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Optical properties of CeO_2 thin films

S DEBNATH, M R ISLAM and M S R KHAN*
Department of Applied Physics and Electronic Engineering, University of Rajshahi, Rajshahi 6205, Bangladesh

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Abstract. **Cerium oxide (CeO_2) thin films have been prepared by electron beam evaporation technique onto glass substrate at a pressure of about 6×10^{-6} Torr. The thickness of CeO_2 films ranges from 140–180 nm. The optical properties of cerium oxide films are studied in the wavelength range of 200–850 nm. The film is highly transparent in the visible region. It is also observed that the film has low reflectance in the ultra-violet region. The optical band gap of the film is determined and is found to decrease with the increase of film thickness. The values of absorption coefficient, extinction coefficient, refractive index, dielectric constant, phase angle and loss angle have been calculated from the optical measurements. The X-ray diffraction of the film showed that the film is crystalline in nature. The crystallite size of CeO_2 films have been evaluated and found to be small. The experimental *d*-values of the film agreed closely with the standard values.**

Keywords. **Transmittance; absorption coefficient; refractive index; optical band gap.**

1. Introduction

Cerium oxide (ceria) films have received considerable interest because of their high transparency in the visible and near IR region and electro-optical performance (Sainz *et al* 1990; Al-Robaee *et al* 1992; Zheng *et al* 1993; Krishna *et al* 1998). It has potential applications in silicon-on-insulator structures, barrier layers and capacitor devices (Park *et al* 1997). It is a highly efficient UV absorber and is used as an additive for glass for protecting light-sensitive materials (Hampel 1960). Films are capable of corrosion protection of metals and as coating for use as a catalyst support (Nelson *et al* 1981). The ability of cerium-doped glass to block out UV light is utilized in the manufacturing of medical glassware and aerospace windows. It is also used to prevent polymers from darkening in sunlight and to suppress discoloration of television glass. In catalytic converters, it acts as a stabilizer for the high surface area alumina, as a promoter of the water–gas shift reaction and as an oxygen storage component. In steel manufacturing, it is used to remove free oxygen and sulfur by forming stable oxysulfides. Ceria films are prepared by a large variety of techniques including sputtering (Bueno *et al* 1997), electron beam evaporation (Baudry *et al* 1990) and sol–gel (Brinker and Scherer 1990).

Several studies were reported on the optical and electrochemical properties of CeO_2 films (Granqvist 1995). Survey of the literature shows that there are some variations of the optical parameters of CeO_2 films fabricated by different techniques. Hence, it was felt worth investigating the optical characteristics of CeO_2 films produced by electron beam evaporation.

*Author for correspondence (msrkhan2003@yahoo.com)

2. Experimental

CeO_2 thin films have been prepared by electron beam evaporation technique onto glass substrate of dimension $3 \times 2{\cdot}5 \times 1$ cm using cerium oxide powder (99·9% purity). The substrates were properly cleaned and dried before it was placed in the deposition chamber of the vacuum coating unit using suitable mask. Films of thickness ranging from 140–180 nm were deposited for optical measurement at a pressure of about 6×10^{-6} Torr. The film thickness was measured by multiple beam interference method. The optical studies (e.g. transmittance, reflectance) were carried out using Perkin-Elmer lamda-19, double beam spectrophotometer. The structure of the films was investigated by X-ray diffractometer, ''X'Pert PRO XRD System'.

3. Results and discussion

The variation of transmittance of cerium oxide (CeO_2) thin films of different thicknesses is shown in figure 1. It is evident from the figure that in the ultra-violet region the transmittance decreases to zero and increases with wavelength in the visible region. The high transmittance is probably due to the existence of an interfacial layer with low refractive index between CeO_2 and glass (Porqueras *et al* 2003). Figure 2 shows the variation of reflectance with wavelength for films of different thicknesses. Absorbance was estimated using transmittance and reflectance spectra and is displayed in figure 3. It is found from these graphs that absorbance has a very high value in the ultra-violet region and decreases sharply with increasing wavelength and becomes almost constant towards the visible region.

The dependence of absorption coefficient of films on wavelength is shown in figure 4. It is seen from the graph that the absorption coefficient increases up to certain values of wavelength in the UV region and then it decreases exponentially and finally becomes constant. It is also found from this graph that absorption coefficient decreases with the increase in film thickness. The values of absorption coefficient were calculated using the relationship

$$\alpha = \ln(1/T)t,$$

where T is the transmittance and t the thickness of the film.

The evaluated value of extinction coefficient of the films shows that it (figure 5) increases up to a certain wavelength and then decreases exponentially and finally becomes constant. It is observed from the figure that extinct-

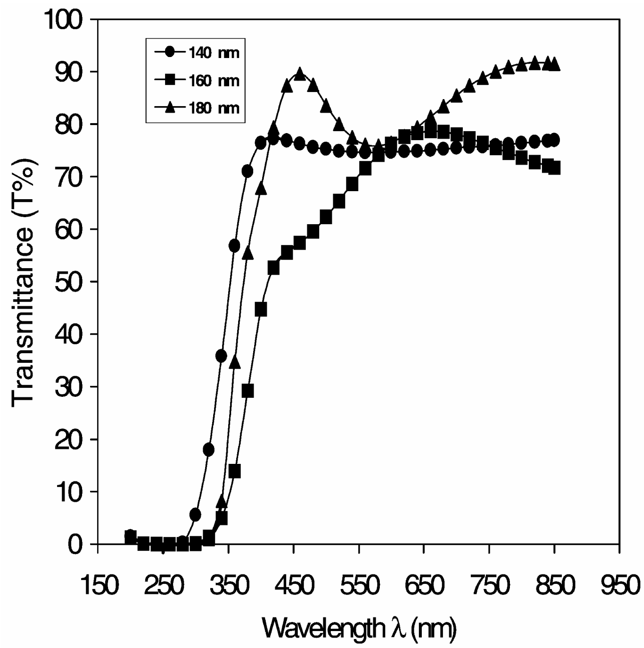

Figure 1. Variation of transmittance with wavelength for different film thicknesses.

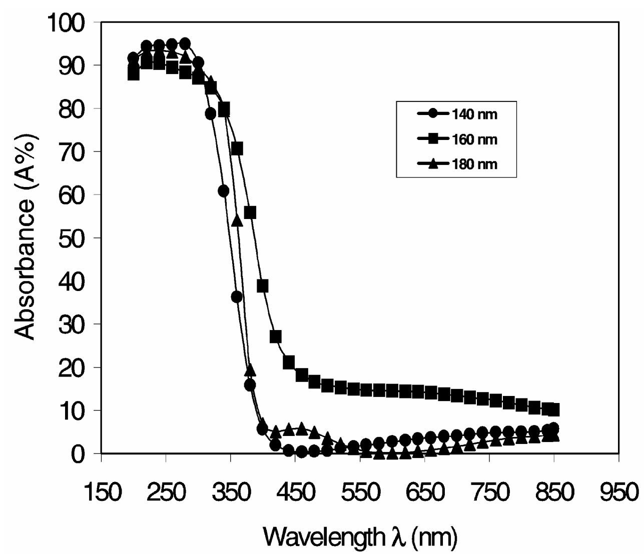

Figure 3. Variation of absorbance with wavelength for different film thicknesses.

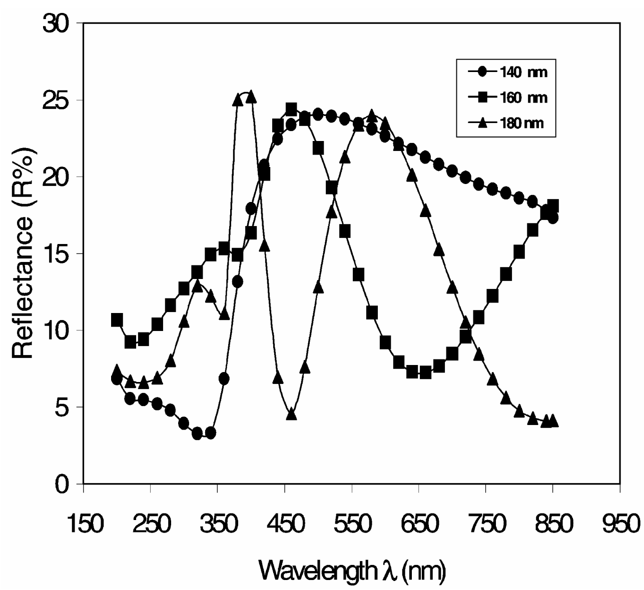

Figure 2. Variation of reflectance wavelength for different film thicknesses.

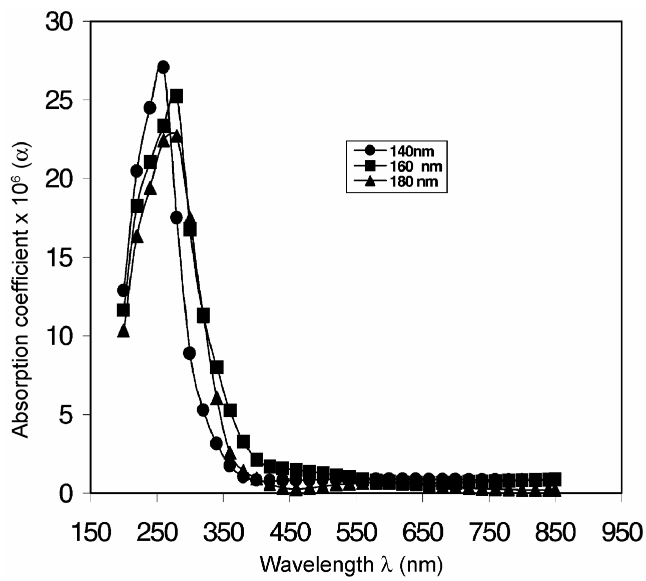

Figure 4. Variation of absorption coefficient with wavelength for different film thicknesses.

tion coefficient decreases with the increase in film thickness. Its value was found to be $\alpha = 0{\cdot}007 \pm 0{\cdot}003$ at $\lambda = 600$ which is in agreement with the reported value (Wooten 1981; Nilgun 2001).

The variation of refractive index, phase angle, dielectric constant and loss angle with wavelength for the films of different thicknesses are shown in figures 6–9, respectively. The refractive index of the film was $n = 0{\cdot}82 \pm 0{\cdot}02$ at $\lambda = 600$ nm which was slightly less than the reported value (Brinker and Scherer 1990; Porqueras *et al* 2004). This low refractive index can be attributed to the singular ear structure, which could grow from first nuclea-

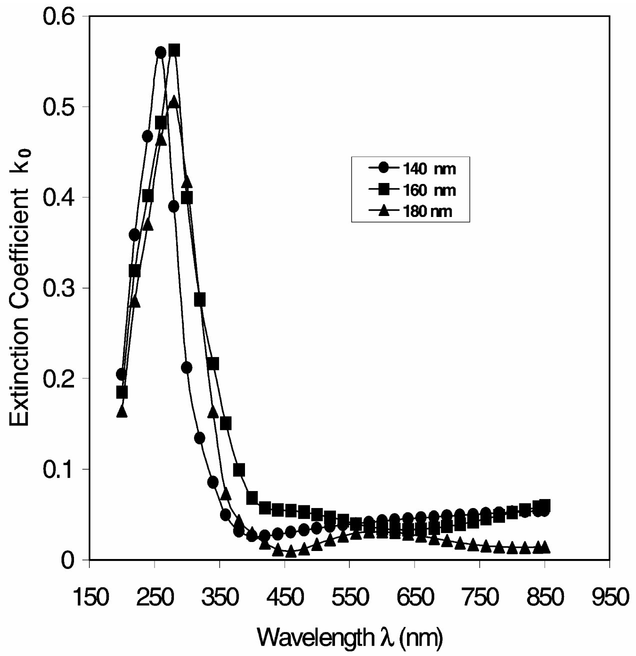

Figure 5. Variation of extinction coefficient with wavelength for different film thicknesses.

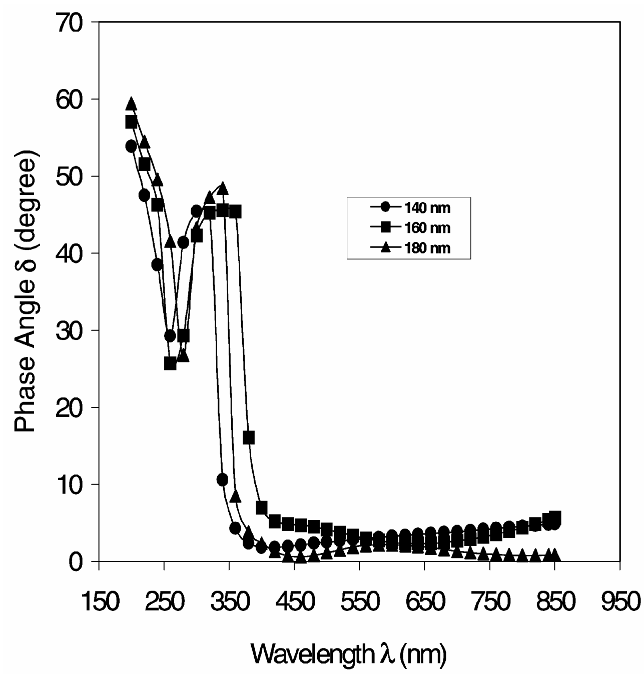

Figure 7. Variation of phase angle with wavelength for different film thicknesses.

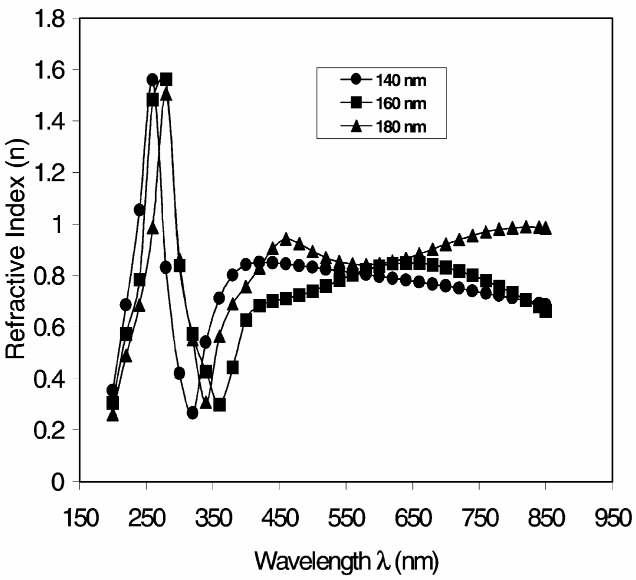

Figure 6. Variation of refractive index with wavelength for different film thicknesses.

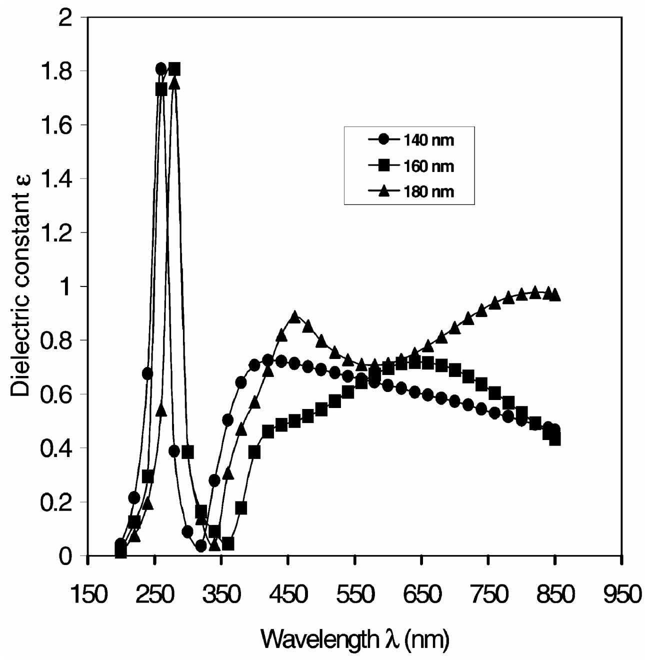

Figure 8. Variation of dielectric constant with wavelength for different film thicknesses.

tion layer (Crnjak Orel and Orel 1996; Porqueras *et al* 2003).

In order to determine the values of optical band gap, $(\alpha h\nu)^r$ vs $h\nu$ curve for three films of different thicknesses have been plotted and the value of $r = 1/2$ had the best fitting. The values of the tangents intercepting the energy axis give the values of optical band gap. From figure 10 the values of optical band gap were found to be 4·11 eV, 3·81 eV and 3·6 eV for 140 nm, 160 nm and 180 nm films, respectively. From these graphs it is found that the optical band gap decreases with the increase in film thickness. These results are in conformity with earlier works (Granqvist 1995; Nilgun 2001; Porqueras *et al* 2003).

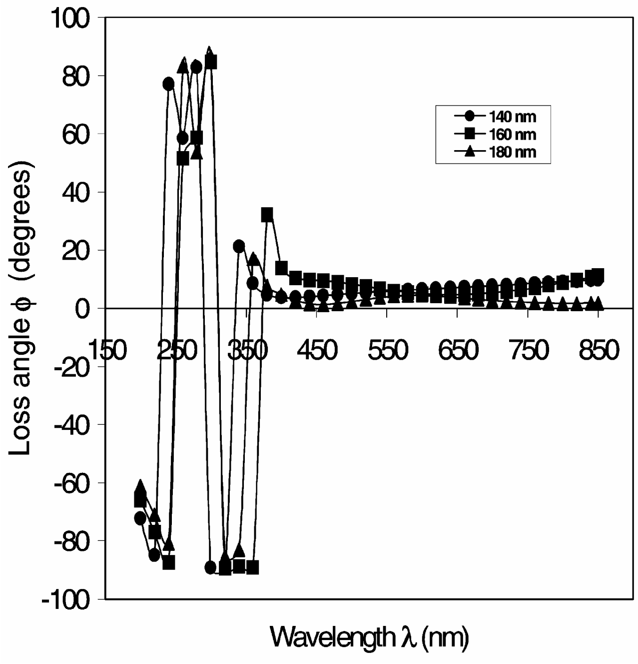

Figure 9. Variation of loss angle with wavelength for different film thicknesses.

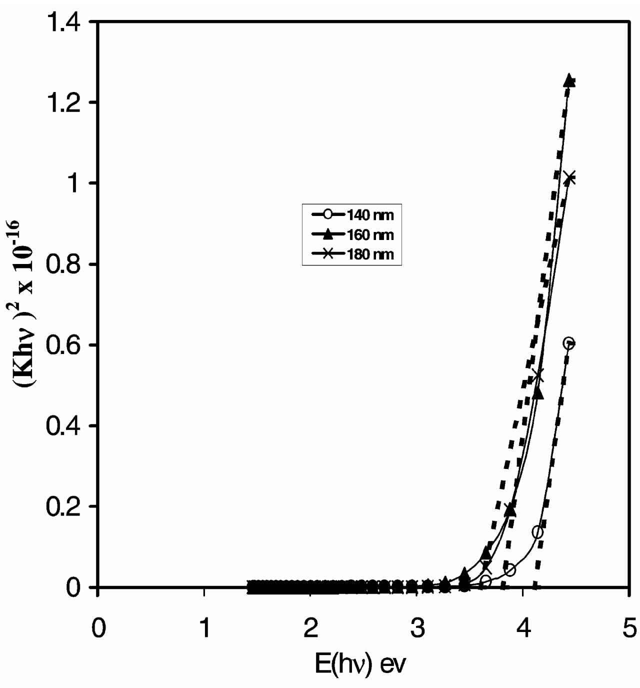

Figure 10. Optical band gap.

4. Crystallite size determination from X-ray diffraction

The X-ray diffraction pattern (figure 11) shows that the film is crystalline with preferred (111) orientation (Wooten 1981). The experimental *d*-spacing values of CeO_2 film were found to be slightly different from those of standard values. This variation may occur due to the difference in the fabrication techniques or may be due to the difference in degree of crystallinity. The crystallite size of the film for (111), (200) and (220) planes were found to be 20·60 nm, 34·79 nm and 14·90 nm, respectively. It is observed from figure 11 that the peaks of their X-ray diffraction patterns are not very sharp except that of (111) plane (Ramirez-Duverger *et al* 1997).

5. Conclusions

Optical studies of CeO_2 films in the wavelength range $200 < \lambda < 850$ nm show that the material is highly transparent in the visible region. It also shows a lower reflec-

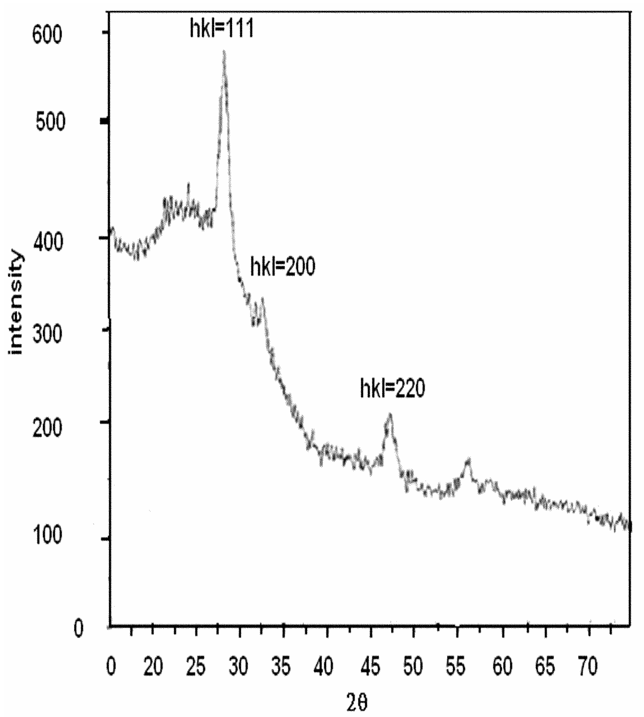

Figure 11. The experimental X-ray diffraction pattern of CeO_2 thin film.

tance in the ultra-violet region whereas a very high absorbance in this region. The optical band gap was found to increase with increase in thickness. The values of absorption coefficient, extinction coefficient, refractive index, dielectric constant, phase angle and loss angle were found to be in conformity with previous works. From the X-ray diffraction studies it is found that CeO_2 thin film has crystalline structure and a smaller crystallite size.

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