Optical properties of filtered cathodic vacuum arc-deposited zirconium oxide thin films

2003 J. Phys.: Condens. Matter 15 7707

(http://iopscience.iop.org/0953-8984/15/45/010)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **15** (2003) 7707–7715 PII: S0953-8984(03)69153-8

Optical properties of filtered cathodic vacuum arc-deposited zirconium oxide thin films

Z W Zhao, B K Tay[1], G Q Yu and S P Lau

School of Electrical and Electronic Engineering, Nanyang Technological University, 639798, Singapore

E-mail: ebktay@ntu.edu.sg

Received 17 September 2003
Published 31 October 2003
Online at stacks.iop.org/JPhysCM/15/7707

Abstract

Zirconium oxide thin films were grown on n-Si(100) and quartz substrates by using an off-plane filtered cathodic vacuum arc without external heating. A Zr cathode was used to obtain the plasma and the deposition rate was varied from 75 to 35 nm min^{-1} corresponding to various oxygen flow rates. Optical properties of as-deposited films are presented as a function of oxygen flow rate and shown to depend greatly on it. The transmittance and optical band gap (E_g) increase with the oxygen flow rate whereas optical constants decrease. Film optical homogeneity is considerably enhanced and good homogeneity is exhibited for the films deposited at oxygen flow rate above 50 sccm. Structural homogeneity remains throughout the film depth even though the respective film structure changes with the different oxygen flow rates. Bulk-like stoichiometric amorphous zirconium oxide film exhibits high E_g (5.0 eV), high transmittance and good optical constants (high refractive index of 2.16 at 550 nm and low extinction coefficient of $\sim 10^{-5}$ at 550 nm) with homogeneous structure.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Zirconia is widely used in optical fields such as high-reflectivity mirrors, broadband interference filters, and waveguides with small losses, and in active electro-optical devices [1, 2], because of its high refractive index, large optical band gap, and low optical loss and high transparence in the 0.3–8 μm range. The properties obtained are dependent on the film chemical composition, impurity and microstructure, which are closely correlated with the deposition technique itself and the deposition conditions. Generally, dense zirconia films with optical and structural homogeneity are desirable, since stability and reproducibility of

[1] Author to whom any correspondence should be addressed.

refractive index in optical thin films are strictly related to the packing density and structural properties.

The inhomogeneity of zirconia films prepared by evaporation has been widely investigated elsewhere [3–7]. The observed inhomogeneity by Klinger *et al* [4] and Harris *et al* [5] arises from the fact that the diameters of the columnar structure in the films change with distance from the substrate side (or surface side) of the film, leading to the changes in the density of the film and a corresponding gradient in the refractive index. A structural inhomogeneity is also noted with a crystallographic phase composition gradient (i.e., monoclinic $\Leftrightarrow$ tetragonal $\Leftrightarrow$ amorphous) from the substrate to the surface, as confirmed by spectroscopic ellipsometry, where a two-layered model structure with a higher refractive index at the bottom and a lower refractive index on the top is favoured during film growth [6]. Improvement in optical and structural homogeneity of zirconia could be achieved by the proper choice of the oxygen partial pressure during reactive evaporation, though inhomogeneity still occurred at high oxygen partial pressures [7]. Many other techniques, such as CVD [8, 9], sol–gel techniques [10], ion-beam assisted deposition [11] and sputtering [12–15], have been used to synthesize zirconium oxide thin films. However, few results have been reported on the homogeneity of zirconium oxide thin films by these various techniques [16].

In this work, zirconium oxide thin films were deposited as a function of oxygen flow rate by filtered cathodic vacuum arc (FCVA), in which unwanted macroparticles are removed by electro-magnetic and mechanical filters [17]. The deposition technique is characterized by its high ion energy (50–150 eV), high ionization rate and high deposition rate of condensing species. The inherent high energy of the depositing species could decrease the void volume of the resulting film by increasing the packing density of the microstructure. The purpose of this paper is to study the optical properties of zirconium oxide films as well as the homogeneity of the films by optical spectroscopy and grazing incident x-ray diffraction (GIXRD). The results reveal that zirconium oxide thin films with good optical properties and homogeneity can be obtained by this technique.

2. Experimental details

Zirconium oxide thin films were deposited by an off-plane double bend FCVA. Details regarding the deposition apparatus have been published elsewhere [18, 19]. The system incorporates an off-plane double bend filter, which effectively removes macroparticles. A Zr cathode with a purity of 99.98% operated at an arc current of 120 A was used to obtain the plasma, and the toroidal magnetic field was fixed at 40 mT. The base pressure of the system was 4×10^{-6} Torr. Oxygen gas with different flow rate from 10 to 98 sccm (corresponding to 1×10^{-4}–4.6×10^{-4} Torr) was introduced into the chamber, leading to the deposition rate varying from 75 to 35 nm min^{-1}. The films were grown on *n*-Si(100) and quartz substrates at room temperature without external heating. During the film growth, the substrate temperature rises due to the plasma bombardment but does not exceed 100 °C.

Transmittance was recorded from 200 to 1100 nm with a spectrometer. Optical constants and film thickness were both obtained by fitting optical spectra with Scout software [20]. Fourier transform infrared spectroscopy (FTIR) was performed on the deposited films in the wavenumber range of 50–7800 cm^{-1}. GIXRD with a Cu Kα source was carried out from $2\theta = 20°$ to 70° at different incidence angles, 0.5°, 1° and 3°, respectively. The phase identification is achieved by comparison with data from the JCPDS international diffraction database.

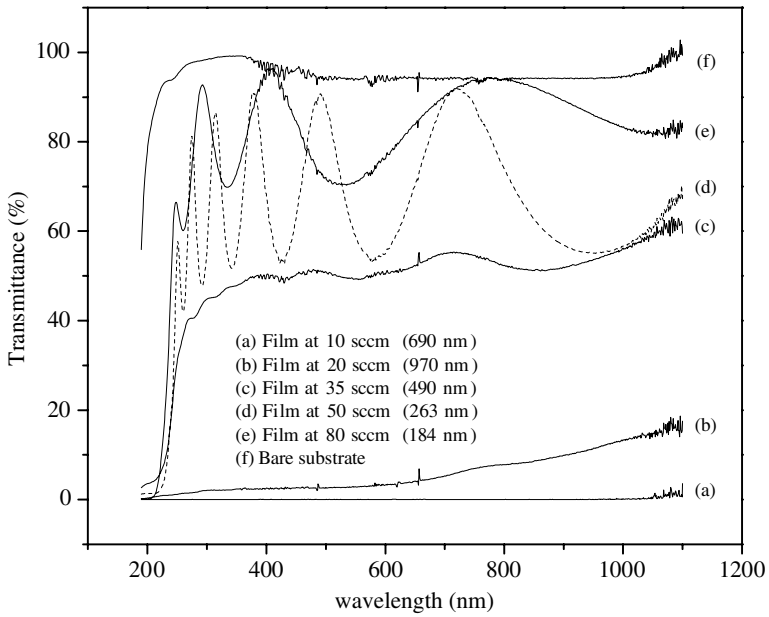

Figure 1. The transmittance of zirconium oxide thin films deposited at different oxygen flow rates.

3. Results and discussion

Figure 1 shows the transmittance spectra of the films prepared on quartz at different oxygen flow rates as well as uncoated substrate. Evidently, the oxygen flow rate has a great influence on film transmittance. At 10 sccm, the film appears dark and the transmittance almost becomes zero. When the flow rate increases to 20 sccm, the transmittance is obviously enhanced, especially in the long wavelength range. Further, at 35 sccm, a great improvement in transmittance is observed as it attains 50%, though the film is not transparent yet. The low transmittance may arise from light absorption by free carriers from zirconium, most of which are not oxidized. In other words, the film deposited at relatively low pressure (corresponding to 20 sccm and below) is severely oxygen deficient. The largely increased transmittance at 35 sccm suggests that most of the zirconium has bonded to oxygen. When the oxygen flow rate is at 50 sccm and above, an interference pattern is clearly seen indicating the films are transparent and a better transmittance could be achieved. In particular for wavelengths above 400 nm, the maximum transmittance is almost constant and as high as that of the substrate (curve (e)), indicative of ideal stoichiometry of the film. For wavelengths below 400 nm, the transmittance decreases gradually as the wavelength approaches the film absorption edge.

The optical inhomogeneity of the films can be evaluated by using optical spectra, such as transmittance or reflectance, of the films compared with corresponding spectra from the bare substrate. The difference ΔT or ΔR between the transmittance or reflectance extremum (T_{max} or R_{min}) of the film and that of the substrate measures the inhomogeneity of the film. For the homogeneous zirconia thin films, the maximum transmittance value (T_{max}) would correspond to the transmittance of the uncoated transparent substrate (T_s). Khawaja *et al* [21] had observed that T_{max} of evaporation-deposited zirconium oxide films was 2% higher than T_s, and ascribed this to the excess of oxygen in the films induced by adsorbed water in air. Martin *et al* [22] also observed substantial vacuum-to-air shifts in the transmittance of zirconium oxide films grown

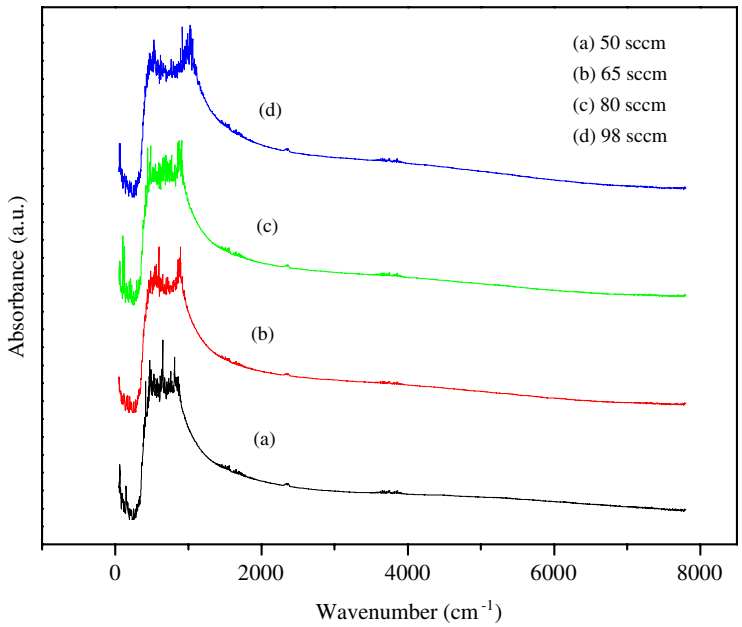

Figure 2. FTIR spectra of zirconium oxide films at and above 50 sccm after exposure to air for 8 months.

at 300 °C by electron beam evaporation, implying that the water adsorption occurred after exposure to air as confirmed by nuclear reaction analysis (NRA). They demonstrated that the shift in transmittance can be diminished by ion beam assisted deposition, and no measurable shift occurred as an O_2^+ ion beam at 1200 eV and 200 μA cm^{-2} was used. In our case, below 50 sccm, considerable ΔT has evidently been observed, which is caused by oxygen deficiency in the films as discussed previously. At 50 sccm, ΔT becomes smaller and is observed to be less than 3%. It is believed that the observed ΔT is caused by the film microstructure, such as the surface morphology and polycrystalline structure. This is concluded from the results of the high roughness parameter with R_{max} of 3 nm obtained by AFM (not shown) and high scattering centre concentration among grain boundaries of polycrystallites as revealed by XRD (this will be discussed next). At and above 65 sccm, no measurable deviation of ΔT can be observed, implying good optical homogeneity and little adsorbed water from air in the film. The high Zr ion energy (116 eV) from plasma would decrease the void volume of the resulting films and thereby yield dense films. Therefore, water incorporation into the films is greatly suppressed. This is further confirmed by FTIR analysis of the films at and above 50 sccm upon exposure to air for 8 months as shown in figure 2. As observed, in addition to the features below 1500 cm^{-1} arising from the ZrO stretching band, no others could be observed around 3400 cm, meaning no detectable OH stretching band in the films, even after a long exposure to air, again implying the high packing density and homogeneous optical properties of the films.

GIXRD patterns with various incident angles could give the information on the phase/structure composition throughout the film depth. Figure 3 shows the GIXRD patterns of respective films at various oxygen flow rates with the incident angle from 0.5° to 3°. For all the crystalline films, with various incident angles, the GIXRD patterns show that only the monoclinic phase is observed as seen in figures 3(a)–(c). Moreover, for each individual film, such as at 50 sccm, in addition to similar features exhibited in these three XRD curves with $\theta = 0.5°$, 1°, and 3°, neither a shift in peak positions nor the presence of new peaks is observed.

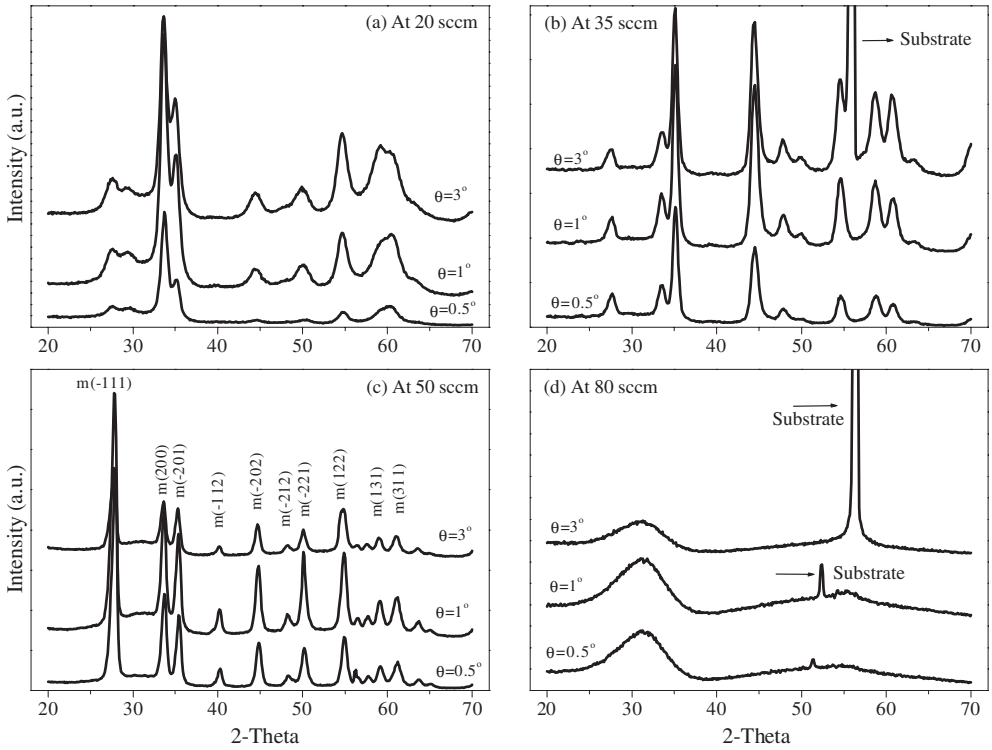

Figure 3. GIXRD patterns of the zirconium oxide films with incident angle of 0.5°, 1° and 3°.

A similar phenomenon can be observed in other films at 20 and 35 sccm, except the additional peak labelled in figure 3(b) at $\theta = 3°$ arising from the substrate due to the enhanced signal from the substrate. At and above 65 sccm, the broad peak centre remains unchanged as the incident angle increases from 0.5° to 3°. Hence, it can be concluded that the independence of film structure on film thickness indicates the homogeneous structure throughout the film depth for all the films. This is different from that of reactive-evaporation-prepared zirconia film reported by Bellotto *et al*, where inhomogeneity exhibited by the films at high oxygen partial pressure [$p(O_2)/p_c(O_2) = 12.5$] was observed and the films consisted of two layers with a bottom layer containing tetragonal zirconia and an upper layer containing monoclinic zirconia [7]. In our work, there is little change with incident angle up to 3°, indicating that the zirconium oxide film with the homogenous structure advances along the growth direction.

Figure 4 shows the variation of optical constants at 550 nm with O_2 flow rate. The refractive index monotonically decreases with increasing flow rate. Based on reported results [7, 16, 21, 23, 24], the refractive index is possibly correlated with the structure, chemical composition, and packing density of film. As depicted previously in figure 3, the film evolves in structure from amorphous to monoclinic phase at 50 sccm, and then to amorphous above 50 sccm. This inconsistent dependence of refractive index and structure on flow rate denotes that the structure is not a significant factor in determining the refractive index. In addition, the film density is believed to decrease with increasing flow rate and to contribute to the decrease of refractive index. As depicted below, the degree of reduction in density is not severe. This is substantiated by the fact that the index (2.16) at 80 sccm is very near the bulk value of 2.2 [25]. Therefore, the composition is a dominant factor in affecting the index. Kao *et al* [23] also reported a similar conclusion.

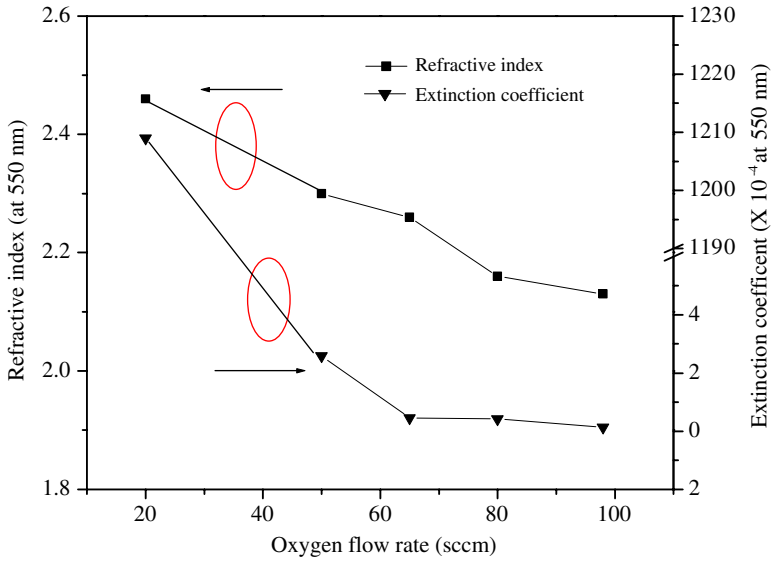

Figure 4. Optical constants as a function of oxygen flow rate.

The FCVA-deposited zirconia film exhibits a higher refractive index compared with those prepared by other techniques as shown in table 1, denoting that a higher packing density could be achieved by using this technique. Normally, using evaporation and sol–gel produces a relatively lower refractive index of less than 2 (see table 1), which might be explained by the fact that the films have a tendency to porous columnar structure formed due to the low adatom mobility, giving rise to lower packing density. Considerable improvement in refractive index could be attained if assisted ion-beam and/or substrate heating are provided during deposition [26]. In our case, neither an ion beam source nor external heating is adopted during film growth. However, as mentioned above, the inherent high ion energy from the cathode source material is expected to evidently decrease the void volume of the grown film by increasing the packing density of the microstructure, hence contributing to the bulk-like refractive index. This could be further confirmed by the stability of film transmittance before and after exposure to air for 8 months as depicted in figure 5. In the visible wavelength range, little shift in intensity could be identified between the spectra of as-grown and the counterpart exposed to air for 8 months. In the range between 400 and 700 nm, Martin *et al* [22] also observed the non-measurable shift in transmittance upon the higher O_2^+ ion beam being used, and ascribed it to the higher packing density. The little shift in transmittance in the visible range, in our case, implies stability in film transmittance and little change in film packing density before and after exposure to air for a long time. That is to say, the higher packing density gives rise to a bulk-like refractive index and results in little water or impurity from the environment in the microvoids of the film even after exposure to air for 8 months, which is supported by the FTIR analysis in figure 2.

On the other hand, the extinction coefficient decreases to approximately zero with increasing flow rate. This tendency is supported by the variation of transmittance in the visible wavelength range in figure 1, and hence is associated with the reduction of oxygen vacancies in the films caused by more incorporation of oxygen. Especially at and above 50 sccm, the film exhibits a sharp drop in the extinction coefficient, denoting the O/Zr atomic ratio approaching 2:1, as confirmed by XPS results analysed in another work [31].

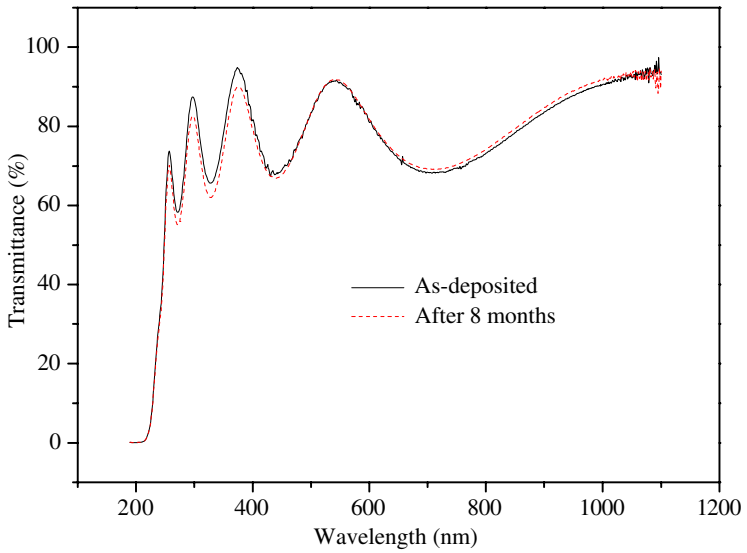

Figure 5. Transmittance comparison of the as-deposited film with that after exposing to air for 8 months.

Table 1. Comparison of refractive index by different techniques.

Technique	n at 550 nm	Remark
Ion beam assisted evaporation [26]	2.1	300 eV ion energy and 220 μA cm^{-2} of current density
Evaporation [27]	1.9	Deposited at room temperature
Sol–gel [28]	1.95	Deposited at 400 °C
Atomic layer deposition [29]	2.08	Deposited at 340 °C
Chemical vapour deposition [30]	2.03 ± 0.17	Deposited at 250–700 °C (at 633 nm)
RF reactive sputtering [12]	2.05	Sputtering power 1000 W
FCVA (current work)	2.16	Deposited at room temperature

For the as-deposited films, the optical band-gap energy, E_g, determined from the Tauc plot [32], is found to increase from 4.1 eV at an oxygen flow rate of 35 sccm to 5 eV as shown in figure 6. The left inset is the plot of $(\alpha h\upsilon)^2$ versus the photon energy $h\upsilon$, where the band gap energy is determined. The right one is the absorption coefficient for the same film. Beyond the optical band gap, the steep increase of the absorption can be attributed to the band–band transitions [33, 34] as shown in the right inset figure. For the films deposited at low oxygen flow rates of 10 and 20 sccm, E_g could not be derived from this method due to the considerable absorption. A similar trend in E_g with the oxygen flow rate was also reported for zirconium oxide prepared by magnetron sputtering [16] as well as for other metal oxides, such as niobium oxide [35] and titanium oxide [36] films.

4. Conclusions

Zirconium oxide thin films have been grown on n-Si(100) and quartz substrates by using off-plane FCVA without external heating. A Zr cathode with high purity was used to obtain the plasma and the oxygen flow rate was varied from 10 to 98 sccm, concurrent with a decrease

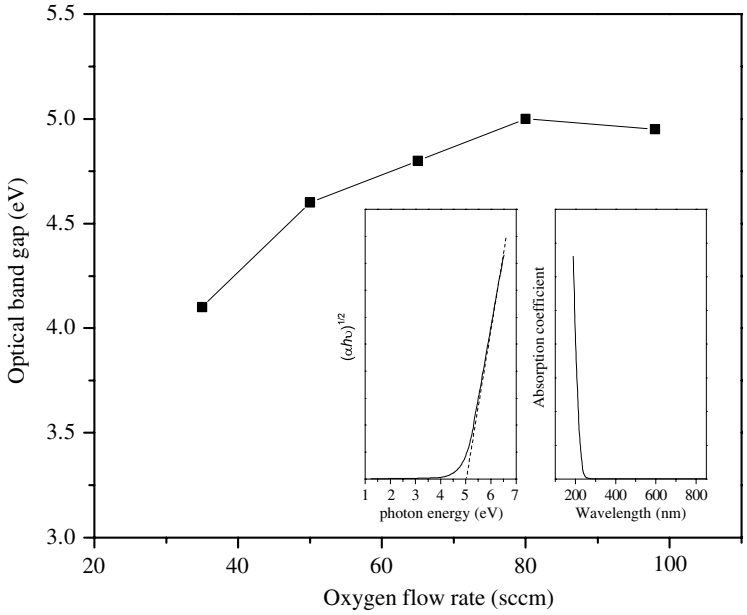

Figure 6. Dependence of E_g on the oxygen flow rate.

in deposition rate from 75 to 35 nm min^{-1}. The optical properties of as-deposited films as well as the film homogeneity have been studied as a function of the oxygen flow rate. The results show that the optical properties are strongly influenced by the oxygen flow rate. The film transmittance increases with the oxygen flow rate as well as the optical band gap, while the optical constants decrease. The film optical homogeneity is improved by increasing the oxygen flow rate, and good homogeneous optical properties are exhibited by the films above 50 sccm, while the film structure remains homogeneous during all the depositions. For the stoichiometric film with amorphous structure, high transmittance, a high optical band gap of 5.0 eV and higher refractive index and lower extinction coefficient are obtained with homogeneous microstructure, implying that there are potential applications for zirconium oxide thin films in optical coatings and for FCVA technology in the deposition of metal oxide optical films.

References

[1] Koch T and Ziemann P 1997 *Thin Solid Films* **303** 122
[2] Jones F 1988 *J. Vac. Sci. Technol.* A **6** 3088
[3] Jahawaja E E and Tomlin S G 1975 *Thin Solid Films* **30** 361
[4] Klinger R E and Carniglia C K 1985 *Appl. Opt.* **24** 3184
[5] Harris M, Mcleod H A, Ogura S, Pelletier E and Vidal B 1979 *Thin Solid Films* **57** 173
[6] Bellotto M, Cremonesi C, Parmigiani F, Scagliotti M and Beretta S 1991 *Mater. Res. Soc. Symp. Proc.* **208** 137
[7] Bellotto M, Carid A, Cereda E, Gabetta G, Scagliotti M and Braga Marcazzan G M 1993 *Appl. Phys. Lett.* **63** 2056
[8] Garcia G, Casado J, Libre J, Cifre J, Figulras A, Gali S and Bassas J 1997 *Chem. Vap. Deposition* **3** 91
[9] Chang J P and Lin Y S 2001 *J. Appl. Phys.* **90** 2964
[10] Chang J P, Lin Y S and Chu K 2001 *J. Vac. Sci. Technol.* B **19** 1782
[11] Matsuoka M, Isotani S, Chubaci J F D, Miyake S, Setsuhara Y, Ogata K and Kuratani N 2000 *J. Appl. Phys.* **88** 3773
[12] Gao P T, Meng L J, dos Santos M P, Teixeira V and Andritschky M 2000 *Vacuum* **56** 143

[13] Ben Amor S, Rogier B, Baud G, Jacquet M and Nardin M 1998 *Mater. Sci. Eng.* B **57** 28
[14] Koski K, Holsa J and Juliet P 1999 *Surf. Coat. Technol.* **121** 303
[15] Edlou S M, Smajkiewicz A and Aljumaly G A 1993 *Appl. Opt.* **32** 5601
[16] Venkataraj S, Lappertz O, Weis H, Drese R, Jayavel R and Wuttig M 2002 *J. Appl. Phys.* **92** 3599
[17] Tay B K, Shi X and Flynn D I 1997 *Surf. Eng.* **13** 213
[18] Shi X, Tay B K and Tan H S 2000 *US Patent Specification* 6031239
[19] Shi X, Tay B K and Lau S P 2000 *Int. J. Mod. Phys.* B **14** 136
[20] Theiss W 2001 *Scout Thin Film Analysis Software Handbook* (Aachen, Germany: Hard- and Software)
[21] Khawaja E E, Bouamrane F, Hallak A B, Daous M A and Salim M A 1993 *J. Vac. Sci. Technol.* A **11** 580
[22] Martin P J, Netterfield R P and Sainty W G 1984 *J. Appl. Phys.* **55** 235
[23] Kao A S and Gorman G L 1990 *J. Appl. Phys.* **67** 3826
[24] Krishna M G, Rao K N and Mohan S 1990 *Appl. Phys. Lett.* **57** 557
[25] Ghanashyam Krishna M, Narasimha Rao K and Mohan S 1992 *Thin Solid Films* **207** 248
[26] Ghanashyam Krishna M, Narasimha Rao K and Mohan S 1992 *J. Vac. Sci. Technol.* A **10** 3451
[27] Ghanashyam Krishna M, Narasimha Rao K and Mohan S 1990 *Appl. Phys. Lett.* **57** 557
[28] Brenier R and Gagnaire A 2001 *Thin Solid Films* **392** 142
[29] Matero R, Ritala M, Leskela M, Jones A C, Williams P A, Bickley J F, Steiner A, Leedham T J and Davies H O 2002 *J. Non-Cryst. Solids* **303** 24
[30] Cameron M A and George S M 1999 *Thin Solid Films* **348** 90
[31] Yu G Q, Zhao Z W, Tay B K and Lau S P 2003 *Appl. Phys.* A submitted
[32] Tauc J 1971 *Optical Properties of Solids* ed F Abeles (Amsterdam: North-Holland) p 71
[33] Nicoloso N, Löbert A and Leibold B 1992 *Sensors Actuators* B **8** 253
[34] Kosacki I, Petrovsky V and Anderson H U 1999 *Appl. Phys. Lett.* **74** 341
[35] Venkataraj S, Drese R, Lappertz O, Jayavel R and Wuttig M 2001 *Phys. Status Solidi* a **188** 1047
[36] Ottermann C R and Bange K 1996 *Thin Solid Films* **286** 32