

Magnesium Oxide Thin Films with Tunable Crystallographic Preferred Orientation *via* Aerosol Assisted CVD**

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Abstract

Magnesium oxide films were deposited on glass *via* aerosol-assisted chemical vapour deposition. Magnesium acetate tetrahydrate was present in ethanol or methanol and depositions were carried out at 400, 500 and 600 °C. The films were analysed by X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy and UV-vis spectroscopy. Growth rate, film thicknesses and crystallite sizes, regardless of the solvent used, increased with temperature. With the exception of the film produced at 400 °C in methanol, the films were crystalline and the crystallographic preferred orientation varied with solvent and temperature allowing fine-tuning of the film for industrial applications. The solvent system and temperature influenced the surface morphology with films deposited using ethanol consisting of smaller surface structures compared with the featureless morphology of the methanol derived films. The refractive index of the films, calculated using the Swanepoel method, was found to be 1.72 and 1.70 for methanol and ethanol systems, respectively.

1. Introduction

Magnesium oxide thin films are of great interest due to their diverse applications attributed to a set of unique properties. The cubic crystalline structure has high thermal and chemical stability ideal for providing the buffer layer for the deposition of superconductive films.^[1] The low dielectric constant ($k' = 9.8$) and a refractive index close to that of glass (1.72) also makes MgO films suitable for ferroelectrics.^[2] Furthermore, the wide band gap (7.8 eV), high secondary electron emission coefficient and the excellent electrical insulating properties account for the successful use of MgO films as a protective layer in AC plasma display panels (PDP).^[3]

MgO films have been deposited by a variety of methods including sol-gel, spray pyrolysis, pulse laser, atomic layer, cathodic vacuum arc and chemical vapour deposition.^[1-7] Chemical vapour deposition (CVD) has a number of advantages over physical methods as deposition can take place at relatively lower temperatures, films are more uniform and the method is simplistic; more suitable for commercial applications.^[4] However, the availability of a suitable volatile precursor can be a limitation. Precursors commonly used for MgO film growth include substituted acetylacetonates, dialkylcarbamates and β -ketoiminates.^[4] Unfortunately, these have also been problematic to use because of their low volatility. In contrast, aerosol-assisted CVD (AACVD) has the added benefit of not requiring the precursor to be volatile which means precursors not suitable for use in other CVD methods can be utilised to great effect.^[8] The main requirement is that the precursor is soluble in the solvent used to generate the aerosol.^[9] Other advantages of AACVD include the use of thermally unstable precursors which increases the choice and availability, the simplification of the delivery and vaporisation of the precursor and the operation of the reaction system at low or atmospheric pressures. The outcome is a low cost method that could be used for the mass production of thin films.

In this work, the effects of temperature and solvent on the deposition of MgO thin films grown on SiO₂ barrier coated float-glass have been investigated. To our knowledge this is the first application of AACVD to deposit MgO films. The films were

analysed for their crystallinity, composition, morphology and optical properties as a function of the conditions of deposition.

2. Results and Discussion

Magnesium oxide thin films were deposited at substrate temperatures of 400, 500 and 600 °C using magnesium acetate tetrahydrate dissolved in either methanol or ethanol by AACVD. The films were highly transparent with uniform coverage across the glass substrate. They were also well adhered to the substrate, passing the Scotch™ tape test. Furthermore, all crystalline films were insoluble in dilute acid and base.

2.1. Growth rates

The variation in deposition growth rate as a function of substrate temperature and solvent is shown in Fig. 1. The rate for both solvent systems increased with substrate temperature. The effect of temperature is in agreement with the kinetics of the reaction.^[7] Bian *et al.* reported a decrease in growth rate with increasing temperature, contrary to the kinetics, which could be a factor of deposition technique or the use of aqueous conditions to deposit the MgO films on the Si(100) substrates.^[10] The growth rates of the films deposited using methanol were between 2-3 times faster than the corresponding films from ethanol. The principal reason for this observation being that the total deposition time when using ethanol varied between 65-80 minutes compared with 30-35 minutes for the methanol systems. This may possibly be due to the ability of methanol to aerosolise more readily compared to ethanol. Films grown at 400 °C were about 40% thicker when produced using methanol (Fig. 2) but the difference in thickness at the higher temperatures between the two solvent systems is less severe (Table 1). As expected, film thicknesses for both solvents increased with deposition temperature due to the decrease in residence time required by the precursors for deposition to take place. Other studies, using AACVD, have also found that higher temperatures produce thicker films.^[11]

Table 1. Thicknesses of MgO films measured from side-on SEM images.

Solvent system	Film thickness /nm at given deposition temperature /°C		
	400	500	600
Methanol	350	400	800
Ethanol	250	450	850

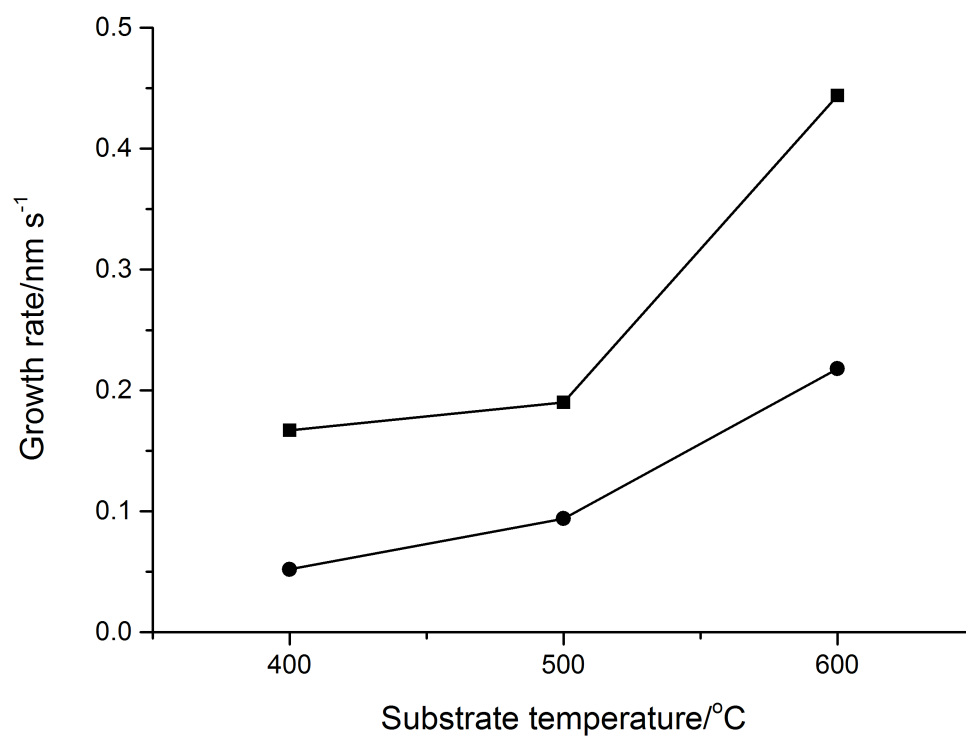


Fig. 1. Deposition growth rate as a function of substrate temperature and solvent: (■) methanol; (●) ethanol.

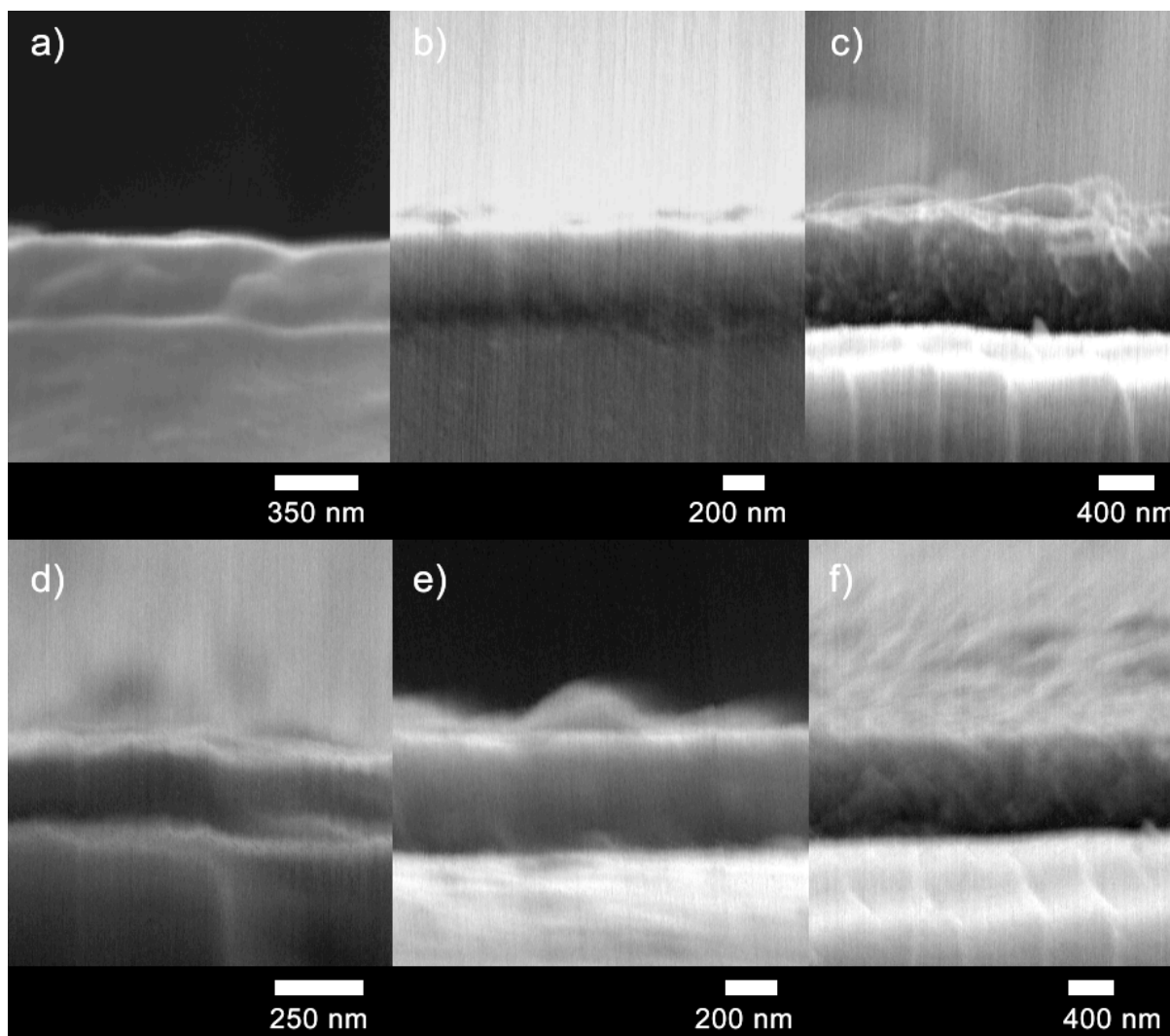


Fig. 2. Side-on SEM images. a) 400°C MeOH; b) 500°C MeOH; c) 600°C MeOH; d) 400°C EtOH; e) 500°C EtOH; f) 600°C EtOH.

2.2. X-ray diffraction

Fig. 3. shows the XRD patterns for the MgO films. The (111) plane shown in the standard (Fig. 3a) was absent in the films. Other authors, using a range of different deposition techniques, have also not detected the presence of this plane.^[3, 6, 12, 13] One study detected the (111) plane at the lowest temperature condition using a spray pyrolysis technique but this peak was absent in the films produced at higher deposition temperatures.^[10] The film produced at 400 °C using methanol was amorphous (Fig. 3b) however, this was not the case when ethanol was used as the solvent (Fig. 3e), indicating that the solvent did indeed have an effect on film crystallinity possibly due to methanol imparting a different decomposition pathway on magnesium acetate to form MgO. In the case of both solvents, the crystallinity of the

films increased with temperature as expected.^[6, 7] Furthermore, with the exception of the amorphous film, the films were found to be insoluble in acid (HNO₃, 0.25 M) and base (KOH, 0.60 M). From texture coefficient calculations^[14] all crystalline films showed a preferred orientation along the (200) plane. Furthermore, it was found that the (200) diffraction peak became more dominant with increasing temperature when films were deposited using methanol. Interestingly, the opposing trend was found when ethanol was used.

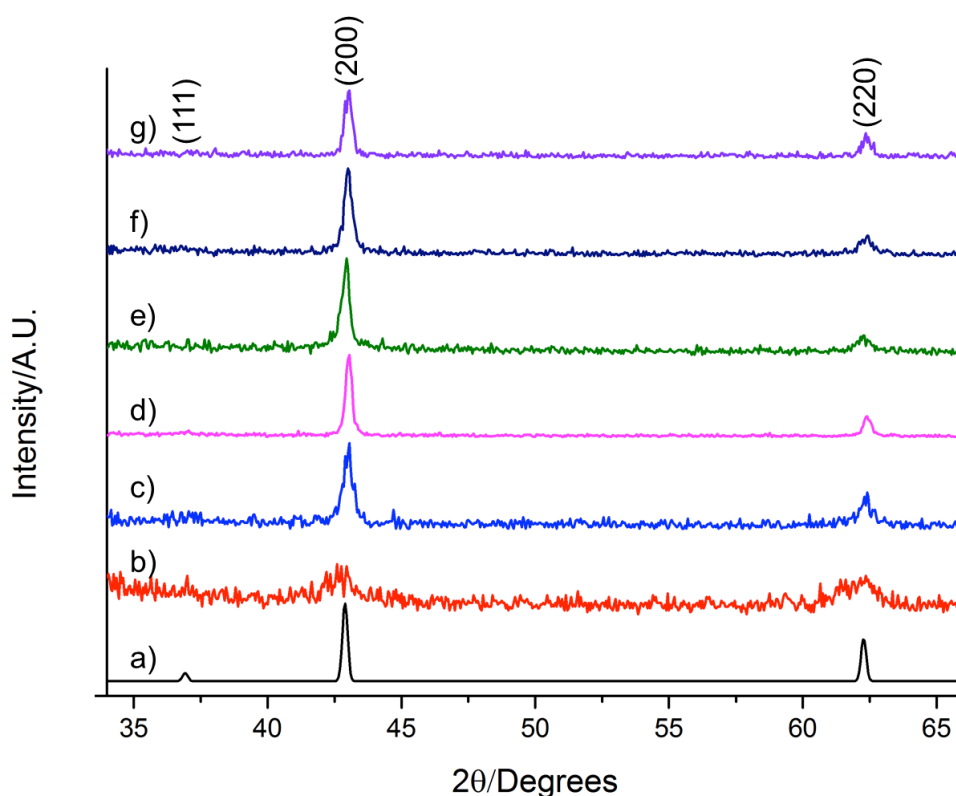


Fig. 3. XRD of MgO films: a) Standard; b) 400°C MeOH; c) 500°C MeOH; d) 600°C MeOH; e) 400°C EtOH; f) 500°C EtOH; g) 600°C EtOH.

Table 2. Average crystallite size calculated using the Scherrer equation.

Solvent system	Crystallite size /nm at given deposition temperature /°C		
	400	500	600
Methanol	amorphous	17	28
Ethanol	19	20	24

The full width at half maximum (FWHM) data of the diffraction peaks were used to calculate the average crystallite sizes of the crystalline MgO films using the Scherrer equation.^[15] The general trend was that the crystallite sizes increased with

temperature for both solvent systems (Table 2). A comparison of both systems at the same temperature showed that the crystallite size was smaller at 500 °C for methanol but the reverse was true at 600 °C. However, the differences in crystallite sizes do not vary significantly.

2.3. Scanning electron microscopy

Representative SEM images of the MgO films show that temperature and solvent do indeed have an effect on the films' morphology (Fig. 4) again most likely due to the different decomposition pathways of magnesium acetate. For the films deposited from a methanol solution the morphology consisted of globular domes (Fig. 4a) that appear to coalesce to form a smooth and continuous film that is largely featureless (Fig. 4b). At a deposition temperature of 600 °C (Fig. 4c), the film contains more structure again with sharp facets that is possibly due to the high growth rate (Fig. 1). The films from the ethanol regime showed surface structure made up of domes that were much smaller than those observed for the methanol system (Fig. 4d – f). With increasing deposition temperature the particles reduced in size and surface area was seen to increase.

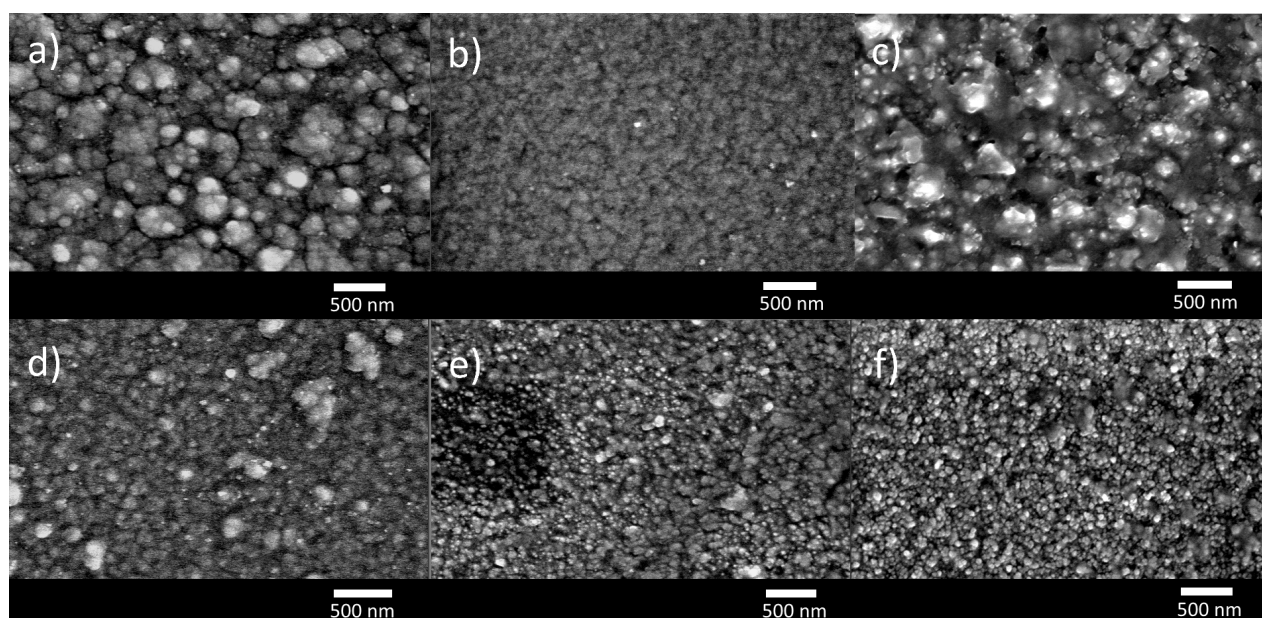


Fig. 4. SEM images of MgO films. a) 400°C MeOH; b) 500°C MeOH; c) 600°C MeOH; d) 400°C EtOH; e) 500°C EtOH; f) 600°C EtOH.

2.4. X-ray photoemission spectroscopy

X-ray photoemission spectroscopy performed on the films showed an Mg 1s peak at 1303.6 eV, matching closely with literature reports for Mg in MgO (Fig. 5).^[4] Furthermore, the Mg 2s and Mg 2p had binding energies at 88.8 eV and 50.1 eV, respectively, which also correspond to transitions expected for MgO.^[4] Deconvolution of the O 1s peak showed the presence of two environments with binding energies at 529.7 eV (O bound to Mg) and 531.9 eV (surface carbonate/hydroxyl groups).^[4]

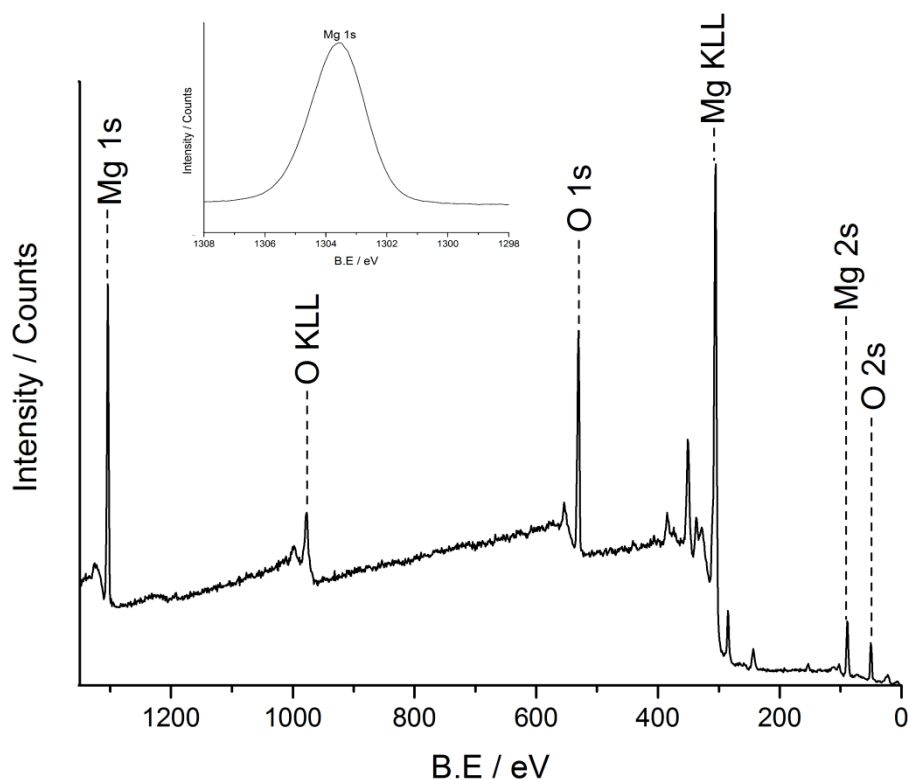


Fig. 5. A typical XPS survey scan and high resolution scan (inset) of the most intense Mg peak (Mg 1s) for MgO films grown via AACVD.

2.5. Refractive index

The refractive index of the MgO films was calculated from the UV-Vis transmission data (Fig. 6) for the films deposited at 600 °C using the Swanepoel method.^[16] The refractive index value of the film produced from the methanol solution was found to be 1.72 at a wavelength of 600 nm and the value for the film deposited using the ethanol system was 1.70 at 400 nm. These values are in close agreement with literature examples.^[2, 13] The film thickness also calculated from the transmission

data via the Swanepoel technique was 800 nm and 850 nm for the methanol and ethanol system respectively being in close agreement with the side-on SEM results (Fig. 2).

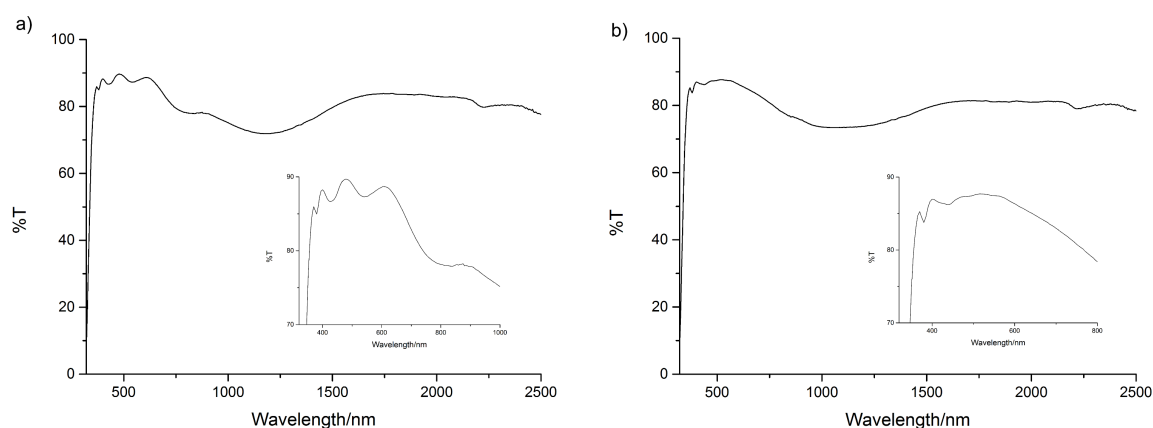


Fig. 6. Transmission curves of the films grown at 600°C used to calculate the refractive index a) Methanol system; b) Ethanol system.

3. Conclusions

This work focused on the effect of solvent system and temperature on the optical properties of MgO films successfully deposited on SiO₂ coated barrier float-glass by aerosol-assisted chemical vapour deposition using magnesium acetate tetrahydrate, a simple and easy to handle precursor. This is the first study to our knowledge that has employed this method of CVD to investigate the effect of solvents on MgO film deposition. A crystalline film was produced, without the need for a post-annealing treatment, at a low temperature using ethanol as the solvent system. The preferred orientation was solvent and temperature dependent which would permit fine tuning of film properties for industrial application. Film thicknesses, surface area and growth rates increased with temperature; the rate being about twice as fast when using methanol compared with ethanol at the higher temperatures. Our findings show that MgO films with favourable characteristics can be deposited using a simple fast and safe method at low temperatures with the ability to alter the film properties by simply modifying the deposition conditions.

4. Experimental Details

Chemicals: Magnesium acetate tetrahydrate was purchased from Sigma-Aldrich. Methanol (MeOH; 99.5%) and ethanol (EtOH; 99.5%) were purchased from Merck Millipore. Compressed air was used as-supplied from BOC. The glass substrate was standard float glass, with a 50 nm thick SiO₂ barrier layer, supplied by Pilkington NSG.

CVD Rig set-up: The depositions were carried out in an in-house built CVD rig. The rig consisted of an open ended quartz tube capped at both ends with stainless steel plates. The steel plates support the upper plate which is placed about 8 mm above the graphite heating block containing a Whatman cartridge heater. The glass substrate was heated to the required temperature and monitored using a Pt-Rh thermocouple. The substrate consisted of SiO₂ barrier coated float-glass (15 cm × 4 cm × 0.3 cm). The coating prevents the ions from within the bulk diffusing to the surface. The glass substrate was first cleaned with detergent and water, followed by propan-2-ol, propanone, and then air dried.

General Procedure: The depositions of the MgO films were achieved by transferring methanol or ethanol (25 mL) to magnesium acetate tetrahydrate (0.25 g, 1.2 mmol) into a Drechsel bottle. Compressed air was bubbled through the solution and an aerosol was generated using a Vicks ultrasonic humidifier. The deposition was started by heating the bottom substrate to the required temperature. The aerosol was passed into the chamber at a flow rate of 1.0 L min⁻¹ monitored using a flow rate meter. Once the precursor solution was used up the air was allowed to pass through chamber until the film reached room temperature. The glass substrate was then removed for film analysis.

Film Analysis: X-ray diffraction (XRD) measurements were obtained using a modified Bruker-Axs D8 diffractometer with parallel beam optics equipped with a PSD LynxEye silicon strip detector to collect diffracted X-ray photons. X-rays were generated using a Cu source with Cu K α 1 and Cu K α 2 radiation of wavelengths 1.54056 and 1.54439 Å, respectively, with an intensity ratio of 2:1 and at 40 kV and 30 mA. The incident beam angle was kept at 1°, and the angular range of the

patterns collected was $10^\circ < 2\theta < 66^\circ$ with a step size of 0.05° counted at 0.5 s/step. The patterns were analysed for crystallinity and preferred orientation. Peak positions were compared to patterns from the Inorganic Crystal Structure Database (ICDS).

Scanning electron microscopy (SEM) was used to determine the film morphology and thickness from a top-down and side-on configuration, respectively, using a JEOL JSM-6301F Field Emission instrument with accelerating voltages ranging from 3-5 keV on Au-coated samples.

X-ray photoelectron spectroscopy (XPS) analysis of the films was carried out using a Thermo Scientific K-Alpha spectrometer fitted with a monochromatic Al-K α . The peaks were modelled using CasaXPS software with binding energies adjusted to adventitious carbon (284.5 eV) in order to compensate for the effects of charging. Survey scans were collected in the range 0–1350 eV (binding energy) at a pass energy of 40 eV.

The refractive index of the film was calculated using UV/Vis/Near IR transmittance data obtained from a Perkin Elmer Precisely Lambda 950 spectrometer using an air background and recorded between 320-2500 nm.

References

- [1] I. C. Ho, Y. H. Xu, J. D. Mackenzie, *J. Sol-Gel Sci. Technol.* 1997, 9, 295.
- [2] S. Vangelista, R. Mantovan, A. Lamperti, G. Tallarida, B. Kutrzeba-Kotowska, S. Spiga, M. Fanciulli, *J. Phys. D-Appl. Phys.* 2013, 46, 9.
- [3] D. Y. Zhu, Y. Liu, C. X. Zheng, M. D. Wang, D. H. Chen, Z. H. He, *Mater. Chem. Phys.* 2012, 134, 1167.
- [4] G. Carta, N. El Habra, L. Crociani, G. Rossetto, P. Zanella, A. Zanella, G. Paolucci, D. Barreca, E. Tondello, *Chem. Vapor Depos.* 2007, 13, 185.
- [5] S. G. Kim, J. Y. Kim, H. J. Kim, *Thin Solid Films* 2000, 376, 110.
- [6] M. Kodu, J. Raud, M. Aints, T. Avarmaa, V. Denks, J. S. Choi, E. Feldbach, R. Jaaniso, M. Kirm, M. S. Lee, A. Maaros, Y. T. Matulevich, H. Mandar, V. Sammelselg, *Thin Solid Films* 2010, 519, 846.
- [7] M. Manin, S. Thollon, F. Emieux, G. Berthome, M. Pons, H. Guillon, *Surf. Coat. Technol.* 2005, 200, 1424.
- [8] P. Marchand, I. A. Hassan, I. P. Parkin, C. J. Carmalt, *Dalton Trans.* 2013, 42, 9406.
- [9] X. H. Hou, K. L. Choy, *Chem. Vapor Depos.* 2006, 12, 583.

- [10] J. M. Bian, X. M. Li, T. L. Chen, X. D. Gao, W. D. Yu, *Appl. Surf. Sci.* 2004, 228, 297.
- [11] D. S. Bhachu, M. R. Waugh, K. Zeissler, W. R. Branford, I. P. Parkin, *Chem.-Eur. J.* 2011, 17, 11613; C. E. Knapp, G. Hyett, I. P. Parkin, C. J. Carmalt, *Chem. Mat.* 2011, 23, 1719; S. Sathasivam, R. R. Arnepalli, B. Kumar, K. K. Singh, R. J. Visser, C. S. Blackman, C. J. Carmalt, *Chem. Mat.* 2014, 26, 4419.
- [12] X. R. Fu, G. M. Wu, S. G. Song, Z. T. Song, X. Z. Duo, C. L. Lin, *Appl. Surf. Sci.* 1999, 148, 223.
- [13] S. H. Tamboli, R. B. Patil, S. V. Kamat, V. Puri, R. K. Puri, *J. Alloy. Compd.* 2009, 477, 855.
- [14] J. Sakaliuniene, J. Cyviene, B. Abakeviciene, J. Dudonis, *Acta Phys. Pol. A* 2011, 120, 63.
- [15] S. J. S. Qazi, A. R. Rennie, J. K. Cockcroft, M. Vickers, *J. Colloid Interface Sci.* 2009, 338, 105.
- [16] R. Swanepoel, *Journal of Physics E-Scientific Instruments* 1983, 16, 1214.

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