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Deposition of ZnO Films on Polycrystalline Alumina Substrates by Spray Pyrolysis

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Abstract

Zinc oxide films have been grown on polycrystalline alumina substrates by a spray pyrolysis method. Film growth was carried out between 200 and 500°C. The concentration of the starting solution ranged between 0·03 and 0·5 mol/litre. The effect of temperature and concentration on the film morphology, growth rate, homogeneity and crystallographic orientation is discussed. The experimental conditions for a good substrate covering are described.

Zinkoxidschichten wurden auf polykristallinen Aluminiumoxidsubstraten durch ein Sprüh-Pyrolyse-Verfahren abgeschieden. Die Temperatur bei der Schichtbildung wurde zwischen 200 und 500°C variiert. Die Konzentration der Ausgangslösung lag zwischen 0·03 und 0·5 mol/liter. Auf den Einfluß der Temperatur und der Konzentration auf die Schichtmorphologie, Wachstumsgeschwindigkeit, Homogenität und kristallographische Orientierung wird eingegangen. Die experimentellen Bedingungen, die zu einem guten Substratüberzug führen, werden beschrieben.

Des films d'oxyde de zinc ont été déposés sur des substrats d'alumine polycristalline par une méthode de pyrolyse par pulvérisation. La croissance du film a été étudiée pour des températures s'échelonnant de 200 à 500°C avec des solutions de départ dont les concentrations étaient comprises entre 0·03 et 0·5 mol/litre. L'effet des paramètres température et concentration sur la vitesse de croissance, la morphologie, l'homogénéité et l'orientation du film déposé sont discutés. Les conditions expérimentales conduisant à un bon recouvrement du substrat sont également exposées.

1 Introduction

Spray pyrolysis is a method of depositing films by spraying a solution which contains the elements desired in the resulting crystallized films on a heated substrate. The final thickness can range from a few nanometers to several microns. One of the advantages of the technique is the low cost of the equipment.

The deposition mechanism depends upon the following parameters: (1) nature of the substrate, (2) temperature, and (3) size of the particles arriving near the heated substrate, which is dependent on the concentration of the starting solution. Literature work[1,2] show that chemical vapour deposition (CVD) is the process leading to good coating in terms of homogeneity, morphology and adherence on the substrate. Usually coatings are made on glass or single crystals.[3–6] In the present work, polycrystalline alumina, which is a substrate currently used for electronic applications, is used. The chosen material for deposition is zinc oxide. Two parameters have been examined: concentration of the starting solution and temperature. Their influence on the growth rate, morphology and crystallographic orientation of ZnO films is studied.

2 Experimental

The experimental setup is derived from the pyrosol process.[7,8] An aqueous solution of zinc acetate was prepared. This precursor was chosen because of its high vapour pressure at low temperature (i.e. about 200°C).[9] Consequently the reaction kinetics on the substrate will be fast. The precipitation of zinc hydroxide is avoided by the addition of a small amount of acetic acid. The solution is contained in a glass vessel and its bottom is fitted with a piezoelectric transducer. The piezoelectric ceramic is excited at 920 kHz (i.e. close to its resonance frequency). A geyser is formed at the liquid surface. The combined effects of cavitation within the liquid and waves at its surface produce an aerosol.[10] Blandenet *et al.*[7] have shown that the droplets produced by this technique have a narrow size distribution. The average diameter, d_{Drop}, can be calculated from Kelvin's relation:

$$d_{Drop} = 0{\cdot}34(8.\pi.\sigma/\rho.f^2)^{1/3} \qquad (1)$$

where σ is the surface tension of water ($\sigma = 69{\cdot}6$ dynes/cm), ρ its density ($\rho = 1$ g/cm^3) and f the ultrasonic frequency ($f = 920$ kHz). At 920 kHz the droplet size is of the order of 4·3 μm.

The aerosol is carried by a gas of controlled flow towards the pyrolysis region enclosed in a glass chamber. The direction of the flow is perpendicular to a horizontal substrate heated by a metallic plate. The selected gas flow and the heating plate design ensure that deposition is a CVD process. The solvent is entirely vaporized close to the substrate. The diameter of the resulting ZnO particles, d_{ZnO}, is related to the concentration C of the starting solution by:

$$d_{ZnO} = (M_{ZnO}.C/\rho_{ZnO})^{1/3}.d_{Drop} \qquad (2)$$

where M_{ZnO} is the molecular weight of zinc oxide ($M_{ZnO} = 81{\cdot}38$ g/mol) and ρ_{ZnO} is the density of zinc oxide ($\rho_{ZnO} = 5{\cdot}61$ g/cm^3).

The substrates are alumina-based materials currently used for electronic applications. The sample surface area is $2{\cdot}54 \times 2{\cdot}54$ cm^2. Prior to deposition the substrates are cleaned with acetone.

The crystallographic nature of the deposited films has been studied at room temperature by X-ray diffraction with an INEL Curved Position Sensitive CPS 120 apparatus (INEL Instrumentation Electronique, France). The sample holder spins on its own axis and is almost parallel to the incident beam. SEM is used to examine the film morphology and determine its thickness.

3 Results and Discussion

3.1 Influence of the concentration at fixed temperature (450°C)

Figure 1 shows a linear dependence between the growth rate and the concentration of the starting solution. It corresponds to a CVD mechanism where the growth rate is diffusion controlled.[1]

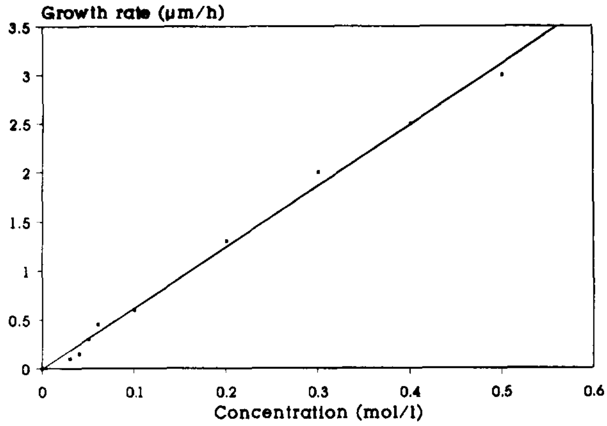


Fig. 1. Growth rate as a function of the starting solution concentration ($T = 450$°C).

The film crystallizes in the hexagonal system. No other phase has been detected. The (002) peak has the greatest intensity (Fig. 2). Therefore the film grows preferentially along the (002) direction. Other works have also mentioned this preferred orientation.[4,5] Such a growth is emphasized at the highest concentrations. The intensity of the (100) and (101) peaks depends on the concentration. In particular, at low concentrations ($< 10^{-1}$ mol/litre), the obtained thicknesses are low and the substrate probably induces a crystal growth in different directions.

The film morphology is related to concentration (Fig. 3). At low concentrations the substrate is covered by a layer of single crystals which follows the surface topography (Fig. 3(a) and (b)). At high concentrations, the film consists of large crystals (5 to 10 μm, Fig. 3(c)). The volume density of the film is high (Fig. 3(d)).

3.2 Influence of the temperature at fixed concentration (10^{-1} mol/litre)

Figure 4 shows the temperature dependence of the growth rate. Four separate temperature dependencies are observed. In region 1, the growth rate is

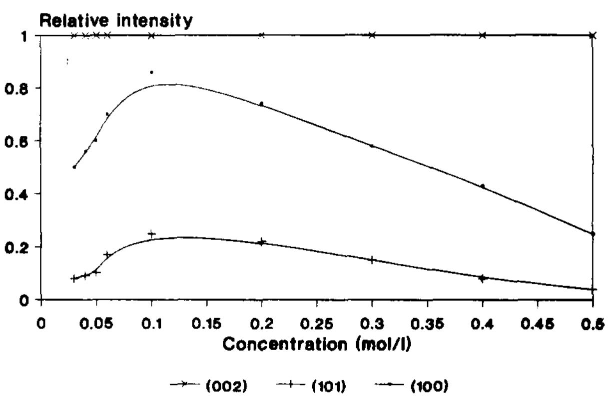
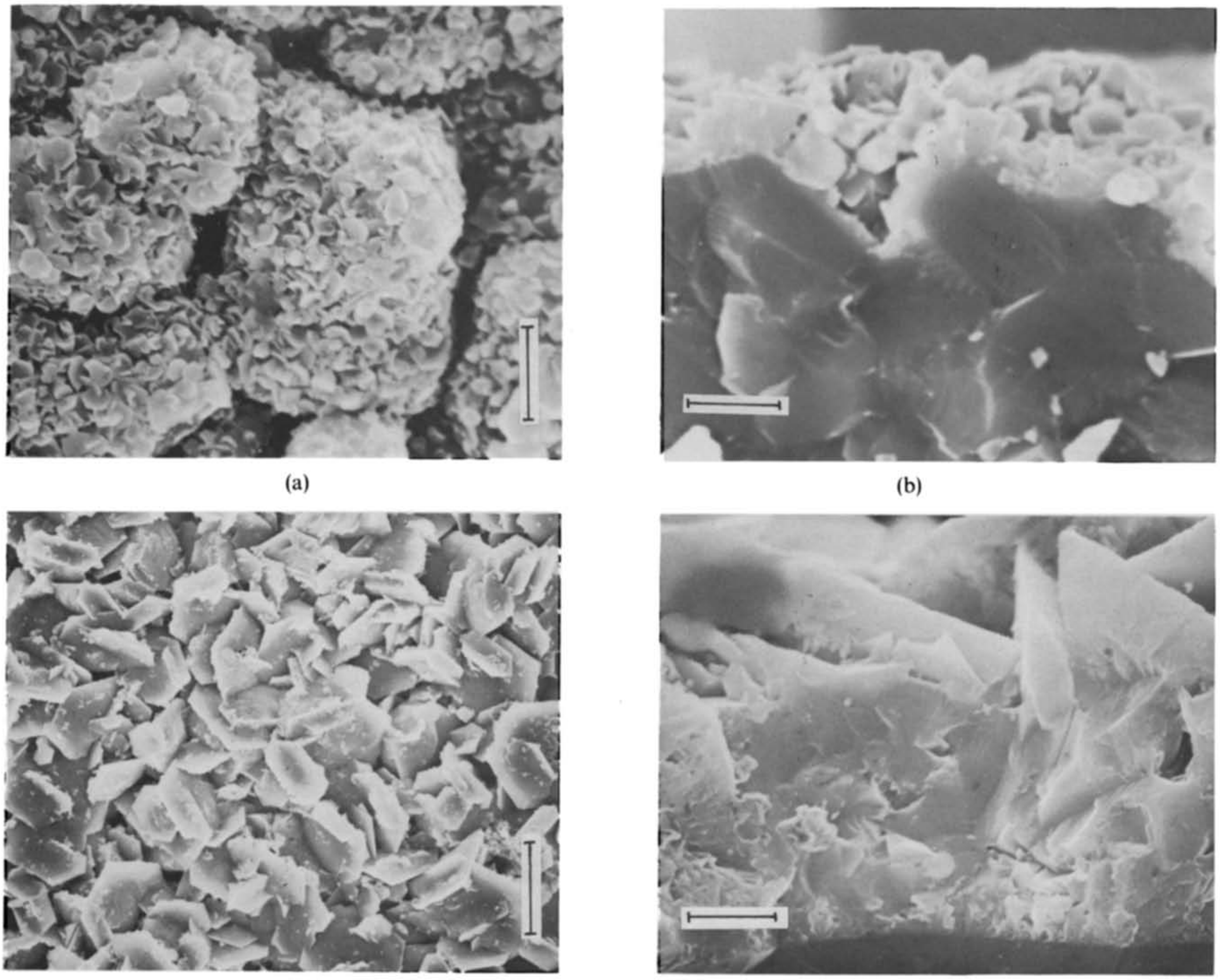


Fig. 2. Intensities of the (100), (101) and (002) diffraction peaks as a function of the starting solution concentration ($T = 450$°C).



(c) (d)

Fig. 3. Film morphology at 450°C for different concentrations of the starting solution. (a) 0·04 mol/litre (bar = 1·5 μm, original magnification × 10 000); (b) 0·04 mol/litre (bar = 1·5 μm, original magnification × 10 000); (c) 0·5 mol/litre (bar = 7·5 μm, original magnification × 2000); (d) 0·5 mol/litre (bar = 1·5 μm, original magnification × 10 000).

low, probably because only a fraction of the starting zinc acetate is vaporized. At 200°C the substrate is covered with a thin layer of crystallized ZnO, whose thickness increases with temperature. A sharp

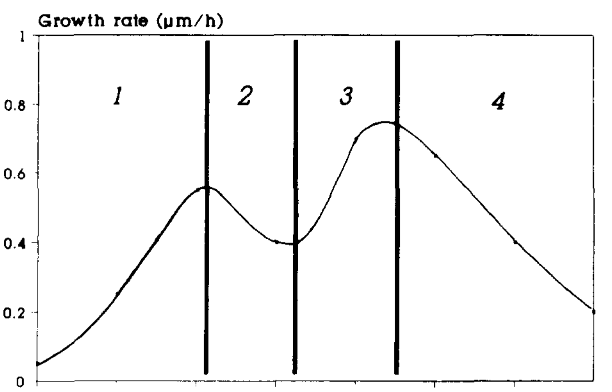


Fig. 4. Growth rate as a function of the deposition temperature (concentration = 0·1 mol/litre).

decrease occurs between 300 and 350°C (region 2) and is followed by an increase between 350 and 430°C (region 3). Such changes have also been reported by Souletie and Wessels.[5] The present results can be explained as follows.

X-Ray diffraction measurements (Fig. 5) indicate that at low temperature the (101) orientation is dominant, followed by the (100) and (002) orientations. Between 300 and about 400°C, the (101) and (100) intensities decrease and the (002) orientation becomes progressively more prominent. Consequently, such a change in the preferred orientation can initially slow down the growth for a deposition temperature < 350°C. Beyond this temperature the (002) orientation has the fastest development and dominates the growth kinetics. In region 4, the growth rate and therefore the obtained thicknesses decrease. This can be explained by a nucleation of ZnO particles in the vapour phase before this vapour

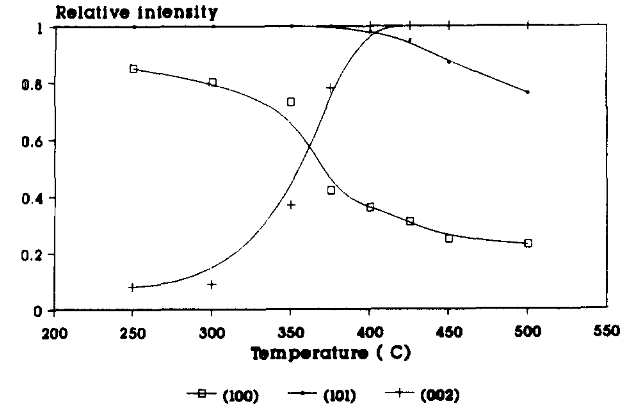


Fig. 5. Intensities of the (100), (101) and (002) diffraction peaks as a function of the deposition temperature (concentration = 0·1 mol/litre).

can reach the heated substrate. Thanks to the design of the apparatus, the so-formed particles do not deposit on the substrate.

The film morphology is very sensitive to temperature. The best films in terms of homogeneity, density and thickness are obtained for deposition temperatures of 400–450°C. At very low temperatures, the crystallite size and shape are not uniform. At very high temperatures the film density is low.

4 Conclusion

The present paper describes the influence of two parameters, namely concentration of the starting solution and temperature of the heated zone, on the characteristics of a ZnO film deposited by spray pyrolysis on polycrystalline alumina substrates. A good substrate covering is obtained for a concentration of at least 10^{-1} mol/litre. The fastest deposition rates occur between 400 and 450°C. In this temperature range the film is uniform, dense and is oriented along the (002) direction. Films of ZnO varistor-based compositions and their electrical characterization are currently under study.

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