JOURNAL OF MATERIALS SCIENCE 27 (1992) 83–88

Effects of oxygen–argon mixing on the properties of sputtered zirconium dioxide film

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Partially stabilized ZrO_2–Y_2O_3 films (PSZ) were deposited using an r.f.-diode cathode sputter deposition system. The variation of film structure according to changes in the deposition parameters is described. The results show that the oxygen concentration of the oxygen–argon sputtering gas used for deposition of PSZ films can be used to control the microstructure of the films and their roughness. We found the optimal oxygen concentration to be 10%, resulting in a dense and homogeneous structure within the film, and a smoother surface. At the optimal oxygen concentration of 10% the refractive index and the absorption coefficient of the films showed a clear maximum and minimum, respectively. We consider that addition of oxygen to neutral argon sputtering gas both decreases the sputtering yield and increases the substrate bombardment by neutral oxygens.

1. Introduction

Partially stabilized zircon films can be applied to refractory metals for use at very high temperatures (2000 °C) as long as the films have a non-homogeneous structure, i.e. the structure must be as dense as possible if they are to act as a diffusion barrier. However, experience has shown that the dense structure is sensitive to heat shocks, whereas an open structure, corresponding to zone 1 of the Thornton (MDT) model [1, 2] is more shock-resistant because of its flexibility. Thus, in practice, a way must be found to modify the microstructure during film deposition. This can theoretically be achieved by changing the substrate temperature according to the MDT model.

In the case of refractory materials such as stabilized ZrO_2–Y_2O_3, this theoretical method would call for the use of very high substrate temperatures, which are incompatible with the proper functioning of a cathode sputtering device. We considered the possibility of altering the microstructure of the sputter-deposited film by changing the oxygen concentration in the oxygen–argon sputtering gas.

We complemented our study with a determination of the optical properties of the film. Variations of the refractive index, n, and the absorption coefficient, α, were studied as a function of deposition conditions.

2. Experimental procedure

Partially stabilized ZrO_2–Y_2O_3 films with thicknesses of 0.35–0.4 μm were deposited using an r.f.-diode cathode sputter deposition system. The substrate was a fused silica wafer measuring 10 mm × 10 mm and polished optically on both sides. Before deposition, the substrate was subjected to a complete cleaning cycle comprising: degreasing with neutral detergent in an ultrasound bath, washing with acetone followed by alcohol, and rinsing with distilled water. The substrate was then heated to a high temperature (500 °C) in a vacuum for 1 h to remove organic matter and gas trapped at the surface. It was then cooled to the deposition temperature. The target consisted of ZrO_2–Y_2O_3 material in the form of a disc of 50 mm diameter. The deposition conditions were varied over the following ranges: oxygen concentration 0%–100%, total pressure 4×10^{-3} torr $< P(O_2 + Ar) < 3 \times 10^{-2}$ torr (1 torr = 1.333×10^2 Pa), r.f. power 25 W $< P_{r.f.} <$ 75 W, substrate temperature $T_s = 400$ °C, substrate to target distance 35 cm.

To characterize the films according to the deposition conditions, we performed the following measurements: X-ray spectrum, micrography of the surface and cross-section of the film by scanning electron microscopy (SEM), surface texture profile by alpha-step analysis and residual stresses deduced from X-ray spectra.

The optical constants n and α were calculated from measurements of transmission in the wavelength range 0.2–0.8 μm, using the method developed by Manifacier *et al.* [3] with a Beckman UV 5240 spectrometer which can be equipped with an integrating sphere to take diffuse light into account.

3. Results

The variation in film structure with changes in the deposition parameters is described below. We began by studying partially stabilized ZrO_2–8% Y_2O_3 (PSZ).

3.1. Variation of the PSZ film structure depending on the pressure of pure argon in the range 4×10^{-3}–3×10^{-2} torr

Analysis of the X-ray diffraction (XRD) spectra of films of comparable thickness showed a predominant preferential orientation in the plane (1 1 1). The degree of crystallinity increased with decreasing pressure, as shown in Fig. 1.

Micrographs (SEM) of the surface show development towards a denser and smoother structure with decreasing pressure. This result is in close agreement with those obtained by XRD spectrum analysis, and has also been observed in studies of cathode-sputtered films on refractory materials [4].

Alpha-step measurements also showed a decrease in roughness with decreasing pressure. Table I gives the roughness amplitude, A_t, from crest to crest and the root mean square (rms) roughness, σ^*, according to total pressure. These results are in agreement with the Thorton model of zones [1, 2]. When the argon pressure increased, the morphology of the film shifted toward zone 1, characterized by a more open structure.

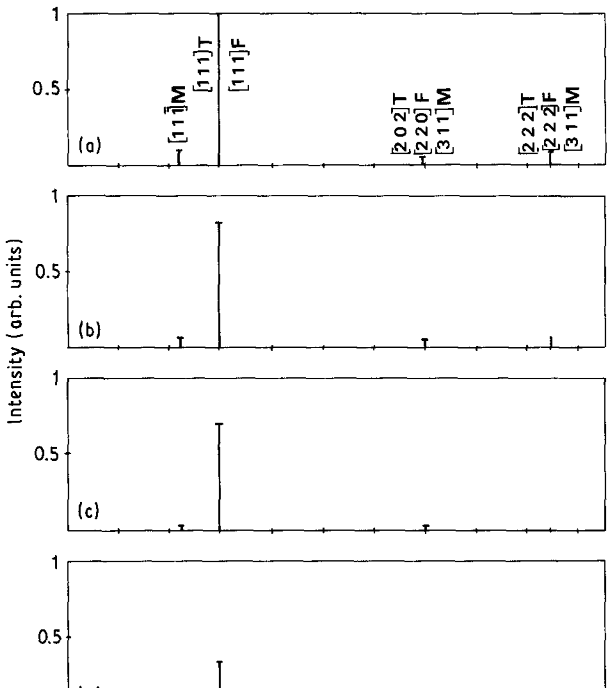

Figure 1 XRD patterns of ZrO_2–Y_2O_3 films sputter deposited at different argon pressures. $T_s = 400\,°C$, $P_{r.f.} = 75$ W and oxygen concentration 0%. P_{Ar+O_2}: (a) 4×10^{-3} torr, (b) 7×10^{-3} torr, (c) 10^{-3} torr, (d) 3×10^{-2} torr.

TABLE I Roughness amplitude, A_t, and mean quadratic value, σ^*, versus total pressure. $T_s = 400\,°C$, $P_{r.f.} = 75$ W and $P\,(O_2) = 0$

	Pressure (torr)		
	4×10^{-3}	7×10^{-3}	10^{-2}
A_t nm	10	25	34
σ^* (r.m.s.) (nm)	1.3	3.1	4.3

Based on the displacement of the lines of the X-ray spectra, the residual stresses in the films can be evaluated [5, 6]. In the pressure range used here, the stresses were compressive: $d_{0\,hkl} = 0.297\,30$ nm. They tended to decrease as pressure increased. These results are given in Table II. This confirms the preceding result by again showing the tendency of the structure to become more open with increasing pressure.

3.2. Variation of the PSZ film structure according to the oxygen concentration of the oxygen–argon sputtering gas

Oxide films obtained in a pure argon atmosphere generally show a lack of oxygen [7, 8]. In our case, zirconium-rich films were produced. Because of this lack of stoichiometry, the physicochemical properties of the films deteriorate. Chemical stability is reduced, as well as the efficiency of the film as a thermal barrier. To overcome this drawback, oxide films must be deposited in the presence of excess oxygen using an oxygen–argon mixture [9].

The effect of oxygen concentration on the properties of the film was studied.

To illustrate the effect of the oxygen concentration in the sputtering gas on the structure of the films deposited, we studied the variation of the XRD spectra of films of comparable thickness (0.35–0.4 μm). All the films had a polycrystalline structure with a preferential orientation of (1 1 1) regardless of the oxygen concentration. The maximum intensity of the (1 1 1) line was obtained at an oxygen concentration of 10%, resulting in a better texture. The intensity of this main line decreased when the oxygen concentration deviated from the optimal 10% concentration. This variation is shown in Fig. 2.

Moreover, spectra obtained with concentrations of 0 and 100% had a strong background noise (results not shown), indicating a poor state of crystallization. The X-rays in the plane (1 1 1) broadened at these extreme concentrations, which is characteristic of a strong lattice distortion related to a high concentration of defects [10, 11]. We also observed a displacement of these X-rays toward small Bragg angles, corresponding to an increase in d_{hkl}, indicating the presence of residual stresses in the films.

Surface and cross-sectional morphology, as characterized by roughness, was studied by SEM and alpha-step analysis. Fig. 3 shows micrographs of the cross-section and surface of PSZ films of comparable thickness and the same enlargement at low oxygen concentrations. The other deposition parameters remained constant. Micrographs of the films obtained

TABLE II Residual stresses and lattice parameter versus total pressure. $T_s = 400\,°C$, $P_{r.f} = 75$ W and $P(O_2) = 0$

	Pressure (torr)			
	4×10^{-3}	7×10^{-3}	10^{-2}	3×10^{-2}
d_{hkl} (nm)	0.299 90	0.299 00	0.298 30	0.298 20
$\sigma(10^{11}$ dyn cm$^{-2})$	− 0.49	− 0.32	− 0.19	− 0.17

with pure argon show an open columnar structure growing normally in the substrate plane, in agreement with the MDT model [1, 2] and having a rough surface texture. The mean quadratic roughness index, σ^* (r.m.s.), determined from surface profile recordings obtained by alpha-step analysis, was 4.3 nm (Fig. 4).

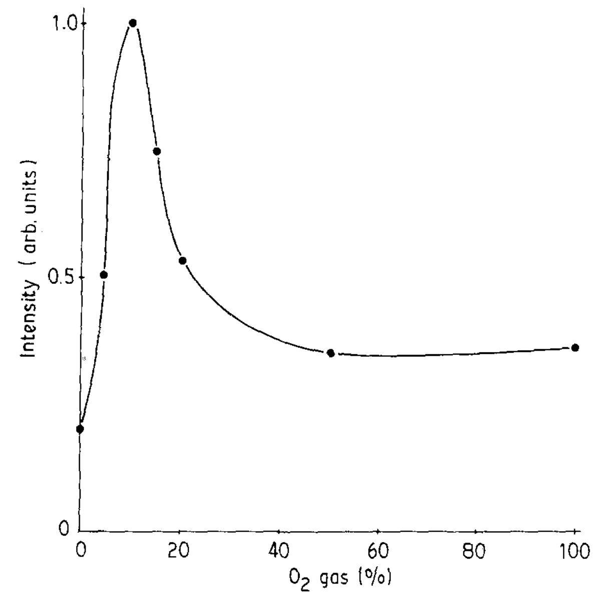

Figure 2 Intensity of the (1 1 1) line versus oxygen concentration.

In the case of the oxygen–argon mixture, 10% oxygen produced a film with a closed microstructure, i.e. more dense and homogeneous, with a clear decrease in surface roughness. Addition of a suitable concentration of oxygen (10%) to the argon inhibited the columnar structure characterizing films obtained with pure argon. Under these conditions, the r.m.s. roughness, σ^*, was of the order of 2 nm. Beyond this optimal concentration, the microstructure became more and more open, and the surface was much rougher. More specifically, micrographic analysis of the film deposited in pure oxygen and its roughness profile show the presence of disturbances and very deep holes. These superficial and deep imperfections affected the physical properties of the film, particularly its refraction index, which is reported elsewhere. In this case, the r.m.s. roughness, σ^*, was of the order of 15 nm.

Table III gives results for the oxygen concentration used for deposition.

The study was completed by determining residual stresses in the film according to the oxygen concentration of the sputtering gas. The XRD method was again

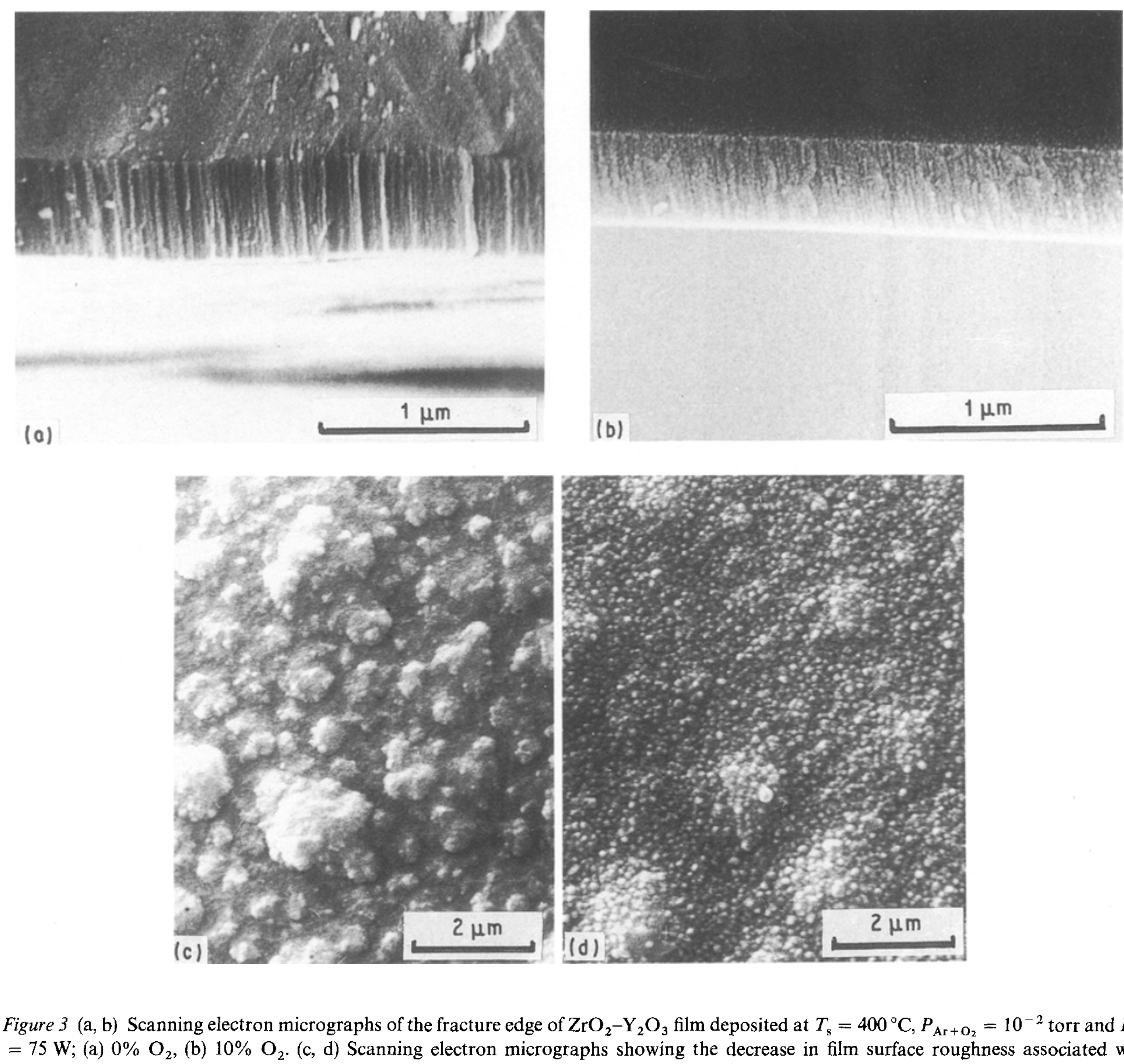

Figure 3 (a, b) Scanning electron micrographs of the fracture edge of ZrO_2–Y_2O_3 film deposited at $T_s = 400\,°C$, $P_{Ar+O_2} = 10^{-2}$ torr and $P_{r.f.} = 75$ W; (a) 0% O_2, (b) 10% O_2. (c, d) Scanning electron micrographs showing the decrease in film surface roughness associated with increasing oxygen concentration; (c) 0% O_2, (d) 10% O_2.

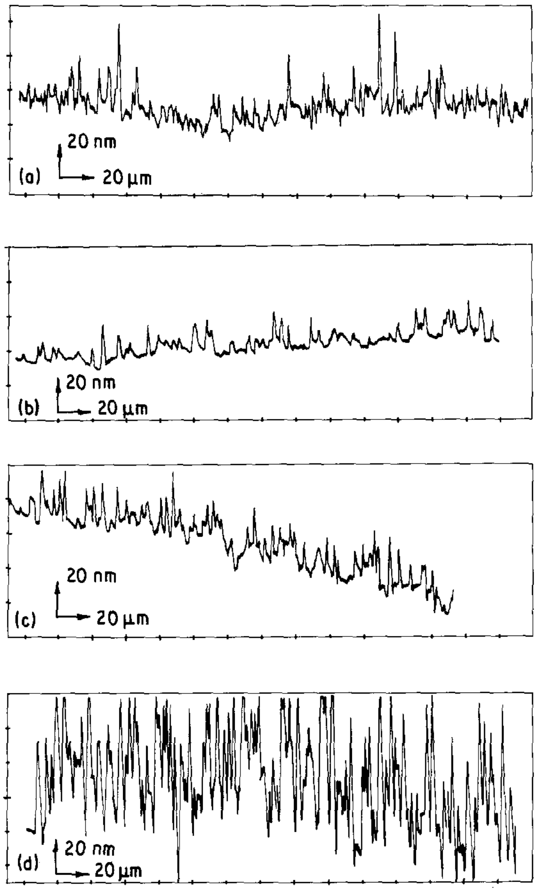

Figure 4 Surface profile recordings as a function of increasing oxygen pressure. $T_s = 400\,°C$, $P_{Ar+O_2} = 10^{-2}$ torr, $P_{r.f.} = 75$ W; (a) 0% O_2, (b) 10% O_2, (c) 20% O_2, (d) 100% O_2.

TABLE III Roughness amplitude and mean quadratic value, σ^*, as a function of the oxygen concentration. $T_s = 400\,°C$

	O_2 concentration %			
	0	10	20	100
R_t (nm)	34	16	36	120
σ^* (r.m.s.) (nm)	4.3	2.0	4.5	15

used, which seems well adapted to this type of analysis. It is based on the shift in the lines of the XRD spectrum with uniform deformation, and a broadening of the XRD peak with non-uniform deformation [11].

Variations of stresses in films deposited on a silica substrate with oxygen concentration are given in Table IV. The stresses were most compressive at an oxygen concentration of around 10% and decreased with deviation from this optimal concentration. The lowest values were obtained with pure argon or oxygen. This variation is in agreement with the more open microstructure of the films and with their optical properties.

The optical constants were determinated from the transmission curves of PSZ films 0.35–0.4 μm thick in the transparency range [3] 0.3–0.8 μm. Fig. 5 shows the variation of the refractive index n with oxygen concentrations ranging from 0–100% with a wavelength $\lambda = 0.6300$ nm. It can be seen that above a certain "threshold", addition of oxygen to the argon sputtering gas considerably changed the optical properties of the deposited films, which was correlated with the microstructural changes.

Under the same deposition conditions, we calculated the variation of the absorption coefficient, α, for the wavelengths $\lambda = 0.63$ and 0.35 μm, with oxygen concentration ranging from 0–20%. The coefficient α reached a very marked minimum at 10% oxygen (Fig. 6). Absorption was generally low in the visible range. In the low ultraviolet range, α increased slightly at 10% oxygen and much more strongly at the other two concentrations. This increase was mostly related to diffusion caused by the increased surface roughness of films obtained at the corresponding oxygen concentration.

3.3. Conclusion

The results show that the oxygen concentration of the oxygen–argon sputtering gas used for deposition of PSZ films can be used to control the microstructure of the films and their roughness.

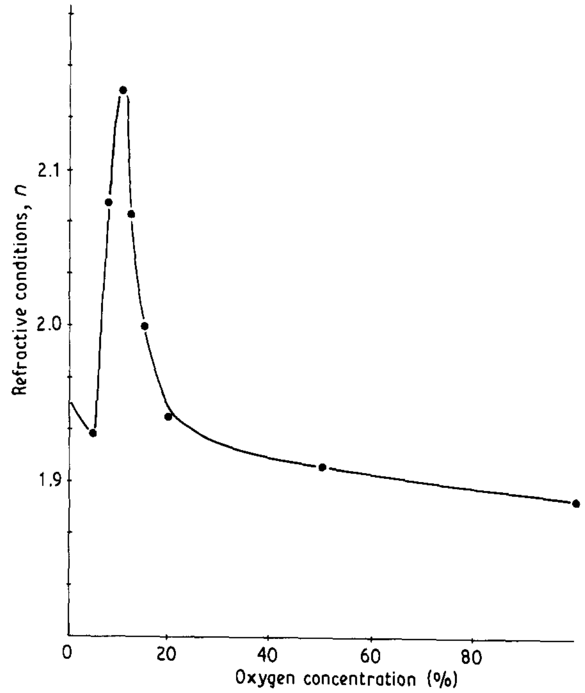

Figure 5 Refraction index as a function of oxygen concentration for ZrO_2–Y_2O_3 thin films. $T_s = 400\,°C$, $P_{Ar+O_2} = 10^{-2}$ torr, $P_{r.f.} = 75$ W, $\lambda = 630$ nm.

TABLE IV Residual stress and lattice parameter versus oxygen concentration. $T_s = 400\,°C$, $P_{(Ar+O_2)} = 10^{-2}$ torr, $P_{r.f.} = 75$ W

	O_2 concentration (%)				
	0	10	20	50	100
d_{hkl} (nm)	0.298 30	0.301 50	0.298 52	0.298 78	0.297 63
σ (10^{11} dyn cm^{-2})	– 0.19	– 0.79	– 0.23	– 0.13	– 0.07

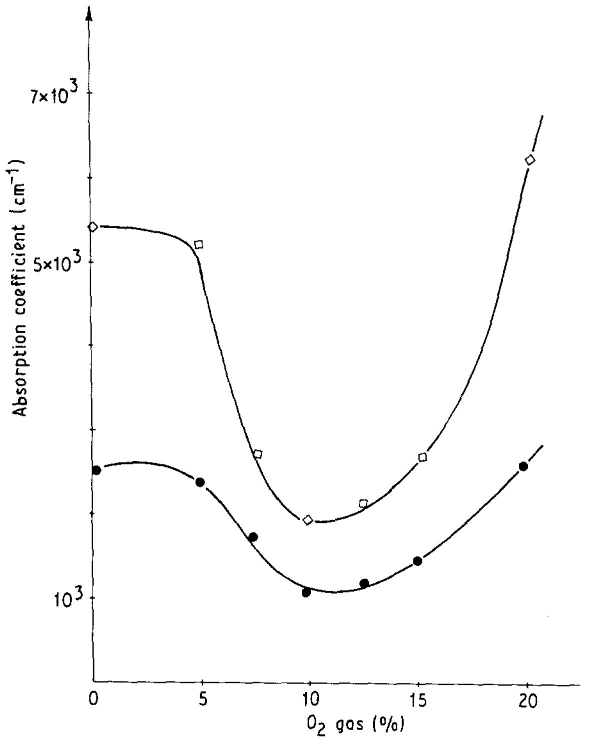

Figure 6 Absorption coefficients versus oxygen concentration at two wavelengths: λ = (◇) 350 and (●) 630 nm. T_s = 400 °C, P_{Ar+O_2} = 10^{-2} torr, $P_{r.f.}$ = 75 W.

The variation of optical properties was found to be related to the corresponding structure under the same conditions.

At an oxygen concentration of around 10% the films were most dense and had the smoothest surfaces.

4. Discussion

The addition of oxygen to the sputtering gas was shown here to cause considerable variation in the microstructure and, consequently, the properties of the films deposited under these conditions. We found the optimal oxygen concentration to be 10%, resulting in a dense and homogeneous structure within the film and a smoother surface. This improvement can be partly attributed to the value of atomic mobility at the film surface during deposition and partly to the rate of re-emission from the deposited film. The increase in re-emission was mostly due to the bombardment of the substrate by neutral oxygen atoms reflected from the target, which removed poorly bonded atoms from the film. However, as the oxygen concentration in the gas mixture rose above the optimal value, found here to be 10%, the concentration of neutrals reflected from the target increased, which reduced the yield of sputtering on to the target, as indicated by the reduced deposition rate. The films obtained under these extreme conditions were of mediocre quality. The improvement of the film structure by neutral bombardment was not enough to compensate for the effect of the reduced deposition rate, which plays a major role in the deposition process.

On the other hand, when the oxygen concentration decreased to zero (pure argon), substrate bombardment decreased, whereas the deposition rate increased, due to the increased sputtering yield. As shown above, the atomic arrangement of the substrate surface was thereby disturbed. The variation of the deposition rate with oxygen concentration is shown in Fig. 7.

Another study has shown an improvement in the microstructure of films when total pressure is increased at a constant oxygen concentration of 10%. Neutrals arriving at the substrate surface are known to be more active at low pressure, when their mean free path is no smaller than the inter-electrode distance. When bombardment is violent at a low deposition rate, the structure is likely to be disturbed, containing many defects, as confirmed by our results. The XRD lines become relatively wide and lose strength.

As pressure rises, the increased probability of collision reduces the number of high-energy particles, which decreases the effect of violent substrate bombardment. The best structure was obtained with a pressure of 3×10^{-2} torr at a deposition rate of 1.1 nm min^{-1}. Fig. 8 shows the relationship between deposition rate and pressure, at an oxygen concentration of 10%.

Analysis of the variation of crystallinity with pressure using pure argon showed a behaviour opposite to that obtained using the oxygen–argon gas mixture with 10% oxygen. At low pressures with pure argon, the microstructure was more homogeneous and dense than at higher pressures. This improvement can be attributed to the effect of substrate bombardment by atoms neutralized near the target by charge exchange, and subsequently reflected. Moreover, under these conditions, the deposition rate was relatively high (1.1 nm min^{-1}) compared to that obtained with the mixture at 10% oxygen (0.585 nm min^{-1}) and the same total pressure of 4×10^{-3} torr. The deposition rate increased with pressure and the increase was then accompanied by a large decrease in substrate bombardment by neutrals, which resulted in a porous structure and rough surface.

Another effect that has to be taken into account is that of film bombardment by secondary electrons,

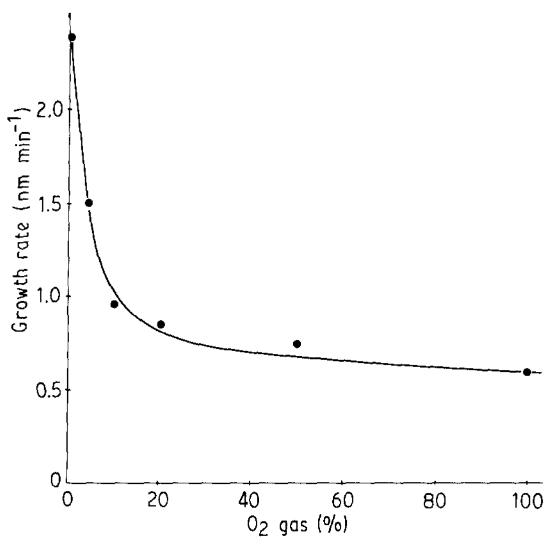

Figure 7 The growth rate of sputter-deposited ZrO_2–Y_2O_3 films as a function of sputtering gas oxygen content. T_s = 400 °C, P_{Ar+O_2} = 10^{-2} torr, $P_{r.f.}$ = 75 W.

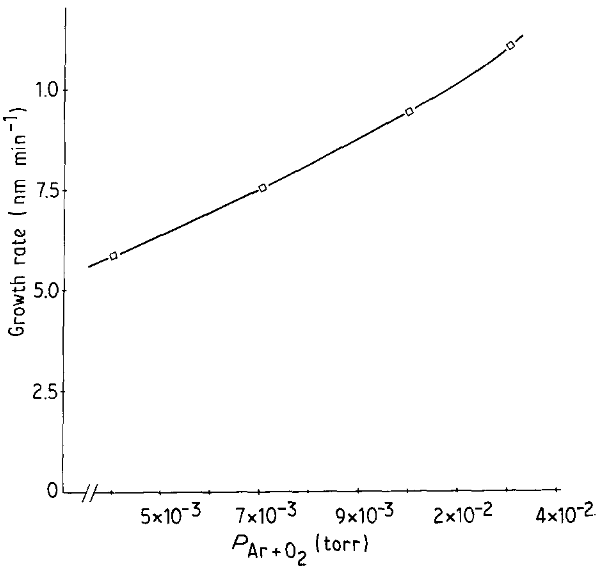

Figure 8 The growth rate of sputter-deposited ZrO_2–Y_2O_3 films a function of total pressure: P_{Ar+O_2}, $T_s = 400\,°C$, $P_{r.f.} = 75$ W, oxygen concentration = 10%.

which can be deleterious to satisfactory film growth [13]. The addition of electronegative oxygen to the sputtering gas produces negative ions (O^-) by attachment of an electron [14]. The neutralization of negative ions is generally of low probability. The overall effect is thus a decrease in the mobility of total negative carriers, now comprising electrons and O^- ions of large mass and low mobility. This decrease in overall mobility increases the probability of collision, thereby producing an apparent increase in pressure. The speed of the electrons is temporarily reduced when they are attached to oxygen atoms, with contractions of the negative column between the electrodes. The negative ions have less tendency to diffuse and thus contribute more effectively to producing a region of charged space in the plasma. The practical result for the deposition phenomenon is a decrease in effective substrate bombardment by secondary electrons.

5. Conclusions

Considering the above results, we consider that addition of oxygen to the neutral argon sputtering gas during deposition of a thin film of zirconium has the following effects.

1. The reflection rate of oxygen neutrals, R_O, from the target is increased. The ratio of energy transmitted to the target to incident energy can be expressed as $R = 4(m_i m_c)/(m_i + m_c)^2$. For oxygen atoms m_i colliding with zirconium atom m_c, $R_O \approx 0.5$, whereas for argon atoms $R_{Ar} \approx 0.8$.

This phenomenon results in a decrease in the sputtering yield, and an increase in substrate bombardment by neutrals.

2. The number of negative O^- ions increases to the detriment of secondary electrons, reselting in an apparent increase in pressure.

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Received 9 July 1990
and accepted 1 May 1991