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Electrophoretic Deposition and Sintering of Thin/Thick PZT Films

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Abstract

Electrophoretic deposition (EPD) is a simple, rapid, and low cost method for forming dense lead zirconate titanate (PZT) films down to 5 μm from particulate precursors. The three main steps of this process are: (1) formation of a charged suspension of the starting PZT powder; (2) deposition of the powder particles on an electrode under the influence of a dc electric field; and (3) fluxing and constrained sintering of the resulting particulate deposit at 900°C to form a dense continuous film. A 10 μm film formed using this process exhibited a polarization hysteresis equivalent to that of a bulk sample formed from the same starting powder, with a remnant polarization of 33 μC cm^{-2}. © 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

Electrophoretic deposition is a method for creating highly uniform ceramic films with thicknesses that are not practical with other techniques.

Electrophoretic deposition (EPD) is a combination of two processes: electrophoresis and deposition. Electrophoresis is the motion of charged particles in a fluid due to an applied electric field. In a dc electric field this migration will cause the particles to accumulate around the oppositely charged electrode (Fig. 1). With the appropriate conditions, these particles, which must repel each other to be stably suspended, will become attached to each other by either Van der Waals attraction or chemical bonding, forming a solid deposit. This particulate deposit can then be sintered to high densities to form structures suitable for sensors and actuators.

Previous work has been done on the EPD of PZT by Sweeny and Whatmore who produced films by repeated deposition-sintering cycles from a suspension in acetone with nitrocellulose and nitric acid.[1]

Comprehensive reviews of the current published literature on EPD have been published recently by Sarkar and Nicholson[2] and Gani.[3]

2 Materials

The PZT powder has a stoichiometry of $Pb(Zr_{0\cdot52}Ti_{0\cdot48})_{0\cdot976}Nb_{0\cdot024}O_3$. It was prepared by reactive calcination of the component powders followed by high energy milling to reduce particle size. Particle size distribution as shown in Fig. 2 was determined by light scattering (Mastersizer S, Malvern Instruments Inc.). Surface area as determined by single point BET adsorption is $3{\cdot}2\,m^2\,g^{-1}$.

Bulk samples of the sintered ceramic were prepared for property comparison. Pellets were dry pressed and sintered in a sealed crucible with a lead source at 1270°C for 2 h. The pellets achieved a final density of 95% theoretical with dimensions of 1·4 mm thick ×11·0 mm diameter.

The PZT films were formed on 25·4×25·4 mm alumina electronic circuit substrates (ADS 996, Coors Ceramics Co.). The substrates were electroded by screen printing platinum paste. The platinum was screen printed, sintered, and polished three times to assure a continuous, pore-free surface. The final surface was then polished to a mirror finish. The resulting electrodes were 5 to 10 μm thick.

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3 Procedure

3.1 Suspension

The suspension is created by dispersing the PZT powder in glacial acetic acid. Three weight percent PZT is added to the acetic acid creating a 0·4 vol% suspension. The powder is dispersed with an ultrasonic horn while stirring for 2 min. In acetic acid the powder develops a positive surface potential of 60 mV with an electrophoretic mobility of 0·21 μm cm/V s as measured by laser doppler velocimetry (DELSA 440, Coulter Electronics of New England, Inc.). This is sufficient to stabilize the suspension for a period of 1–2 days. However, due to the density of the particles (8 g cm^{-3}), particles larger than 0·4 μm dia. will not be kept in suspension by Brownian motion, with particles greater than 2 μm settling rapidly.

Lead oxide on the surface of the powder will react with the acetic acid to form lead acetate and water. The acid also reacts with zirconium to a lesser extent, leaving a titania rich surface which becomes positively charged by accepting protons from the solvent. After 30 h, some supernatant was removed for analysis by dc plasma emission spectroscopy to determine the extent of dissolution/reaction of the particles. The following quantities were determined, expressed in mole percent of each element in the original powder: Pb 2·4%, Zr 0·6%, Ti 0·25%, Nb 0·9%. There was also some sodium remaining from the surfactant used during milling. The dissolved sodium in the supernatant was 0·01% of the total weight of the powder added.

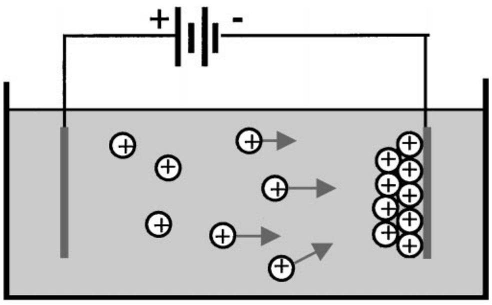

Fig. 1. Positively charged particles will migrate to, and deposit on, a negatively charged surface.

The conductivity of the acetic acid is 0·03 μS cm^{-1} prior to the addition of the PZT (Fisher Accumet Model 20). The conductivity of the suspension is 0·05 μS cm^{-1}. This small increase in conductivity indicates that the ionic strength of the solution is likely only due to surface effects and any species created by dissolution from, or reaction with, the particle surface do not exist as dissociated ions in the solution.

3.2 Deposition

Deposition is done in a 6 cm inside diameter Pyrex beaker. The anode is a 6 cm dia. Inconel disk placed at the bottom of the beaker. Analysis of the supernatant after deposition did not detect any dissolution of ions from the anode. Deposition occurs on the cathode which is the electroded ceramic substrate. It is mounted horizontally 2 cm above the anode in a square mask that exposes 5·4 cm^2 of its surface. During deposition the particles must move upward to deposit on what is effectively the ceiling of the deposition cell. Deposition is carried out at a constant 300 V. This results in a current density of 45 μA cm^{-2} based on deposition electrode area. With repeated depositions the current increases for each subsequent deposition. During the deposition the current declines by less than 5%.

Because of the density and size of the particles, they will begin settling out immediately after stirring is stopped. To insure reproducible results deposition should be started at the same elapsed time from the end of the sonication and stirring. With this precaution the thickness deposited is linearly proportional to the deposition time. To form the 10 μm film for which the properties are shown below, the suspension was allowed to settle for 7 min after sonication and the deposition was carried out over 2·5 min at 250 V.

3.3 Sintering

The films are all sintered in covered, cement sealed alumina crucibles with lead source. The lead source is a 1:1 molar mixture of $PbCO_3$ and ZrO_2 powders. During sintering the powders will calcine to form $PbZrO_3$. The vapor pressure of PbO from the

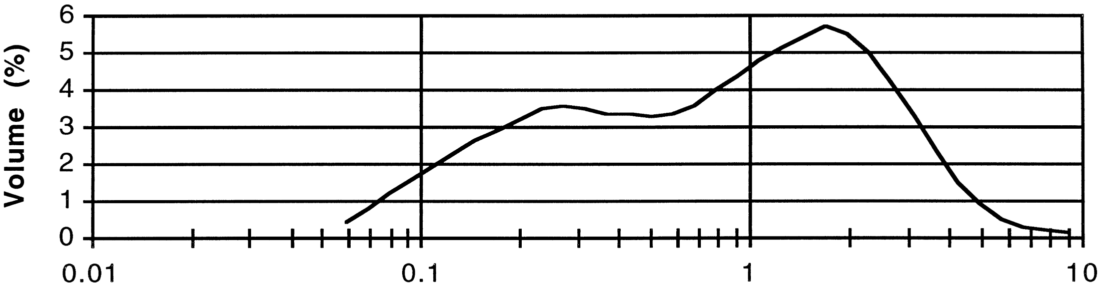

Fig. 2. Particle size (μm).

$PbZrO_3$ is higher than the equilibrium vapor pressure above PZT. Therefore PZT in the same environment should retain a stoichiometric lead ratio as lead is lost from the lead zirconate powder above 840°C.

Sintering of depositions with no sintering aids showed increasing density and grain size with increased sintering temperature. However, before reaching a temperature where the film might be expected to reach full density ($\approx 1250°C$), the film decomposed, losing almost all lead from the PZT, in spite of the presence of the lead source.

To decrease the required sintering temperature two sintering aids were used, Li and PbO. The exact mechanism by which lithium works has not been proven, however experiments have shown that it significantly improves the sintering of the PZT and has been necessary to achieve high density in all of the films formed so far. The excess lead oxide provides a transient liquid phase during sintering. The majority of the excess lead evaporates during sintering, leaving stoichiometric or near stoichiometric PZT.

These sintering aids were added to the powder after deposition. The dried deposition is re-wetted using a spray atomizer with methyl ethyl ketone containing lead ethylhexanoate and lithium acetate with a small addition of methanol to dissolve the acetate. The solvents evaporate leaving behind the metal organics. The organics were then burned out by heating at $1°C\,min.^{-1}$ to 450°C.

4 Results

4.1 Sintering

In Fig. 3 using procedures similar to those above[4] we have been able to produce films at 900°C, as shown below, with no visible porosity on substrates with sputtered platinum electrodes. Unfortunately, during the sintering of this film the thin sputtered platinum electrode de-wetted the interface, remaining as small spherical inclusions scattered along the PZT–alumina interface. Without a bottom electrode, electrical measurements on this film are not possible. To form stable, non-porous electrodes it was necessary to use screen printed platinum paste as detailed above.

Shown in Fig. 4 is a crossection of the film for which the properties are reported and which generated the hysteresis loop. The sintering aids added to the deposition prior to sintering were: lithium—approximately 5 mole% of the $Pb(Zr,Ti)O_3$ and lead ethylhexanoate sufficient to generate, after burnout, lead oxide equivalent to 15 wt% of the deposition. The film was sintered at 900°C for 30 min with a $20°C\,min^{-1}$ heating and cooling rate. The average grain size, as determined by inspection of a fracture crossection of the film, is 0·7 to 0·8 μm.

4.2 Film composition

The X-ray diffraction pattern for the film indicates that the film is phase pure PZT with no evidence of remaining crystalline lead oxide or of reaction with the substrate.

4.3 Electronic properties

The charge/voltage hysteresis loop for this film is shown in Fig. 5. The maximum field is 86 $kV\,cm^{-1}$ with a saturated polarization of 43 $\mu C\,cm^{-2}$. The remnant polarization is 33.6 $\mu C\,cm^2$ with an average coercive field of 21 $kV\,cm^{-1}$.

Capacitance was measured on an HP 4275A Multifrequency LCR Meter at 1 kHz with an applied electric field of 0·1 $kV\,cm^{-1}$. This resulted in a dielectric constant of 750, with a loss tangent of 0·034. The dielectric constant was measured after the hysteresis measurement, so the film was effectively poled at the time of measurement. However, on a section of the substrate that was cut out and depoled by heating to 425°C, repoling reduced the capacitance by 4% and reduced the loss from 0·055 to 0·041

The pyroelectric coefficient of 25 $nC\,cm^{-2}\,K^{-1}$ at 25°C was determined by cooling and re-heating a portion of the sample over a range of ±125°C at a rate of $4°C\,min^{-1}$. Prior to measurement the film was poled by the application of a 100 V potential for 1 min at room temperature. The pyroelectric

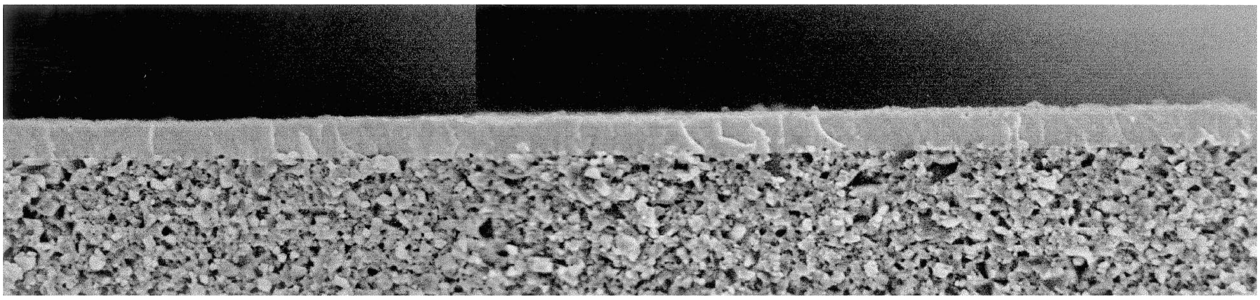

Fig. 3. Fracture surface crossection showing a 6 μm PZT film deposited on a dense alumina substrate with a sputtered platinum electrode (not visible) and sintered to full density at 900°C.

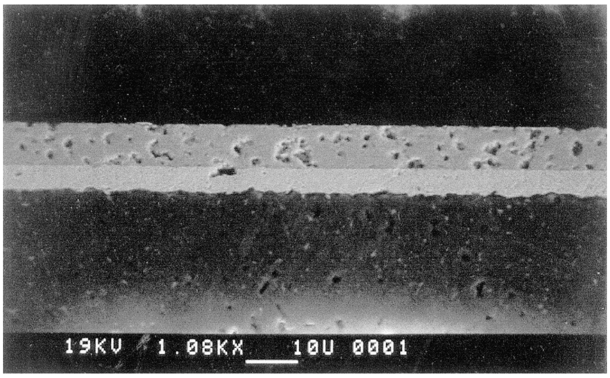

Fig. 4. Crossection of 10 μm PZT film on Pt electrode.

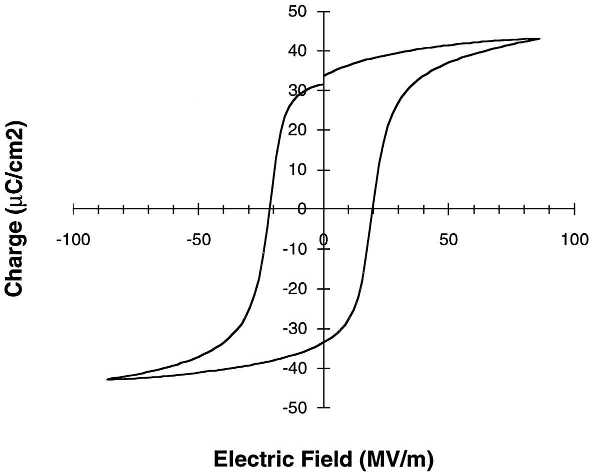

Fig. 5. Polarization hysteresis of 10 μm film.

coefficient was determined by the same procedure for the bulk sample with symmetric sputtered gold electrodes.

When heating the film to 425C at 4C min^{-1} it exhibited an anomalous discharge behavior above 180°C, similar to that documented previously in Ref. 5 and observed previously for a similar film with a silver/palladium electrode in Ref. 4.

Preliminary measurements of the d_{33} coefficient for this film indicate that its behavior is strongly clamped with no extrinsic contributions to its piezoelectric behavior, as was found for a 14 μm PZT film on a silver/palladium electrode in Ref. 4

5 Conclusion

Intermediate thickness, thin/thick, films of PZT have been produced by electrophoretic deposition and sintering of a starting powder with controlled stoichiometry. Using this method a 10 μm film was formed which exhibited polarization switching behavior almost exactly the same as a bulk ceramic prepared from the same starting powder and sintered at a much higher temperature.

The remaining problems to be addressed are: uniform distribution of the sintering additives, accurate measurement of the piezoelectric coefficients of these films, and understanding of the high temperature electrochemical reactions within the PZT film.

Acknowledgements

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