

Characterization of MgO Layers on Different Alumina and Glass Substrates by Grazing Incidence Diffractometry and Grazing Incidence X-ray Reflectometry

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Magnesium oxide thin films were deposited at an average evaporation rate of 1.8 nm s^{-1} onto different crystalline alumina substrates and amorphous float glass. The deposits were made in an electron-beam evaporator at substrate temperatures between 25°C and 190°C under different oxygen partial pressures. Films of 0.1, 0.5 and $1 \mu\text{m}$ thickness were deposited. These coatings were investigated by grazing incidence diffractometry (GID) to vary the depth of penetration. For films $0.1 \mu\text{m}$ thick the additional use of grazing incidence x-ray reflectometry (GIXR) was possible. The deposited films were polycrystalline with different $\langle 100 \rangle$ textures depending on the substrate temperature. All the MgO thin-film reflexes measured were strongly broadened compared with the reflexes of a standard polycrystalline MgO material. The crystal size and the microstrain of the MgO coatings were calculated by profile analysis using the Fourier transformation method. It was demonstrated that the x-ray profiles of the MgO reflexes are influenced by the roughness of the substrate surface. Only small gradients were found in the particle sizes and microstrains within the deposited films. The oxygen partial pressure did not significantly influence the film properties measured by GID. The GIXR roughness and mass density measurements agreed with the results of GID. Magnesium oxide films deposited at higher temperatures show a diminished crystallinity and less interface roughness.

INTRODUCTION

The application of a surface coating to a workpiece provides a method of changing its surface properties independently of the bulk material and extends the use of components manufactured by conventional processes to many new applications in a diverse range of technological areas. Lattice defects as imperfections of the first and second type in thin films influence the properties of films. It can be assumed that gradients of chemical, physical and structural properties exist between the film layers on the substrate and the outermost layers. The purpose of this study is to prepare thin MgO films and characterize their structure and defect structure by non-destructive x-ray methods. X-ray data are influenced by different types of lattice defects. The first type of imperfection, such as point defects, displacement disorders or substitution disorders, does not change the long-range order in the crystals. In the second type of imperfection there is, on the contrary, no long-range order. If the arrangement of close neighbours is very loosely ordered, we have amorphous bodies. These crystal structure characteristics are partially or wholly manifested by diffraction intensity, lineshape or the change in lineshape with respect to the diffraction angle 2θ . The term 'shape' includes peak breadths at half-maximum height (FWHM) or integral breadth, the symmetry or lack

thereof around the intensity maximum and the mathematical form of the diffraction profile, which may be Lorentzian or Gaussian or an intermediate form. To extract the pure lineshape from the experimental profile, procedures were required for removing instrumental effects. The influence of the apparatus was separated from the experimental profile by deconvolution. Another aim of this study is to check the influence of comparable small substrate temperatures in the range from room temperature to $\sim 200^\circ\text{C}$ to prevent structural and optical changes of the substrate material.

Magnesium oxide crystallizes in the rock salt structure. It has been widely used as a substrate material for the thin film growth of high-temperature superconductors because of its lattice matching to $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and its low chemical reactivity.¹ Recently, MgO buffer layers on silicon, fused silica and sapphire have been deposited by various methods.^{2–5} Strong $\langle 100 \rangle$ orientation of MgO was observed on alumina-coated sapphire when deposited by spray pyrolysis of $\text{Mg(2,4-pentanedione)}_2$ from alcoholic solutions at 47°C .⁶ Berezin *et al.*⁷ prepared MgO buffer layers on sapphire at temperatures as low as 370°C by electron-beam evaporation. Little or no diffusion occurs between the substrate and the MgO layers. At a substrate temperature of 300°C , MgO films were deposited on several semiconductors by r.f. sputtering of a pure MgO target.⁸ Apart from epitaxy, MgO grows with strong preferential $\langle 100 \rangle$ orientation regardless of the substrate selection. The authors report that the substrate

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temperature strongly affected the surface morphology of 3 nm thick layers. On reducing the substrate temperature, mirror surfaces were obtained. However, the surface of 40 nm thick MgO deposited under the same conditions had a number of spotty defects that were 2–4 μm in diameter.

X-RAY PROCEDURES

The penetration depth of x-rays is an important parameter in the analysis of surface layers, specially if gradients of structure parameters are observed. In ultrathin films the x-ray beam penetration exceeds the layer thickness. The film information depth T strongly depends on the thickness of the layer.⁹

$$T = \frac{1}{\mu Z} (1 - e^{-\mu x Z}) \quad (1)$$

where $Z = 1/(\sin \Omega) + 1/\sin (2\Theta - \Omega)$, μ is the mean linear absorption coefficient, and x is the film thickness.

Figure 1 shows the information depth of Cu K α radiation at varying incidence angles calculated for 0.1, 0.5 and 1 μm thick MgO films. In the grazing incidence diffraction (GID), the penetration depth is independent of the glancing angle Θ if the incidence angle Ω is small.

An important application of x-ray diffraction to polycrystalline thin films is the use of line broadening analysis to evaluate domain size and microstrain in deposited coatings. For peak analysis the Fourier transformation procedure¹⁰ is applied to x-ray data in order to obtain a peak profile free of instrumental effects from the broadened and standard profile. The method used to interpret size-strain broadening of x-ray diffraction lines is that used by Warren and Averbach.^{11,12} In the WA model it has been shown that the Fourier transformation $F(L)$ of a pure line profile can be written for a particular L as

$$F(L) = A^S(L)F^D(L) \quad (2)$$

where: $A^S(L)$ expresses the so-called size broadening term, which is independent of the order of (hkl); and $F^D(L)$ depends on microstrains. The manner in which $F(L)$ is separated differs according to various authors. However, the resulting differences are believed to be small.¹¹ Series expansion of $F^D(L)$ and restriction to the

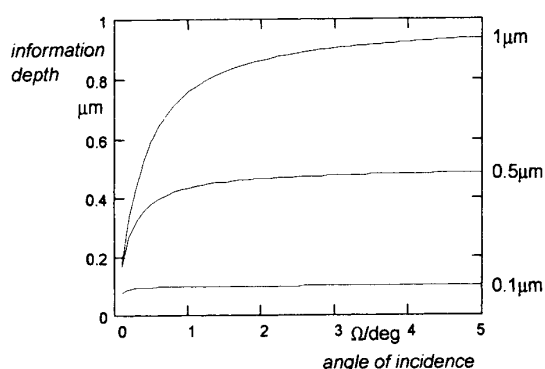


Figure 1. Information depth of Cu K α radiation depending on incidence angles, calculated for 0.1, 0.5 and 1 μm MgO films.

leading term with respect to strain gives

$$|F(L)| \approx A^S(L) \{1 - 2\pi^2(L/d^2)(\langle \varepsilon^2(L) \rangle - \langle \varepsilon(L) \rangle^2)\} \quad (3)$$

where $\varepsilon(L)$ is the strain resulting from the displacement of two unit cells at a distance L . If two orders of an (hkl) plane are available, $A^S(L)$ and $\langle \varepsilon^2(L) \rangle - \langle \varepsilon(L) \rangle^2$ are obtained from a plot of $F(L)$ vs. $1/d^2$. If the centroid of the line profiles of the broadened and standard reflection are properly determined and the origin of the unfolded profile coincides with its centroid, $\langle \varepsilon(L) \rangle = 0$. Thus, values of $A^S(L)$ and $\langle \varepsilon^2(L) \rangle$ as a function of L can be determined. If reflexes of a higher order are not present, as in this study, the investigation of microstrain and size must be carried out by a Fourier method for a single peak.¹³ The mean apparent size S in a direction perpendicular to the diffraction planes considered is obtained from the initial slope of the curve of $F(L)$ vs. L .

$$\frac{1}{S} = \left| \frac{dF(m)}{dL} \right|_{L=0} \quad (4)$$

where $L = m\lambda/2 (\sin \Theta_2 - \sin \Theta_1)$. The disorder coefficient estimated at $L = S/2$ is used to calculate $\langle \varepsilon^2(L) \rangle_{S/2}$ according to

$$F_{S/2}^D = 1 - \pi^2 m^2 \langle \varepsilon^2(L) \rangle_{S/2} S^2 / 2d_0^2 \quad (5)$$

where m is the reflection order, S is the domain size and d_0 is the net plane distance.

The measurement of x-ray reflectivity around the critical angle for total reflection allows the accurate determination of film thickness and interface roughness, irrespective of the crystalline structure. Grazing incidence x-ray reflectometry (GIXR) is equally well applicable to crystalline, polycrystalline and amorphous materials; it only requires a sufficiently flat sample. The value for the critical angle can be evaluated according to Eqn (6) from a plot of Θ^2 vs. m^2

$$\Theta_m^2 = \Theta_c^2 + \frac{\lambda^2}{4x^2} m^2 \quad (6)$$

This equation gives the position of the m th influence maximum as a function of the critical angle of total reflection Θ_c of the wavelength λ and the film thickness x . The exact value for the critical angle of total reflection Θ_c can be used to determine the mass density ρ of a deposited film¹⁴

$$\Theta_c = \sqrt{2\sigma} \quad (7)$$

and

$$\sigma = \sqrt{\frac{N_A r_0 \rho \sum (Z + f')}{2\pi \sum A}} \lambda \quad (8)$$

where N_A is the Avogadro constant, r_0 is the classical electron radius, $(Z + f')$ is the atomic scattering factor, and A is the atomic weight.

All GID and GIXR measurements were performed with a Siemens D 5000 diffractometer equipped with a thin-film attachment and using Cu K α radiation.

DEPOSITION PROCEDURES

Substrate preparation

The alumina and glass substrates were rinsed in hot water and then boiled with concentrated H_2SO_4

(99.997%) for 10 min, washed with distilled water and then etched in a solution of $\text{NH}_4\text{OH}-\text{H}_2\text{O}_2-\text{H}_2\text{O}$ for 10 min. All the wafers were rinsed in hot distilled water once more, dried in $\text{C}_3\text{H}_7\text{OH}$ vapour and introduced into the deposition chamber.

Magnesium oxide deposition conditions

Magnesium oxide films were deposited by electron-beam evaporation of MgO pellets using a modified UNIVEX 450 evaporator (Leybold). An electron beam unit ESV-6 with a 6 kW electron gun and 9 kV supply voltage was used. The substrates were heated by two infrared radiators. The substrate temperatures ranged from 25 °C to 190 °C. The temperatures were measured with a thermocouple element fastened to the substrate holder. During growth, the substrate temperature is held constant. The partial pressure of oxygen was measured by a mass spectrometer Quadrex 100 SCU (Inficon Leybold). It was varied from 1×10^{-2} Pa to 1×10^{-3} Pa. The vacuum before the deposition procedure was 9×10^{-5} Pa. The thin-film growth (rate 1.6–2 nm s^{-1}) was registered during the evaporation by means of a piezoelectric crystal.

EXPERIMENTAL RESULTS AND DISCUSSION

Thin MgO films of about 0.1, 0.5 and 1 μm thickness were deposited on flat float glass and different alumina substrates. Figure 2 shows GID patterns ($\Omega = 1$) of MgO deposited at room temperature on polycrystalline alumina, polished sapphire (110) and float glass. These coatings are $\sim 0.5 \mu\text{m}$ thick. All the films were optically transparent, chemically homogeneous and polycrystalline. The MgO coatings on all the investigated substrates were chemically and structurally stable over a long period.

The MgO reflex intensity ratios on polycrystalline alumina substrates were comparable to the MgO x-ray

powder patterns calculated and independent of the x-ray penetration depth. The integral intensities of MgO decreased and those of $\alpha\text{-Al}_2\text{O}_3$ (PDF 10–173) rose. The crystallites showed random orientation in these layers. In comparison, the MgO patterns on glass and sapphire substrates showed a $\langle 100 \rangle$ preferred orientation. The rocking curves of MgO (200) profiles at this deposition temperature were broad and also indicate only a small orientation along $\langle 100 \rangle$. The effects of processing parameters on MgO film properties were investigated at different oxygen partial pressures and substrate temperatures. The oxygen pressure did not significantly influence the GID patterns. The influence of the substrate temperature was obvious. Figure 3 shows the (200) reflexes of 500 nm thick MgO films on glass substrates deposited at different temperatures. Whilst a complete temperature study was not done, a number of simple observations were made. The crystallinity and the $\langle 100 \rangle$ preferred orientation increased strongly to a medium substrate temperature of about 50 °C or decreased if the substrate temperature was held at higher temperatures. Figure 4 shows three patterns of MgO on glass at different incidence angles. The substrate temperature was 135 °C. No preferred orientation was observed. Many authors^{7,5,15} have grown MgO of epitaxial quality at higher substrate temperatures on different substrates. Obviously, the deposition system and all the processing parameters influence the growth of MgO layers more than the chemical composition of the substrates. This suggests that only small or no intermixing with the substrates occurs.

To study the influence of the substrate temperature on the crystal growth, MgO coatings (~ 100 nm thick) on polished sapphire (110) deposited at 25 °C and 150 °C were investigated by GID and GIXR (Figs 5 and 6). Magnesium oxide films at low temperatures were polycrystalline with a small $\langle 100 \rangle$ texture. The MgO coatings at 150 °C showed a poor crystallinity. Only very flat and broad (200) and (220) reflexes were observed, which indicated small crystallite sizes. It is not quite clear if differences in the partial pressure of

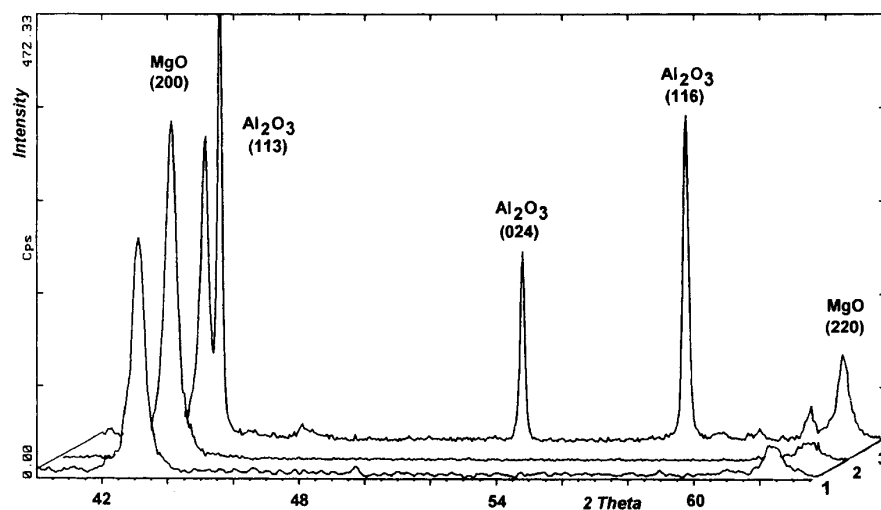


Figure 2. Grazing incidence diffractometry patterns of 500 nm thick MgO films deposited on (1) float glass, (2) sapphire (110) and (3) polycrystalline $\alpha\text{-Al}_2\text{O}_3$.

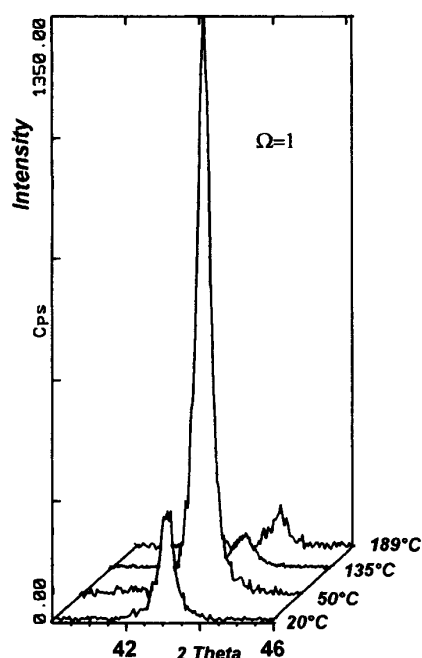


Figure 3. Magnesium oxide (200) reflexes on float glass deposited at different substrate temperatures.

oxygen influence the film properties characterized by x-ray diffraction. The integral intensities of the MgO peaks could be caused by differences in the film thickness and therefore by various amounts of crystallites with domain sizes that affect the x-ray patterns. The GIXR measurements of roughness and mass density agreed with the GID results. Rough interfaces in low-temperature deposited MgO films reduced the reflectivity. Only a slight roughness was observed in the films grown at higher substrate temperatures. Roughness and domain size in polycrystalline coatings changed in the same way. In the examples given (Table 1), only the low-temperature sample deposited without oxygen had a critical angle of total reflection that turned out to be smaller than the bulk value for pure MgO. The void fraction increased as a consequence of nucleation events

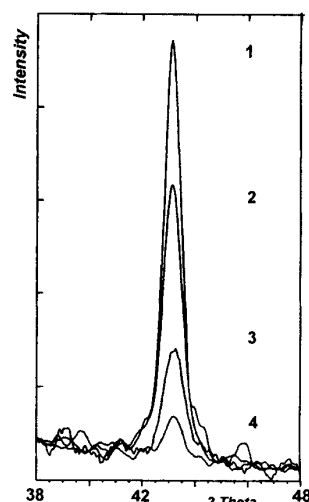


Figure 5. Grazing incidence diffractometry patterns of ~ 100 nm thick MgO films on sapphire (110) deposited at different temperatures and oxygen partial pressures: (1) 25 °C with oxygen; (2) 25 °C without oxygen; (3) 152 °C with oxygen; (4) 150 °C without oxygen.

associated with non-stoichiometry. No such effects were observed for higher growth temperatures. Yatavali *et al.*¹⁶ described similar problems in the low-temperature growth of MgO using molecular beam epitaxy. These film investigations show that the nucleation process depends on the substrate temperature. At higher substrate temperatures (> 100 °C) the nucleation takes preference over the crystallite growth. The slight roughness is due to minute MgO particles. Interface and layer surface are very smooth. The films consist of small and

Table 1. Parameters of GIXR measured samples

Temperature (°C)	Oxygen	Integral intensity (cps)	Film thickness x (nm)	Θ_c (degree)
25	Yes	13	80.4	0.273
25	No	8.5	73	0.265
150	Yes	4.5	101	0.273
150	No	2	83.9	0.276

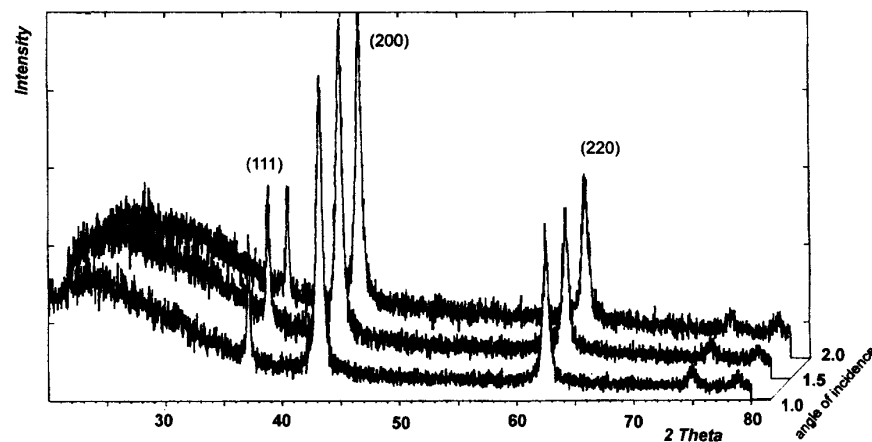


Figure 4. Magnesium oxide grown on glass at 135 °C measured at different incidence angles.

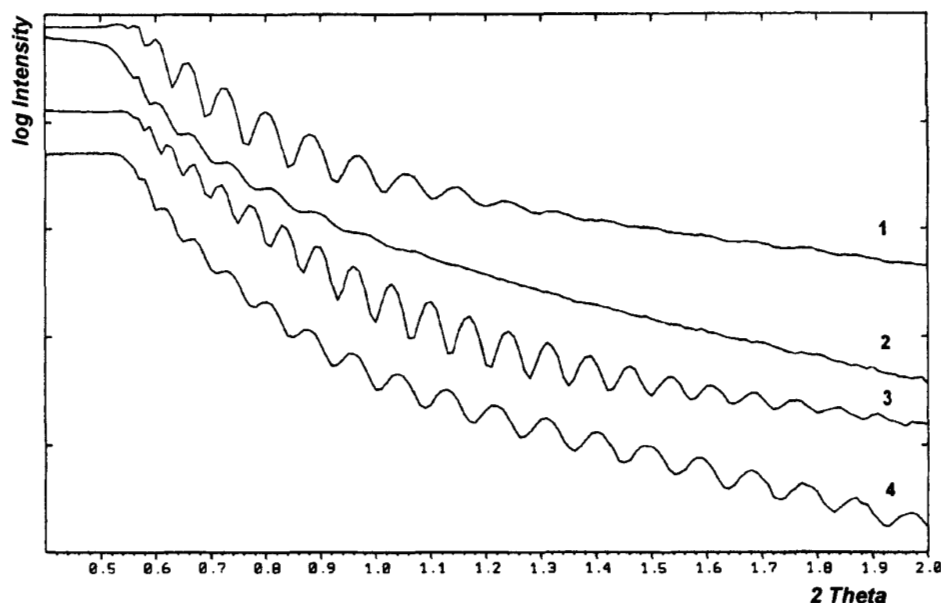


Figure 6. Grazing incidence x-ray reflectometry measurements of thin MgO films (~ 100 nm) on sapphire (110) deposited at: (1) 25 °C with oxygen; (2) 25 °C without oxygen; (3) 152 °C with oxygen; (4) 150 °C without oxygen.

partial crystalline particles. The favourable condition for the crystal growth in our experiments was a temperature of ~ 50 °C irrespective of the substrates. Under these evaporation conditions, strong $\langle 100 \rangle$ textured MgO crystallites are found.

That these MgO films are not of epitaxial quality is shown by the calculation of domain size and microstrain from the Fourier transformation. All the reflexes of the films were strongly broadened. Figure 7 shows the (200) profiles of polycrystalline MgO used as standard material and of a film deposited at room temperature on sapphire (GID, $\Omega = 1$). Figure 8 shows the Fourier coefficients as a function of L for MgO depos-

ited on polished and unpolished sapphire at an incidence angle $\Omega = 1$, and in Fig 9 the Fourier coefficients are plotted versus L of MgO deposited on polycrystalline alumina at different incidence angles. Table 2 shows the domain sizes and microstrains calculated from the single-line Fourier analysis. The crystal sizes change with the surface roughness of the substrates. The crystallites increase from the very smooth polished sapphire (surface roughness 25 nm) to a polycrystalline alumina surface with a mean particle size fraction of ~ 20 μm . With increasing MgO crystallite size the microstrains decrease and the crystalline quality becomes more perfect. The contributions of the various

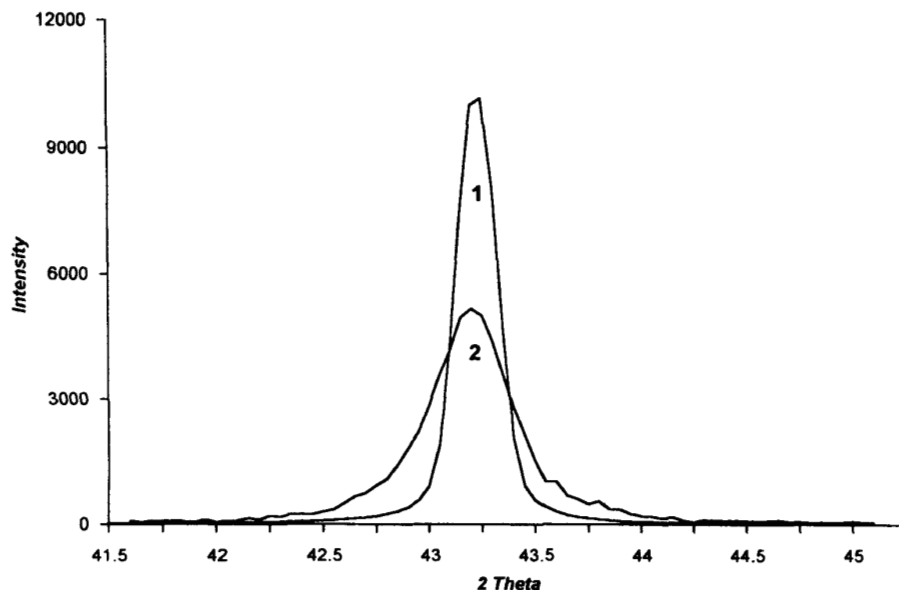


Figure 7. Profiles of MgO (200) peaks of the standard substance (1) and of a deposited film on sapphire (2).

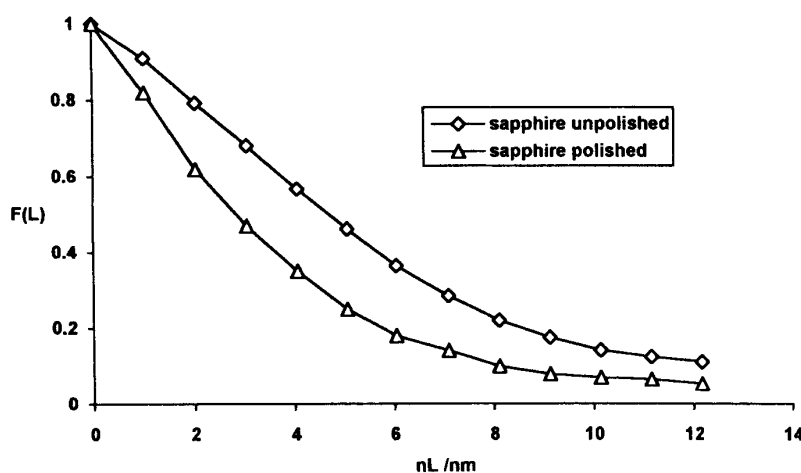


Figure 8. Fourier coefficients as a function of L for polished and unpolished sapphire at an incidence angle $\Omega = 1$.

types of imperfection (dislocations, stacking faults) that cause the microstrain cannot be unravelled. To quantify each of these causes, an analysis of a variety of independent diffraction data is generally required. No shifting of MgO Bragg angles and only a small gradient of the calculated physical parameters was observed at varying x-ray penetration depths on all substrates tested. This suggests that no intermixing with the substrate material and no stress occurs. The calculated mass density supports this assumption. The mass densities were calculated from the critical angle of total reflection [Eqn (8), Table 1]. For pure MgO the Θ_c value is 0.273° . This value corresponds to a density of 3.58 g cm^{-3} .

The external grain structures, together with the internal defects or voids, are determined not only by the deposition conditions but also by the grain structure and the surface morphology of the substrates. On rugged surfaces an island film formation is preferred to a layer growth. Island growth occurs when the smallest stable clusters nucleate on the substrate and grow in three dimensions to form islands. This happens when atoms or molecules in the deposit are more strongly bound to each other than to the substrate or when the extension of the smallest stable nucleus is hindered due to geometric and perhaps energetic barriers. Further nucleation is handicapped and diminished nucleation

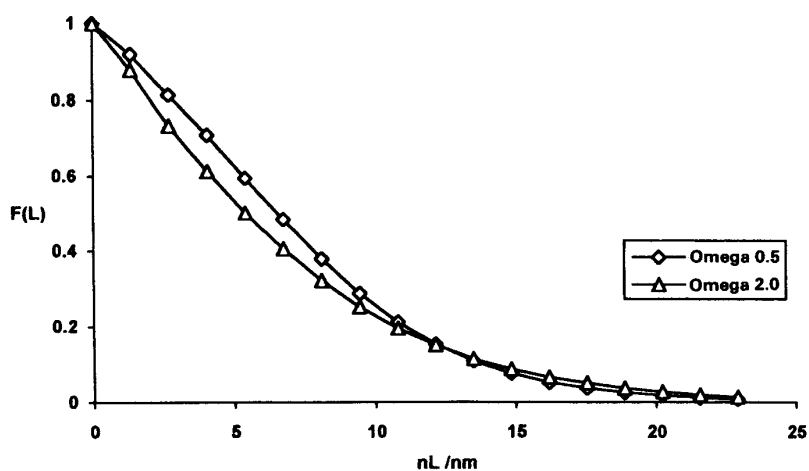


Figure 9. Fourier coefficients of MgO deposited on polycrystalline alumina at different incidence angles $\Omega = 0.5$ and $\Omega = 2$.

Table 2. Physical parameters of the deposited MgO films

Substrate	Sapphire polished		Glass		Sapphire unpolished		Polycrystalline alumina	
Incidence angle Ω	0.5	2	0.5	2	0.5	2	0.5	2
Domain size (nm)	5.5	6.5	7.7	6.6	9.5	9.1	15	12
Microstrain ($\times 10^3$)	11.8	10.5	8.8	9.8	7.0	7.2	4.8	5.5

events could promote a more perfect polycrystalline crystal growth.

CONCLUSION

Thin films of magnesia were deposited on glass and alumina with different substrate roughness by electron-beam evaporation. The films were optically clear, adherent and uniform. Rapidly deposited films are less influenced by the underlying chemical composition of the substrate. From single-line Fourier analysis, domain sizes and microstrains were determined. Both param-

eters change with the substrate roughness. On rugged surfaces, polycrystalline MgO grows with better polycrystalline quality. On smooth surfaces, the deposited coatings have small domain sizes and higher microstrains. Strongly $\langle 100 \rangle$ preferred orientation was observed for MgO films deposited at a substrate temperature of $\sim 50^\circ\text{C}$.

Acknowledgement

The present investigation was supported by Contract Wu 216/1-1 of the Deutsche Forschungsgemeinschaft (Germany).

REFERENCES

1. M. Gurvitch and A. T. Fiory, *Appl. Phys. Lett.* **51**, 1027 (1987).
2. K. Harada, N. Fujimori and S. Yazun, *Jpn. J. Appl. Phys.* **27**, L1524 (1988).
3. S. Witanachi, S. Patel, D. T. Shaw and H. S. Kwok, *Appl. Phys. Lett.* **55**, 295 (1989).
4. B. S. Kwok, E. P. Boyed, K. Zhang, A. Erbil and B. Wilkins, *Appl. Phys. Lett.* **54**, 2542 (1989).
5. D. K. Fork, F. A. Ponce, J. C. Tramontana and T. H. Geballe, *Appl. Phys. Lett.* **58**, 2294 (1991).
6. W. J. De Sisto and R. L. Henry, *J. Cryst. Growth* **109**, 314 (1991).
7. A. B. Berezin, C. W. Yuan and A. L. de Loganne, *Appl. Phys. Lett.* **57**, 90 (1990).
8. M. Tonouchi, Y. Sakaguchi and T. Kobayashi, *J. Appl. Phys.* **62**(3), 961 (1987).
9. H. Wulff, J. Klimke, V. Krasemann and H. Steffen, *Mater. Sci. Forum*, **313**, 166 (1994).
10. A. P. Stokes, *Proc. Phys. Soc.* **B61**, 382 (1948).
11. R. Dehlez, Th. H. de Keijzer and E. J. Mittemeijer, *Fresenius Z. Anal. Chem.* **312**, 1 (1982).
12. B. E. Warren, *X-Ray Diffraction*. Addison Wesley, Reading, MA (1969).
13. H. K. Nandi, H. K. Kou, W. Schlosberg, G. Wissler and J. B. Cohen, *J. Appl. Cryst.* **17**, 22 (1984).
14. B. Lengeler, *Microchim. Acta* **1**, 455 (1987).
15. Y. W. Zhao and H. Suhr, *Appl. Phys.* **A54**, 451 (1992).
16. S. Yataavalli, M. N. Yang and C. P. Flynn, *Phys. Rev.* **B41**, 7961 (1990).