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Electrophoretic deposition of MgO thick films from an acetone suspension

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Abstract

Mechanism and kinetics of electrophoretic deposition in an MgO/acetone cell were studied. Linear relations of the deposition yield with voltage applied, time and particle concentration was experimentally verified at both very low concentration levels (~0.02 wt.%) and short deposition times (~5 s). Deposition was constantly cathodic with a particle mobility of 2.5×10^{-4}cm^2/V.s. Results were similar for all substrate materials employed. An optimum voltage range for obtaining uniform and sufficiently adherent films was established. Scanning electron micrograph observations revealed each particle to be independent in both migration and deposition processes. Under clean conditions, finely porous MgO films were reproducibly formed in suspensions of low concentrations. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Electrophoretic deposition; MgO; Suspensions; Films

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1. Introduction

Electrophoretic deposition (EPD) has been used for the preparation of thick films of many electroceramic materials.[1–3] Sarkar and Nicholson in their feature paper[4] have thoroughly covered the background literature. The deposition of MgO thick films on metal substrates, as heat resistant insulators, is of technical significance.[5–7] Such films are also finding applications in fabrication of Josephson devices.[8] Hamaker prepared MgO films by EPD in a methanol suspension,[5] Avgustinik et al. in ethylalcohol,[6] and Rao and Subbarao formed MgO bodies by EPD in benzyl alcohol and dichloromethane.[7] Acetone, due to its low viscosity (η) and high dielectric constant (ϵ_r) 3.1×10^{-4} Pa s and 20.7 respectively, both at 25°C, is one of the popular solvents for EPD.[1,2,9] However, it has been neglected in the case of MgO, perhaps, because of the low value of the electrokinetic potential (ζ) previously reported.[10]

In this work we investigated the electrophoresis of MgO particles in acetone. The aim was to obtain higher levels of precision, reproducibility and control in the EPD process, to facilitate deposition of micro-thick high temperature insulators on semiconducting and metallic substrates. In this respect, relationships between the deposition process and the related basic parameters were studied. These studies were extended down to very low MgO concentrations (~0.02 wt.%) and short deposition periods (~5 s).

2. Experimental

The MgO powder used was "light extra pure" grade (MERCK, 105862). Our XRD analysis revealed the powder to be periclase. The particle size distribution was studied by a laser particle size analyser (Fig. 1). The particles were also examined by SEM, showing that they were flaky with thicknesses below 0.1 μm. The solvent used was a "residue analysis" grade acetone (MERCK, 12) with a purity stated as 99.8 wt.%. The exposure of the powder, solvent, and suspensions to the open air was minimized. To avoid the effect of impurities our

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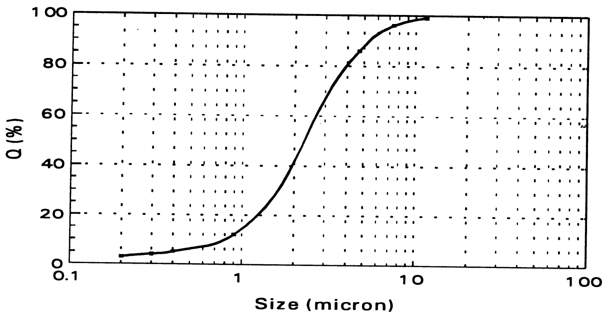

Fig. 1. Particle size distribution of the MgO powder used.

experiments were carried out on a clean bench normally used for hybrid circuit fabrication.[11]

A suspension of ~5 wt.% MgO in acetone was prepared in an airtight borosilicate glass container. It was placed in an ultrasonic bath for 15 min. Five min were allowed for the sedimentation of the larger particles. The slurry of finer particles was then poured into a second similar vessel. The concentration of the latter was adjusted to about 2.0 wt.% by the addition of more acetone. This suspension was our supply slurry and its concentration was monitored frequently by weighing the residues obtained by drying 1 cc samples. Suspensions of lower concentrations were prepared by adding proper volumes of the supply slurry to the acetone in the cell. The suspensions were stable within the duration of each experiment.

The electrophoresis cell consisted of a borosilicate glass beaker, within which glass holders for the cathode and the anode had been constructed. The electrodes were both made of glass slides. One face of each was covered with a gold thick film, deposited by pyrolysis of a commercially available gold resinate (Degussa, GZ11712). The effective surface areas of both cathode and anode were 4 cm^2 each. The distance between the anode and the cathode (d) was constantly 15 mm. The schematic diagram of the cell and the circuit used for the electrical measurements is presented in Fig. 2.

The voltage source was a regulated D.C. power supply. A storage oscilloscope was used to record the electric current vs. time, $I(t)$, curves. The voltmeter was temporarily disconnected during such recordings to eliminate its leakage current. These curves proved to be useful for monitoring the contaminations[11] and cell conductivity, facilitating comparison of the results from different experiments. A typical example of observed $I(t)$ curves is given in Fig. 3. Since the electric field intensity (E) within an electrophoresis cell is far from constant,[4] our experimental results are presented with respect to the applied voltage (V) rather then E. An average E value can be deduced from V/d in each experiment. Deposition time (t) was controlled by an electronic timer connected to an electromechanical switch. The mass deposited on the cathode was obtained from the difference in the cathode weights before and after each experiment. The EPD yield (Y) was calculated by dividing the said mass by the effective surface area of the cathode. All of the measurements were carried out at room temperature (25°C). The cell temperature, monitored by a thermometer, was usually about 5°C lower, due to acetone evaporation.

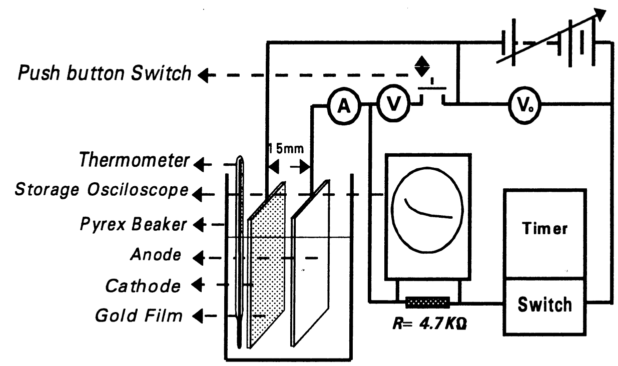

Fig. 2. Schematics of the electrophoresis cell employed and the supporting electric current.

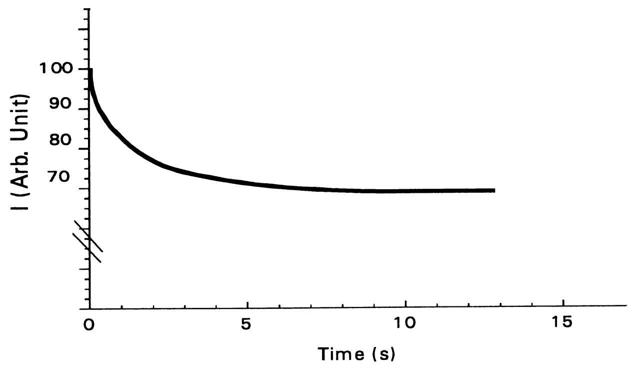

Fig. 3. A typical $I(t)$ curve observed on the storage oscilloscope.

3. Results and discussion

In order to prevent the particles from possible interactions during their migration,[6,7] suspensions with concentration levels of $c<0.6$ wt.% were employed. At such concentrations the possibility of various flocculation mechanisms caused by the migrated ions near the cathode,[12] would have also been removed. The deposition was constantly cathodic. The adherence of the deposit to the cathode was adequate for $V>60$ V. For $V<40$ V the adherence was not acceptable and the deposits were partially washed away as the cathode was being extracted from the cell.

The experimental relationships of Y with V, t, and c are shown graphically in Fig. 4(a)–(c), respectively. The dotted lines have been drawn by assuming linear relationships between the respective parameters and a constant particle mobility (μ) of 2.5×10^{-4}cm^2/V.s. The results obtained basically support Hamaker's linear model of the process.[5] This is the first experimental verification of validity of these proportionalities at very low concentration and short deposition times.

The nonlinear behavior of $Y(V)$, observed particularly at low voltages [Fig. 4(a)], can partly be attributed to the errors caused by a weak adherence of the deposit to the cathode. A gradual decay in deposition rate due to both solution depletion at long deposition runs[13] and electrode covering by layer deposited[14,15] is also observable in Fig. 4(b) and (c). However, the intensity of these hindering effects are subsided by the low concentration levels and short deposition time employed. Apart from gold substrates, EPD yield measurements were carried out on aluminum, stainless steel, graphite and silicon wafer with similar results.

A rough estimation of the ζ-potential is then afforded through $\zeta = \mu\eta/\varepsilon, \varepsilon_r$,[16] where ε, is permitivity of vaccum. The result, $\zeta = +42$ mV, is about an order of magnitude higher than the result of a previous measurement.[10] MgO/acetone cell is very impurity sensitive[11] and such discrepancies can be attributed to the effect of impurities.

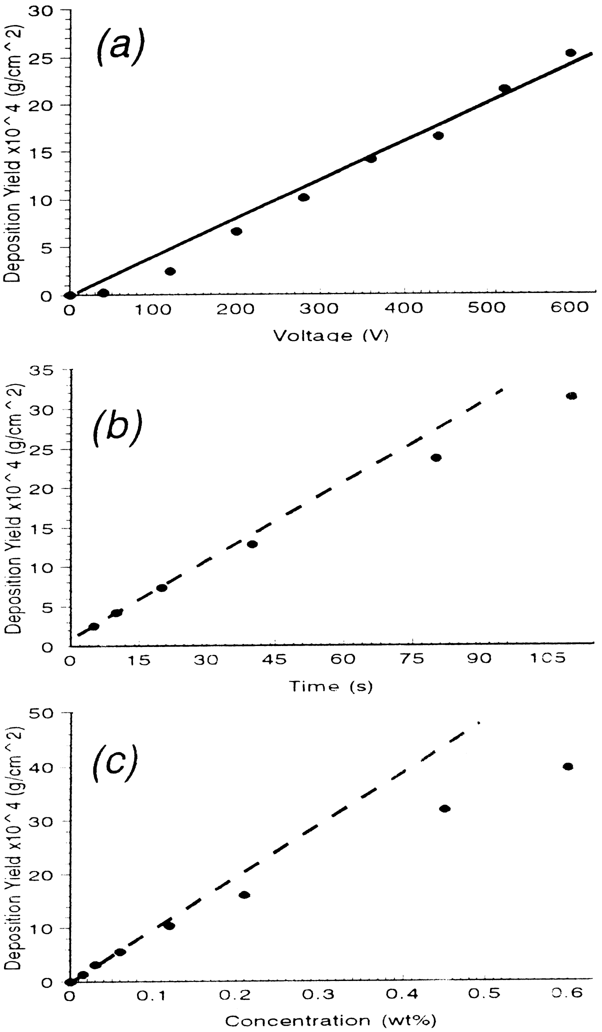

Fig. 4. The variation of deposition yield vs. (a) applied voltage at $t = 30$ s and $c = 0.1$ wt.%, (b) duration of deposition at $V = 250$ V and $c = 0.1$ wt.% and (c) concentration of suspension at $V = 250$ V and $t = 30$ s.

The SEM micrographs of the deposits formed on the cathode, at various stages of a deposition process, are shown in Fig. 5(a)–(d). These, and many more similar micrographs studied, support the concept of independent migration and deposition of the particles in an EPD process. This rules out the occurrence of the deposition due to various flocculation mechanisms near the cathode.

These micrographs also revealed that at the lower end of the voltage range applied (e.g. ~80 V), particles tended to be deposited on the bare cathode surface, resulting in uniform deposits. At a medium V (e.g. 200 V), the positioning of the particles occurred randomly and were not influenced by the already deposited particles. However at $V > 400$ V, particles favoured deposition on the already deposited particles rather than the bare cathode surface, resulting in a rough surface for the layer

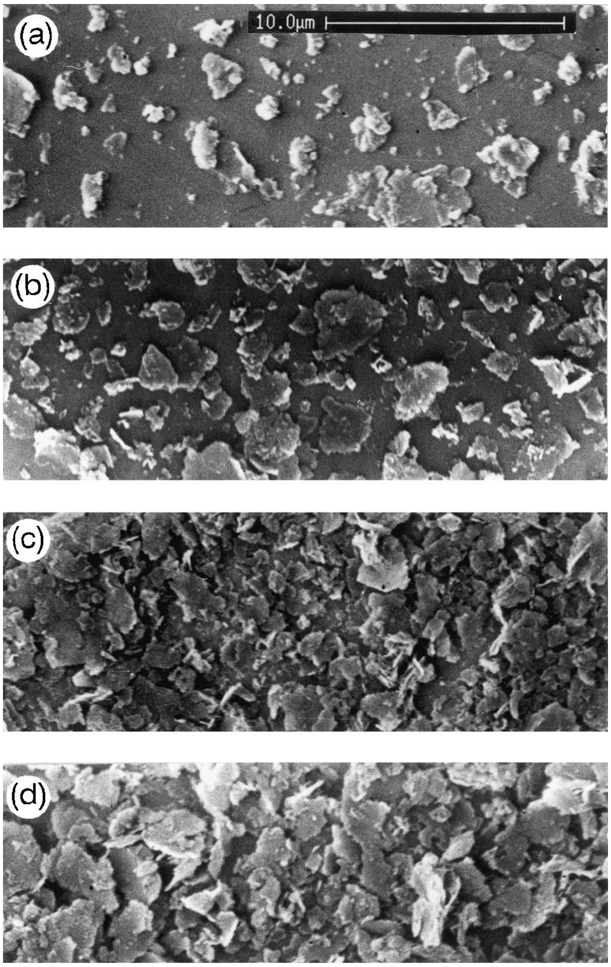

Fig. 5. SEM micrographs of the deposits obtained at $V = 100$ V, $c = 0.03$ wt.% and (a) $t = 0.5$ s, (b) $t = 2$ s, (c) $t = 7$ s and (d) $t = 30$ s.

deposited. By a further increase in V the roughening intensified and as the process progressed, strings of particles were formed along the lines of force, within the liquid. Observation of such particle strings had also been mentioned by other workers[17]. Furthermore, at low voltages, the flaky particles were deposited on the cathode mainly with their base parallel to the surface of the substrate. The directional deposition could be maintained for a few particle layers. This indicates the potentials of the EPD for forming anistropic ceramic layers.[18,19]

Thus an optimum range of V, $60\ \text{V} < V < 400\ \text{V}$, for the deposition of uniform and acceptably adherent thick films was experimentally established. Films deposited at the optimum conditions are uniform but porous as shown in Fig. 5d. Working on a clean bench and in low solid concentration suspensions, deposits of reproducible uniformity and pore texture were obtained. Particle by particle deposition mechanism renders a uniform micropore distribution, making the technique attractive for the fabrication of devices such as ceramic gas sensors.

4. Conclusions

A. Acetone was found to be a suitable medium for the EPD of MgO thick films.

B. An optimum voltage range for depositing uniform and acceptably adherent thick films was experimentally established.

C. Deposition yield was proportional to V, c and t at very low concentration levels and short deposition periods.

D. EPD yield measured was independent of the materials employed as substrates.

E. Particles were deposited independently on the substrate; no flocculation or coagulation of the particles prior to deposition, was observed.

F. Control of the EPD process was achieved by adjustments of the c, V and t in clean conditions. Trade offs between these parameters were also possible. Lower concentrations afforded further precision and reproducibility.

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