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Synthesis and properties of zirconia thin films

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Abstract. Thin films of zirconia have been synthesized using reactive DC magnetron sputtering. It has been found that films with good optical constants, high refractive index (1·9 at 600 nm) and low extinction coefficient can be prepared at ambient temperatures. The optical constants and band gap and hence the composition are dependent on the deposition parameters such as target power, rate of deposition and oxygen background pressure. Thermal annealing of the films revealed that the films showed optical and crystalline inhomogeneity and also large variations in optical constants.

Keywords. Magnetron sputtering; zirconia.

1. Introduction

The low temperature synthesis of technologically useful materials in thin film form has been the subject of considerable interest in recent times. This not only enhances applicability of preparation processes but also that of the materials prepared using these processes. Plasma based thin film deposition processes such as sputtering, ion plating etc have traditionally found use in processing of such materials because they allow lower processing temperatures as a consequence of energetic particle bombardment during synthesis. Reactive magnetron sputtering, due to its high deposition rate, reduces target oxidation and offers better control over film composition. Since energetic bombardment of substrates is low, the substrate temperature rise during processing is low. It has, thus, been used successfully to prepare a number of oxides such as titania and zirconia in thin film form at low temperatures. The process has been discussed in detail in recent reviews (Westwood 1989) and hence will not be done here.

Zirconia films are ideal for various technologically important applications because of their durability, hardness, low thermal conductivity, high refractive index, low optical losses etc (Martin *et al* 1983). Since it exhibits polymorphic behaviour, each crystalline modification of zirconia, i.e. monoclinic, tetragonal and cubic, has found application in various areas.

Thus, it is of great interest and importance to prepare and characterize thin films of zirconia. To this end, in this paper we report the preparation of zirconia thin films using DC magnetron sputtering, the optical and structural properties of the films so deposited will also be reported. A study of the thermal stability of these films in respect of optical and structural properties will also be reported.

2. Experimental

The films were prepared in a chamber which was pumped using a diffusion pump (fitted with a liquid nitrogen trap) and rotary pump combination to a pressure of

10^{-6} torr. The target was a 152 mm diameter zirconium plate (99·8% purity). The system was arranged in a sputter up configuration with a target to substrate distance of 65 mm. High purity oxygen (4N) and argon (5N) were used as the reactive and sputter gases respectively.

The target was sputter cleaned for 30 min prior to sputtering. The substrates used were 25 mm diameter fused silica plates. The films were coated to a thickness of 200 nm. The spectral transmittance was recorded in a Hitachi (model 330) spectrophotometer operating in the range 200 to 2500 nm. The refractive indices, extinction coefficient and inhomogeneity in the films were determined using techniques described earlier (Swanpoel 1983; Suhail *et al* 1992). The band gap was calculated from a model proposed by Tauc (1974) for amorphous semiconductors. The X-ray diffraction patterns were recorded in a powder diffractometer using Co–Kα radiation (λ = 0·179 nm).

The films were finally annealed in air over temperature range from 300 to 900°C and characterized for the same properties.

3. Results and discussion

As stated earlier, one of the main advantages of magnetron sputtering is the high rate of deposition (calculated from the total thickness and sputtering time) that it provides. From figure 1a, where the rate of deposition is plotted as a function of target power, it is seen that rates as high as 50 nm/min can be achieved routinely.

The deposition rate as a function of background oxygen pressure has been plotted in figure 1b at a constant target power of 450 W. Initially, as the oxygen pressure is increased the rate of deposition remains constant up to a value of 3×10^{-5} torr, there is a steep drop beyond that and the rate of deposition then becomes constant at and above a pressure of 4×10^{-5} torr. The pressure at which the drop occurs is called the critical oxygen pressure and the drop beyond that point is attributable to target oxidation, because the corresponding oxide will have a lower deposition rate. Blickensderfer *et al* (1976) reported a similar effect during rf sputtering from a Zr target. They have observed a drop from 20 to 4 nm/min at critical pressure of 0·2 mtorr as against the 35 nm/min to 25 nm/min drop observed in the present case. Schiller *et al* (1984) also observed the presence of a critical oxygen pressure during the processing of titania thin films.

The effect of changing pressure and hence the related change in deposition rate on the refractive index of these films (at 600 nm) is shown in figure 2a. The refractive index also appears to be constant up to the critical oxygen pressure but shows a more gradual drop in its value beyond the critical pressure. Further, no saturation is observed in the index value. This clearly indicates that the refractive index is strongly dependent on both the oxygen pressure and the deposition rate (figure 2b) and can be modulated using either of these process parameters thus enhancing the applicability of the process. The values of refractive index obtained, 1·93 at the critical pressure 3×10^{-5} and 1·84 at the highest pressure used in the study 4×10^{-5} torr, are lower than the bulk value of the material (2·21). The value 2·08 obtained at 50 nm/min and the critical pressure however, compares favourably with the bulk value. The low values indicate that the films are porous and probably non stoichiometric. Indirect evidence for stoichiometry is presented in figure 3,

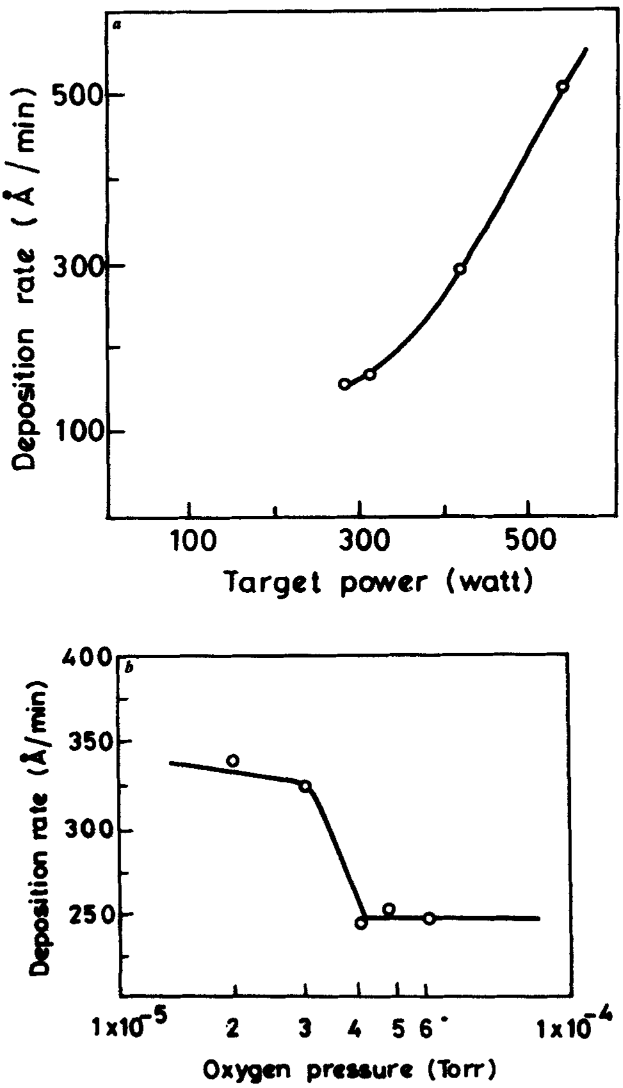

Figure 1. Variation in deposition rate as a function of a. target power and b. oxygen pressure.

where the band gap is plotted as a function of oxygen background pressure. It is seen that as the pressure is increased, initially there is a sharp rise in the optical band gap from 4·7 to 5·1 eV at the critical pressure, 3×10^{-5} torr, and saturates thereafter. This quite clearly indicates that the film composition approaches stoichiometry at this pressure and that further oxygen input does not affect the composition significantly. The highest value of 5·1 eV however, is lower than the bulk value and thus suggests that the films are only nearly stoichiometric and not completely so. This is reflected in the refractive index values also. Demiryont and Sites (1984) had earlier reported that the optical band gap of ion beam sputtered

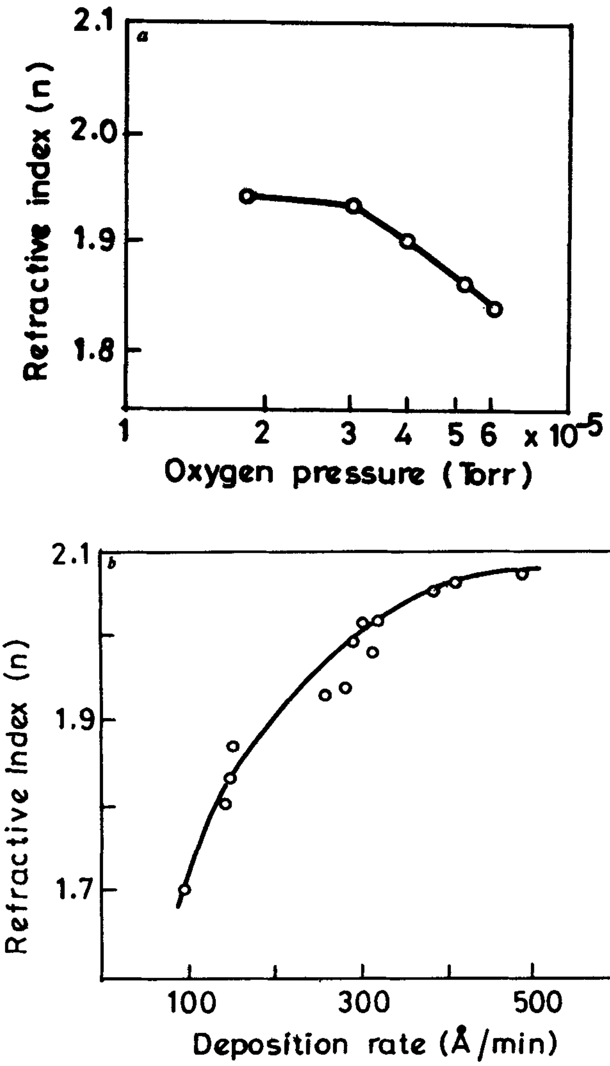

Figure 2. Variation in refractive index as a function of **a.** oxygen pressure and **b.** deposition rate.

titania films is a strong function of oxygen content in the films and hence the premise that the films in present case are stoichiometric at the critical oxygen pressure seems justified.

Rutherford backscattering spectroscopy done on samples prepared at 3×10^{-5} torr, indeed show that the films are nearly stoichiometric (figure 4).

Thus, it appears that stoichiometric films of zirconia can be synthesized at low temperatures using magnetron sputtering. Significantly, the observed temperature rise during deposition was not more than 40°C even at the highest power conditions. The reaction therefore, apparently, proceeds by an energetic particle induced diffusion and mixing mechanism. Netterfield *et al* (1988) had earlier reported that in ion

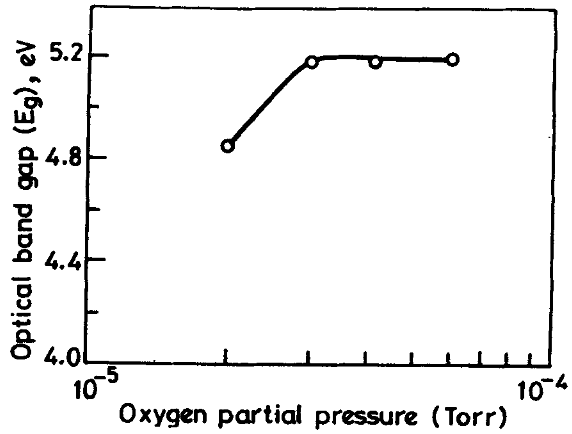

Figure 3. Variation of optical band gap as a function of oxygen pressure.

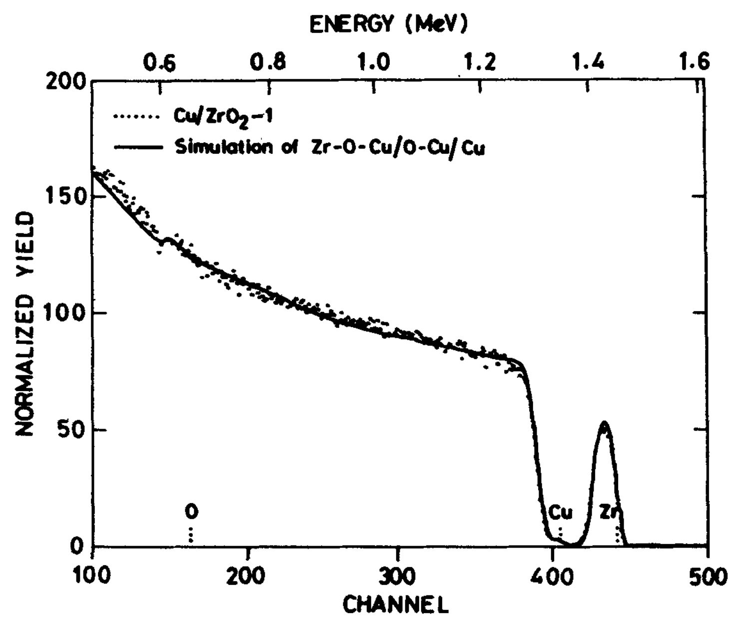

Figure 4. RBS spectra of zirconia films deposited at optimized conditions.

assisted deposited films of AlN, the compound formation is due to diffusion of nitrogen into the growing film and that it is accelerated due to ion bombardment. They also observed that it was a strong function of the ion to atom arrival ratio, which in the present case is determined by the oxygen backfill pressure, deposition rate and target power. Unlike in ion assisted deposition, however, these parameters cannot be independently controlled in magnetron sputtering. The exact dependence of compound formation of these factors independently is therefore difficult to determine.

Another factor of significance is the existence of a critical oxygen pressure above which the properties of the films seem to be optimal. The pressure of oxygen can, thus also be used to modulate the optical properties of oxide films deposited using reactive magnetron sputtering.

All further studies were carried out on films deposited at the critical oxygen pressure of 3×10^{-5} torr and a total pressure of 2×10^{-2} torr, a deposition rate of 32 nm/min corresponding to a target power of 450 W.

One of the main problems related to the growth of zirconia thin films is intrinsic optical inhomogeneity. Optical inhomogeneity can be defined as the variation of refractive index across the thickness of a film, as a result of process parameters, changes in microstructure or composition or a combination of these. A material is considered to show positive inhomogeneity with respect to thickness if the refractive index increases from the film-air interface to the substrate-film interface and negative inhomogeneity in the reverse case. This translates into higher reflectance than the bare substrate for the film, in the former case and lower in the latter case.

Figure 5 shows the spectral reflectance curves for the films deposited at the optimized conditions (stated above), in their as deposited state and then post deposition annealed to temperatures indicated in the figure. It can be seen that while as deposited films show positive inhomogeneity, presumably due to non stoichiometry in the films, the films annealed to 300°C show almost homogeneous behaviour. Further annealing to 500°C and 850°C results in negative inhomogeneity. This can be attributed to the grain growth resulting from annealing, which in turn results in increased grain size across the thickness of the film.

The behaviour of refractive index and extinction coefficient as a function of post deposition temperature shown in figures 6a and b respectively at three different wavelengths is illuminating. It is observed that up to a temperature of 300°C both the refractive index and extinction coefficient do not show very drastic changes as in the case of inhomogeneity. However beyond 300°C while the index drops, the extinction coefficient rises sharply and saturates beyond 500°C, both the optical constants show another step beyond 800°C. This signifies the fact that the optical constants are not stable to thermal annealing and show large changes in their values. Initially, however, they seem to be stable up to 300°C, as they approach

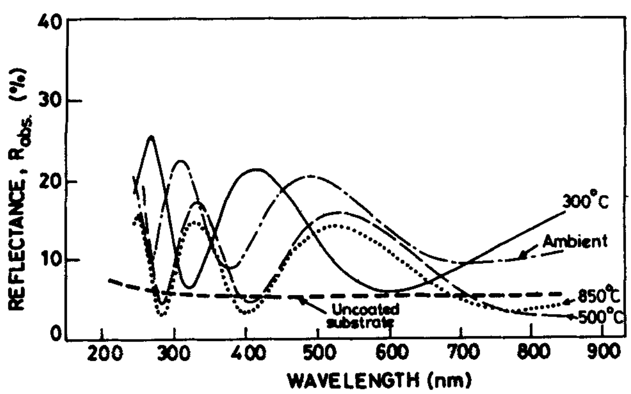

Figure 5. Spectral reflectance characteristics for as deposited and annealed zirconia films.

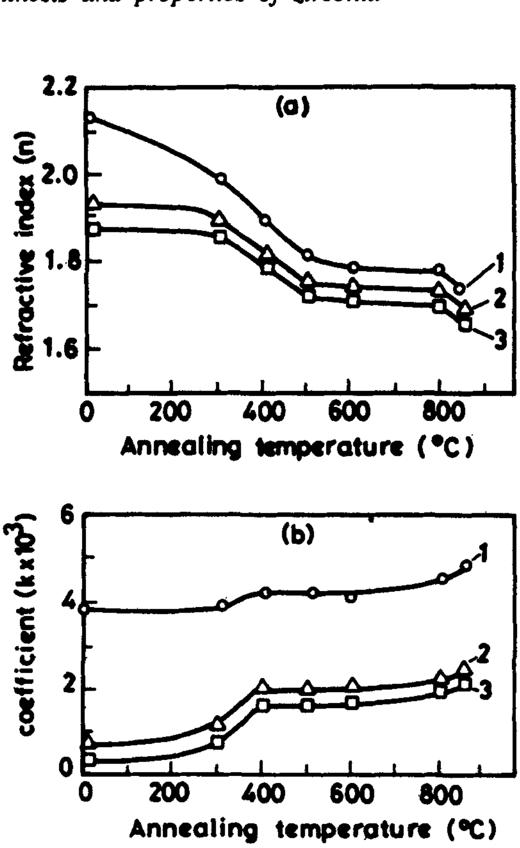

Figure 6. Optical constants as a function of post deposition annealing temperatures at (1) 350 nm, (2) 550 nm and (3) 850 nm.

zero inhomogeneity. Thus the inhomogeneity, the microstructure and the optical constants seem to, in conjunction, contribute to the instability of these films to thermal annealing.

The structural behaviour of these films is shown in figure 7, using X-ray diffraction. It was found that up to 400°C the films were completely amorphous and at this temperature they made a transition to a crystalline phase which was a mixture of tetragonal and monoclinic phase (figure 7a). The films were polycrystalline with small grain sizes, of the order of 12 nm (as estimated from the full width at half maximum of the peaks). At 600°C (figure 7b) the films were still polycrystalline with only a slight increase in grain size and finally at 900°C (figure 7C) they were almost single phase monoclinic, with a grain size of 24 nm. Two significant points that can be observed is that the films are mainly biphasic, i.e. they exhibit crystalline inhomogeneity in addition to optical inhomogeneity. Further the reduction in intensity of the tetragonal seems to be accompanied by an increase in grain size. This indicates a possible grain size dependent tetragonal to monoclinic phase transition. Such a transition has been observed earlier by Farabaugh *et al* (1987). It would thus appear that the instability to thermal annealing of zirconia with respect to its optical and structural properties is interrelated and that to exactly determine the cause for such behaviour would require further studies. Similar

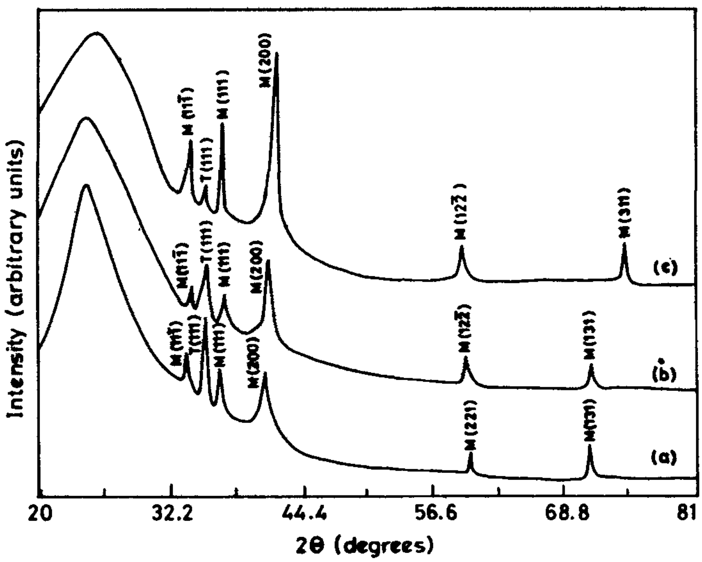

Figure 7. X-ray diffraction patterns for films annealed at **a.** 400°C, **b.** 600°C and **c.** 900°C.

observations have been made by Ghanashyam Krishna *et al* (1990) and Rujkorakarn and Sites (1986).

4. Summary

In summary, it has been demonstrated that zirconia films with reasonably high index and low optical absorption can be deposited at low temperatures by reactive DC magnetron sputtering. The composition of the films deposited under optimized conditions shows that the films are nearly stoichiometric. The refractive index, optical band gap and extinction coefficient are strong functions of the deposition parameters. The thermal stability of these films, however needs to be improved to enable larger applications of these films.

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