Synthesis of sols for the production of La-modified PbTiO₃ thin films

N. J. ALI
School of Materials, University of Leeds, Leeds LS2 9JT, UK

P. CLEM
Department of Materials Science and Engineering, University of Illinois, Urbana, IL, USA

S. J. MILNE
School of Materials, University of Leeds, Leeds LS2 9JT, UK

The electrical properties of lead titanate and modified lead titanate thin films are of interest for a number of device applications, including pyroelectric sensors and bulk acoustic wave filters and oscillators. The favourable piezoelectric and ferroelectric properties of unmodified PbTiO₃ stem from the large c lattice distortion and high polarization of the tetragonal polymorph. However, this distortion makes it difficult to pole the films and they often undergo electrical breakdown before the switching voltage is reached. Lattice substitutions can be carried out to reduce the c/a ratio, allowing for easier poling; provided reasonable values of polarization can be retained, the modified films may exhibit favourable electrical properties for device applications.

Partial substitution of La on the Pb site is one means of reducing the lattice distortion, but a number of other substitutions, such as Ca and Mn, also find widespread use. A wide compositional range of La₂O₃-PbTiO₃ tetragonal solid solutions up to ~28 mol % La₂O₃ have been reported [1].

There are a number of methods available for depositing ferroelectric thin films, including chemical and physical vapour deposition techniques and solution based sol–gel methods. Examples of the latter have been demonstrated for the deposition of PbTiO₃ sol–gel routes referred to, the limiting thickness of single-layer large crack-free films is <~0.1 μm. Thicker layers, if required, have to be built up using multiple deposition procedures.

We have previously illustrated a sol–gel route based on diol chemistry for the synthesis of PT and PZT films [6-8]. Here we have modified the route to incorporate La into the starting sols.

Starting reagents used were lead acetate trihydrate Pb(CH₃COO)₂·3H₂O, lanthanum 2,4-pentanedionate, (La(CH₃COCHCOCH₃)₃), titanium disopropoxide-bis 2,4-pentanedionate (Ti(C₅H₇O₂)₂)(CH₃COCHCOCH₃)₂ and propanediol (all from Aldrich Chemical Co.). All sol synthesis procedures were carried out in air. Infrared (IR) spectroscopy was used to help identify some of the products of the sol synthesis reaction, whilst reflectance fourier transform IR (FTIR) provided a means of following the thermal decomposition of the coatings. Two PLT compositions were considered: 10 mol % La₂O₃–PbTiO₃ and 28 mol % La₂O₃–PbTiO₃; sols were prepared according to the base formula Pb₁₋ₓLaₓTiO₃.

The films were deposited onto platinized silicon substrates using a spin-coating technique. Samples were pre-fired on a hotplate set at 300 °C before firing for 30 mins in a tube furnace set at 600 °C. Phase analysis was performed using a Philips APD X-Ray diffractometer. Microstructures and film thickness were examined by means of a Hitachi SP700 scanning electron microscope (SEM); elemental analysis was performed using a Camscan series 4 instrument fitted with an energy-dispersive X-ray (EDAX) facility. Initially, sols were prepared using a similar method to that used for PbTiO₃ sol synthesis. Pb(CH₃COO)₂ and HO(CH₂)₃OH were heated under reflux conditions before adding a diol solution of Ti(OC₃H₇)₂(CH₃COCHCOCH₃) and (La(CH₃COCHCOCH₃)₃. Unfortunately, when this approach was adopted a precipitate separated from the sols after refluxing the combined solutions. The problem appeared to be more severe in the case of the 28 mol % La₂O₃ sols.

This precipitate was collected and washed with propanol; the carbon and hydrogen contents of the precipitate were determined using standard microanalytical techniques. Unfortunately, this gave no conclusive evidence as to the composition of the precipitate because the C,H data did not fit any of the likely products, such as La(CH₃COO)₃, La(CH₃COCHCOCH₃), Pb(CH₃COO)₂, Pb(CH₃COCHCOCH₃), or 3Pb(CH₃COO)₂·PbO.

Subsequent IR analysis of the precipitate produced a trace showing a close resemblance to the trace of a sample of La(CH₃COCHCOCH₃), but...
the results of SEM/EDAX analysis of the calcined precipitate indicated the presence of Pb along with La.

These results imply the precipitate to be mainly 
La(CH\textsubscript{3}COCHCOCH\textsubscript{3})\textsubscript{3} combined with a small fraction of a Pb-containing phase. This was possibly Pb(CH\textsubscript{3}COCHCOCH\textsubscript{3}), since tests have shown that it, too, is relatively insoluble in HO(CH\textsubscript{2})\textsubscript{3} OH.

Using an empirical approach, we arrived at conditions that avoid precipitate formation. The reaction conditions for the formation of the initial Pb(CH\textsubscript{3}COO)\textsubscript{2}, La(CH\textsubscript{3}COCHCOCH\textsubscript{3})\textsubscript{3} HO(CH\textsubscript{2})\textsubscript{3}OH solution were modified by distilling off by-products at 125–200 °C after 1 h reflux reaction. The titanium reagent was refluxed separately with HO(CH\textsubscript{2})\textsubscript{3}OH in a molar ratio of 1:1 for 1 h and then distilled at 85–90 °C to remove volatiles before combining the solutions and refluxing the mixture for a further 3 h.

The resulting sols remained stable against precipitation for at least 3 months. The concentration of sols used for coating purposes was 1 m. Fig. 1 shows the changes in the FTIR reflectance spectra of coatings of the 28 mol % La composition immediately after spinning and after heating for 30 min at temperatures up to 650 °C. The main absorption bands in the as-spun coating are labelled in the caption to Fig. 1. (As the samples were heated slight shifts in IR absorption peaks were detected.)

After the films were heated at 175 °C the absorption at 1750 cm\textsuperscript{-1} due to COO stretching (\nuCOO) had all but disappeared, implying the volatilization of acetic acid or an ester. These would have been formed from solvent exchange reactions during the sol synthesis reaction. Analysis of related diol systems suggests an isopropyl acetate ester is formed from isopropanol and acetic acid (formed from exchange reactions between Pb(CH\textsubscript{3}COO)\textsubscript{2} with HO(CH\textsubscript{2})\textsubscript{3} OH) and isopropanol (present as a solvent in the starting titanium reagent and also formed from exchange reactions); ester formation from the reaction of acetic acid and propanediol is also possible.

Heating at 225 °C resulted in a continued diminution of the remaining absorption bands, while increasing the heat-treatment temperature to 275 °C caused the elimination of bands due to \nuCH, but a carbonyl stretch band, \nuCO, persisted. The C = O groups are likely to be due to pentanedionate derivatives, but the absence of CH and the presence of broad MO bands may also suggest the formation of a metal carbonate at this temperature. After firing at the next temperature, 400 °C, there was only a faint broad absorption in the carbonyl stretch region and there was still some evidence of a faint OH absorption band. The pattern for the 500 °C sample was similar to that of 400 °C, but by 600 °C the \nuCO band had disappeared and only a narrow metal–oxygen stretch band was evident.

Hence, the reflectance FTIR data indicate that the final decomposition of the coatings to form the desired ceramic film occurs between 500 and 600 °C, a result that is consistent with previous thermogravimetric analysis data on bulk PT and PZT precursor gels [7, 8].

The XRD patterns of the films were pseudo-cubic (Fig. 2); data for bulk ceramics [1] indicates that the 10 mol % composition should clearly reveal a tetragonal structure, but broadening due to crystallite size and strain effects may mask any tetragonal splitting in the films.

SEM examination of cross-sections of the films indicated a thickness of ~0.5 μm for a single-layer deposit (Fig. 3a). The surface microstructure of a 10 mol % La film is shown in Fig. 3b. There is an indication of an ~0.5 μm \textquotedblleft grain\textquotedblright size but by analogy with PbTiO\textsubscript{3} [7] it is possible that what appear to be grain boundaries are actually boundaries between