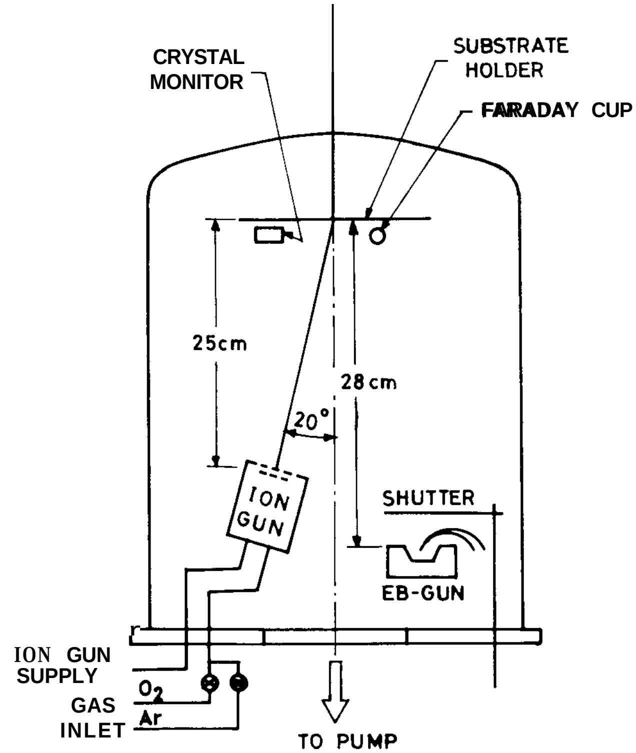

FIG. 1. Schematic view of the experimental chamber.

The extinction coefficient of these films was negligibly small ($< 10^{-4}$) at all pressures. This study reconfirms that for the preparation of highly transparent films of CeO_2, reactive evaporation is not necessary. Figure 2 also shows that the rate of deposition (15–18 nm/min) has only a slight influence on the refractive index.

The deposition conditions, i.e., oxygen pressure (1×10^{-4} mbar) and rate of deposition (15–18 nm/min) have been used for further investigations on CeO_2 films. The pressure was determined by the stability of ion source operation, and by also the fact that reasonably high current densities could be obtained at this pressure.

Figure 3(a) shows the measured spectral transmittance of the films deposited at oxygen ion energies of 0 (no ions), 500,600, and 700 eV, with a current density of 220 $\mu A/cm^2$.

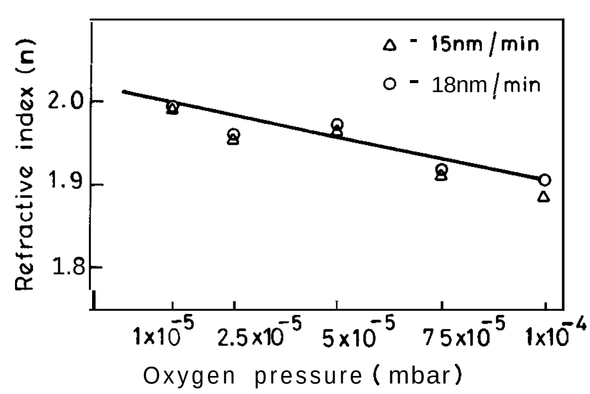

FIG. 2. Variation of refractive index with oxygen backfilling pressure for two rates of deposition 15 and 18 nm/min.

clearer when it is plotted as a function of ion energy and current density as shown in Figs. 5(a) and 5(b). The refractive index increases from 1.98 at 300 eV to 2.3 at 600 eV, and then decreases to 2.0 at 700 eV with an ion flux of 220 $\mu A/cm^2$. A similar variation in the refractive index has also been observed in films deposited at current densities of 50, 100, and 150 $\mu A/cm^2$. The influence of the ion current density is more pronounced at energies greater than 400 eV than at lower energies. The increase in index over a current density range from 50 to 220 $\mu A/cm^2$ is 1.93–2.05 at 400 eV, whereas it varies from 2.05 to 2.3 over the same range at 600 eV. The reduction in index of the films at 700 eV may be due to preferential sputtering of oxygen atoms from the film during ion bombardment, or incorporation of excess oxygen in the films.

The packing density was calculated using the relationship between the packing density and refractive index which is approximately linear. The packing density variation with oxygen ion bombardment at different ion current densities and ion energies is shown in Figs. 6(a) and 6(b). Figure 6(a) shows that as the current density (at 600 eV) increases, the packing density also increases. It increases from 0.84 at 50 $\mu A/cm^2$ to 0.97 at 220 $\mu A/cm^2$ for an ion energy of 600 eV. It is clear from Fig. 6(b) that as the ion energy increases, the packing density increases, reaching a maximum at 600 eV ion energy and then starts decreasing.

In the discussion that follows, the composition of the argon–oxygen gas mixture is represented in terms of the percentage of argon in the mixture.

The influence of argon–oxygen ion bombardment mixtures for different compositions (0%, 25%, 75%, and

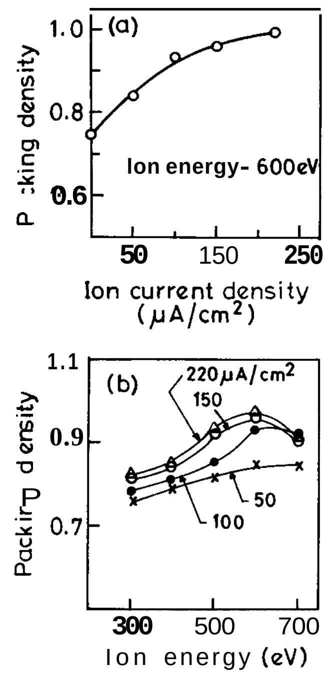

FIG. 6. (a) The variation in packing density with current density at an ion energy of 600 eV. (b) The variation in packing density as a function of ion energy at current densities of 50, 100, 150, and 220 $\mu A/cm^2$.

100%) on the optical properties of the films is shown in Figs. 7 and 8. Figure 7(a) represents the measured spectral transmittance characteristics for the films deposited at 600 eV ion energy and 220 $\mu A/cm^2$ ion flux. The spectral reflectance of these films is shown in Fig. 7(b). It is clear that the films deposited with 0% and 25% argon-ion bombardment show reflectances very near to the substrate reflectance; the films deposited at 75% and 100% argon-ion bombardment show higher reflectances than the substrate. This can be attributed either to the inhomogeneity or high absorption in the films.

The variation of refractive index and extinction coefficient as a function of wavelength for these films is shown in Figs. 8(a) and 8(b). It is observed that although the extinction coefficient for the films deposited with 0% argon ions and 25% argon-ion films is a minimum, the refractive index in the latter case is higher. The 0% argon IAD film had a refractive index of 2.30 at 550 nm, whereas the 25% argon ion film had an index of 2.35. Further addition of argon in the gas mixture only induced an increase in the extinction coefficient and a decrease in refractive index. The initial increase in refractive index at 25% argon might be due to the increase in packing density without affecting the stoichiometry of the films. At higher argon-ion content, the deterioration in optical constants can be attributed to preferential sputtering of oxygen from the growing films, resulting in nonstoichiometry and the incorporation of argon in the films.

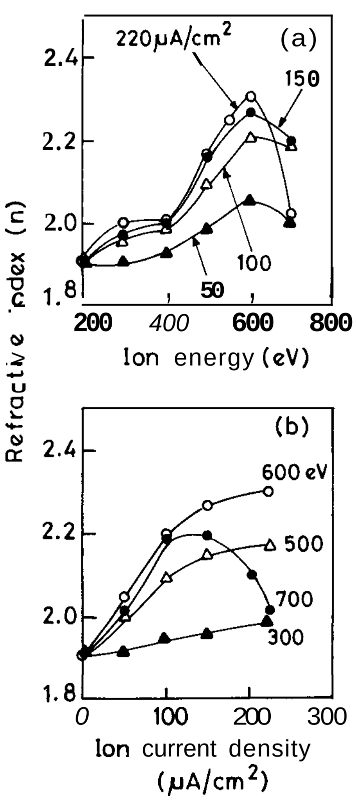

FIG. 5. (a) The variation in refractive index for the films deposited at oxygen ion current densities of 50, 100, 150, and 220 $\mu A/cm^2$ as a function of ion energy at a wavelength of 550 nm. (b) The variation in refractive index plotted as a function of current density for the films deposited at 300, 500, 600, and 700 eV at a wavelength of 550 nm.

IV. SUMMARY

In summary, we find that CeO_2 films with exceptionally bulk-like refractive indices and low absorptions can be reproducibly fabricated by oxygen-ion assisted electron beam evaporation. It has been found that the refractive index increases steadily with increasing ion energy (upto 600 eV) and ion current density. The packing density also shows a

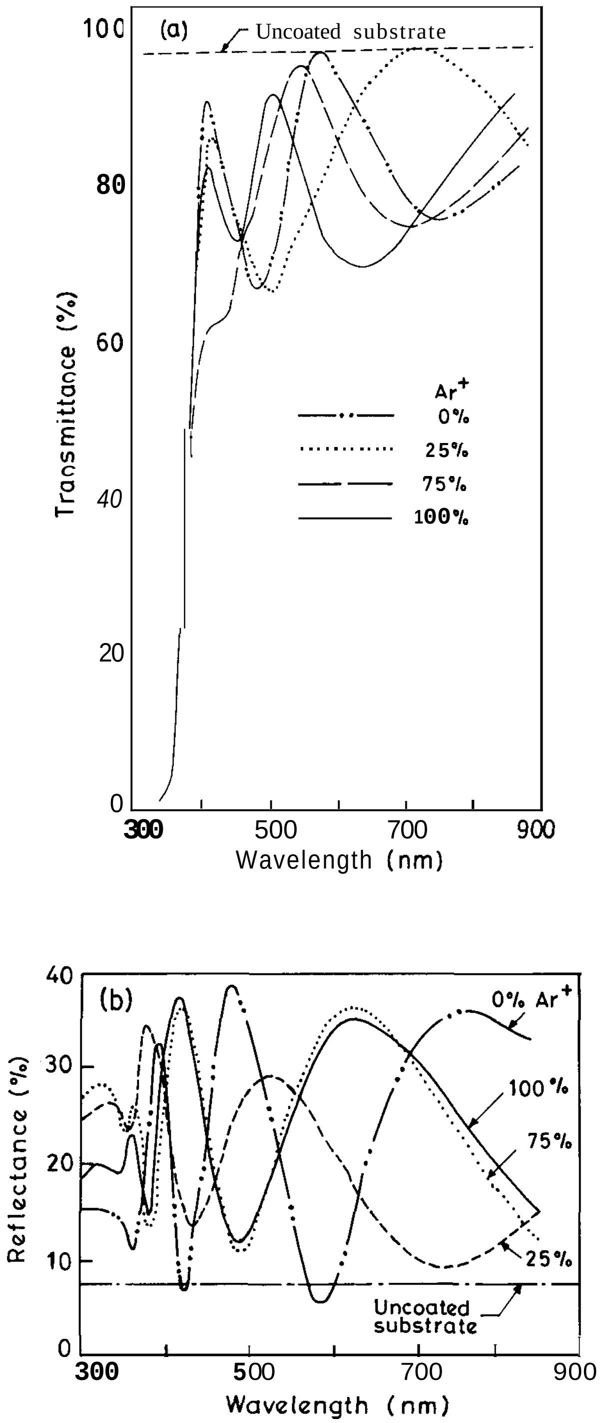

FIG. 7. (a) The measured spectral transmittance curves for the films deposited in an argon-oxygen ion gas mixture with 0%, 25%, 75%, and 100% argon in the mixture at an ion energy of 600 eV and a current density of 220 $\mu A/cm^2$. (b) Measured spectral reflectance curves for the same films.

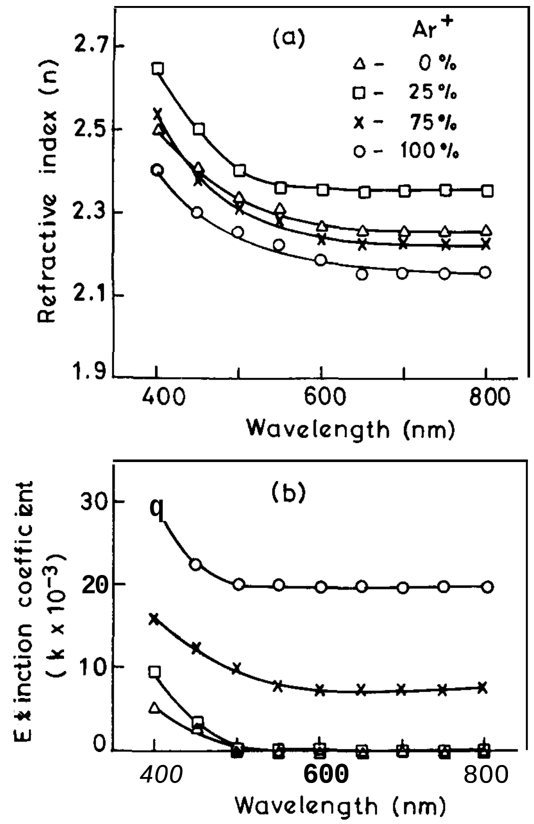

FIG. 8. (a) The dispersion curves for the films deposited in an argon–oxygen ion gas mixture with 0%, 25%, 75%, and 100% argon in the mixture at an ion energy of 600 eV and 220 $\mu A/cm^2$. (b) The variation in extinction coefficient with wavelength for the same films.

similar behavior. The absorption in these films is lower at energies of 600 eV and below, in the case of oxygen-ion bombardment. The films deposited at an energy of 600 eV and ion current density of 220 $\mu A/cm^2$ seem to exhibit the best optical behavior with the highest index, packing density and low absorption. Films produced by argon-oxygen ion bombardment (25% argon) resulted in films with even higher refractive indices and minimum extinction coefficients. The extinction coefficients increased as the content of argon ions increased in the mixture. It has been demonstrated that the film properties can be improved significantly by the addition of small amounts of argon in the oxygen-ion beam.

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