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Laser-transfer processing of functional ceramic films

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Abstract

Pulsed excimer laser irradiation through a UV-transparent fabrication substrate has been successfully employed to separate PZT thick films from their sapphire host substrates. Films of 20 μm in thickness were prepared by a hybrid particle sol–gel synthesis route. The microstructure, morphology and ferroelectric properties of the thick films after laser-transfer have been examined. Films were irradiated with a 248 nm, 15 ns pulse, and transferred to a platinised silicon substrate (Pt/Ti/SiO_2/Si). A laser fluence of 250 mJ/cm^2 was sufficient to delaminate the original PZT/sapphire interface. The pulsed energy density used here is lower than reported by other groups utilising a laser-transfer process for PZT. This is believed to be due to higher levels of porosity at the film/substrate interface in this study.

Keywords: Sol–gel processing; Ferroelectric properties; PZT; Functional applications; Laser lift-off

1. Introduction

High density thick films of a few 10s of micrometers thick are of technological interest for a range of micro-electromechanical systems (MEMS) including accelerometers, transducers and actuators.[1,2] The films can be produced on a variety of substrates, including silicon, at temperatures between 650 and 750 °C using a composite sol–gel technique.[3] By combining PZT powder with a PZT forming sol to create an ink, it is possible to produce a system where the conversion of sol to ceramic is used to bind both the PZT particles and the substrate. In this process the conventional high temperature sintering stage, requiring significant atomic diffusion, can be reduced in severity allowing PZT ceramic to be co-processed with a range of other materials.

Pulsed excimer laser lift-off has recently been shown to be a viable alternative to a direct deposition process for the integration of dissimilar materials. The high temperatures required for direct deposition of high quality ferroelectric materials (550–700 °C) make this type of processing unfeasible for applications requiring integration onto semiconductor or polymer substrates. Laser-transfer processing (LTP) utilises a pulsed laser beam, directed through a transparent growth substrate, to delaminate a ceramic film highly absorptive to the same wavelength. The technique was originally developed for the separation of epitaxially grown GaN thin films from sapphire to Si-based substrates and electronics.[4,5]

The laser-transfer process (LTP) is advantageous as it allows the ferroelectric to be fabricated on a compatible high-temperature substrate, prior to transfer onto a selected receiver substrate. The end-use substrate is not heated to high temperatures. Bonding of the original top surface of the film to the transfer substrate, prior to laser treatment of the PZT/sapphire bottom interface, involves temperatures of less than 200 °C. This opens up the possibility of using ferroelectric films on polymers or semiconductors.

In this study, microstructures and polarisation–electric field loops are evaluated for PZT films deposited directly onto a Pt/Si fabrication substrate using a hybrid particle sol–gel route, and for comparable PZT films laser-transferred from a sapphire fabrication substrate.

2. Experimental methods

PZT thick films were deposited using a composite sol–gel approach whereby an ink was produced by mixing together PZT powder, a PZT producing sol, a sintering aid (PbO/Cu_2O) and dispersant (KR55 Kenrich Petrochemicals). The composition of the PZT powder and sol–gel

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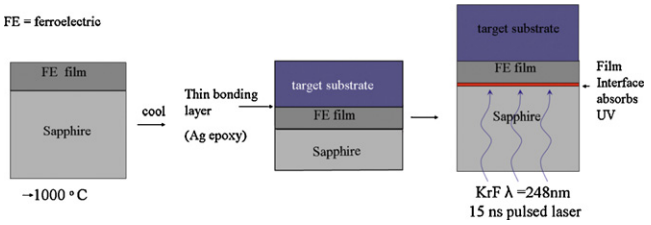

Fig. 1. Schematic of the laser-transfer process.

derived PZT was matched to produce a film of homogenous composition—$Pb_{1.05}(Zr_{0.48}Ti_{0.47}Nb_{0.015}Sb_{0.015}Mn_{0.015})O_3$. The powder to sol ratio of the inks was maintained at 1.5 g of PZT powder/1 ml of 1.1 M sol.[3] 4.7 wt% sintering aid (relative to PZT powder) was also included in the ink to aid sintering.

The films were deposited using a spin coating method. Two composite ink layers were spun at 2000 rpm for 30 s with a drying stage at 300 °C and a pyrolysis stage at 450 °C for each layer. Subsequently the composite layer was infiltrated four times using 0.55 M sol again drying and pyrolysing between infiltrations. In total four of these two composite + four sol-infiltration layers were deposited to produce a film approximately 20 μm thick. The complete film was sintered at 720 °C for 2 min in a box furnace to develop the perovskite structure and densify the microstructure.

A schematic of the laser-transfer process is shown in Fig. 1. The PZT thick films on sapphire were bonded to a Pt/Si substrate via a conductive silver epoxy resin. The Pt/Si was selected for convenience as a standard demonstration substrate. A single 15 ns laser pulse from a KrF excimer laser (λ = 248 nm) was then directed through the sapphire substrate. The fluence was varied until the threshold for film release was identified (250 mJ/cm^2).

The particle size and grain morphology were evaluated using a scanning electron microscope (SEM; LEO 1530 FEGSEM, Cambridge, United Kingdom). The ferroelectric response of the films was measured using a Sawyer Tower circuit. For electrical characterisation, samples were not poled prior to examination. Samples were tested at a frequency of 10 Hz and maximum potential of 500 V; resulting in maximum applied fields of ∼250 or 350 kV/cm. Thermally evaporated gold electrodes (shadow mask method) were applied: area $\sim 3.1 \times 10^{-6}$ m, with an electrode thickness of ∼300 nm.

3. Results and discussion

Scanning electron microscopy (SEM) images were obtained for a standard PZT sample deposited directly onto Pt/Si (Fig. 2) and a similar film deposited on sapphire and laser transferred to a Pt/Si substrate, as shown in Fig. 3. From the low magnification SEM image of the film deposited directly onto Pt/Si using the hybrid route it is noticeable that there is a relatively high level of micro-cracking evident on the film surface (top surface). This is attributed to high levels of strain inherent in the film during processing this type of hybrid particle sol–gel coating, due to: the shrinkage of the gel 'binder' during the gel–ceramic conversion; partial sintering (at 700 °C); and the interfacial constraint of the Pt/Si substrate. Micro-cracking offers a strain relaxation mechanism. At 700 °C it is not possible to achieve high densification and high mechanical strength in the film structure.

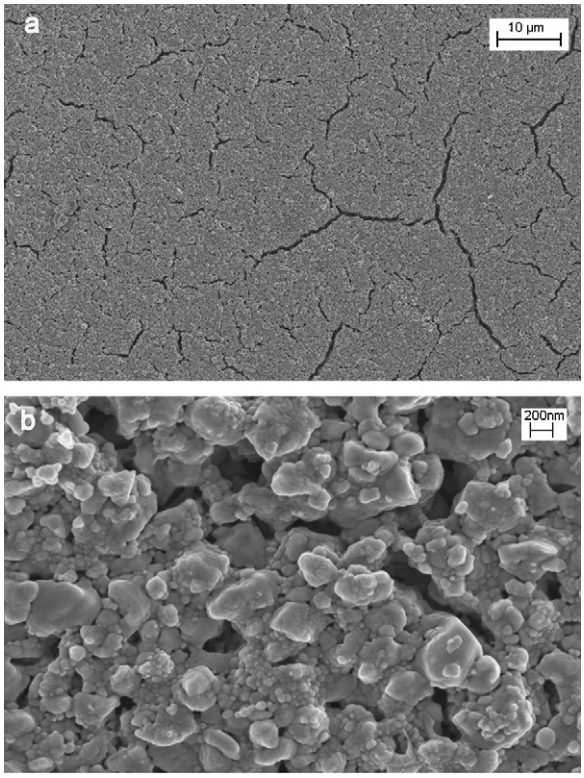

Fig. 2. SEM images of top surface microstructure of a PZT film deposited directly onto platinised silicon: (a) low magnification and (b) high magnification.

Fig. 3 shows an image of the laser-irradiated interface for a PZT film transferred from sapphire to Pt/Si. As Fig. 3 is an image of the original PZT/sapphire interface whilst Fig. 2 shows the top surface of the PZT film deposited directly onto Pt/Si, it is not possible to draw direct comparisons. However, there are major differences between the two microstructures which are probably associated with local heating of the PZT interfacial region adjacent to the sapphire during laser irradiation. Firstly, the discrete grains observed in the PZT sample shown in Fig. 2 are not observed in Fig. 3. Instead the laser-irradiated interface appears as a continuous network with micron scale voids. This infers that

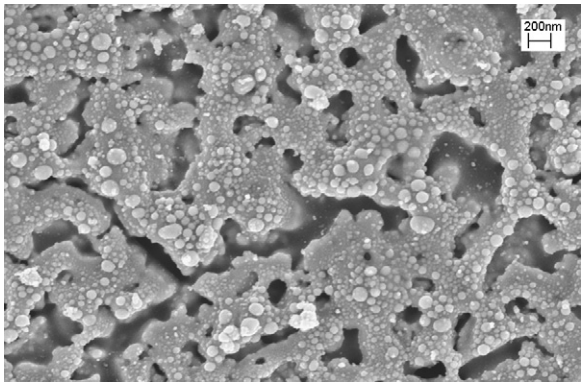

Fig. 3. SEM images of laser-exposed surface of a PZT film, deposited on sapphire and laser transferred to platinised silicon.

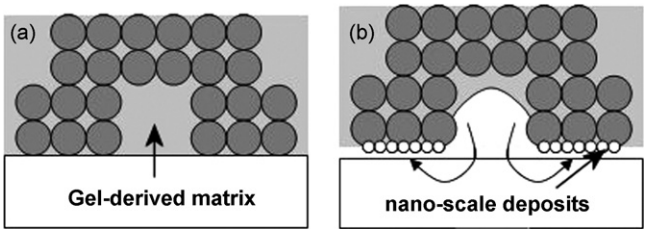

Fig. 4. Schematic images of proposed void formation mechanism during LTP.

melting has taken place during the laser treatment, changing the local microstructure. It is possible that some of the void spaces apparent at the laser-released surface were originally filled with fine-grain PZT resulting from the sol-infiltration process. The level of porosity at the interface was higher than for the film as a whole (Fig. 5).

Secondly, spherical, light contrast nanoscale deposits appear at the laser-irradiated interface (Fig. 3). They are presumed to be PbO, formed due to thermal vaporisation of PbO during laser irradiation. If the voids are present prior to laser irradiation, the vapour can be confined within voids at the PZT interface and as the sample cools, the PbO condenses from the vapour phase resulting in the characteristic sub-200 nm spherical condensates shown in Fig. 3. Alternatively, some of the voids may themselves be formed by the laser irradiation when the PbO is vaporised and condenses, on cooling, in clusters of characteristic sub-200 nm condensates. Such preferential vaporisation can be accounted for by the smaller grain size of material derived from the gel component, and by the lead rich composition (5 at.% excess) (Fig. 4).

The temperatures at the interface during irradiation are not known, but simple calculations based on the heat capacity of PZT indicate temperatures of several thousand °C are possible (ignoring heat dissipation effects). Hence film-substrate delamination, allowing the PZT film to be transferred to another substrate, is most probably a result of localised melting at the interface,[4,5] and weakening of the original chemical bonds that form between the PZT and sapphire during *in situ* fabrication heat-treatment.

Fig. 5 shows an oblique cross-sectional SEM image of a standard PZT film, deposited on sapphire. A focussed ion beam system (FIB) has been used to partially mill away a portion of the film to reveal a cross-section. The inherent porosity in the hybrid sol–gel PZT film is thought to explain the lower laser fluence, 250 mJ/cm^2, necessary for delamination of a PZT film from sapphire, compared to literature values of 400–700 mJ/cm^2.[6–8] Even though this increase in laser energy density may be partially explained by small variations in wavelength of radiation used

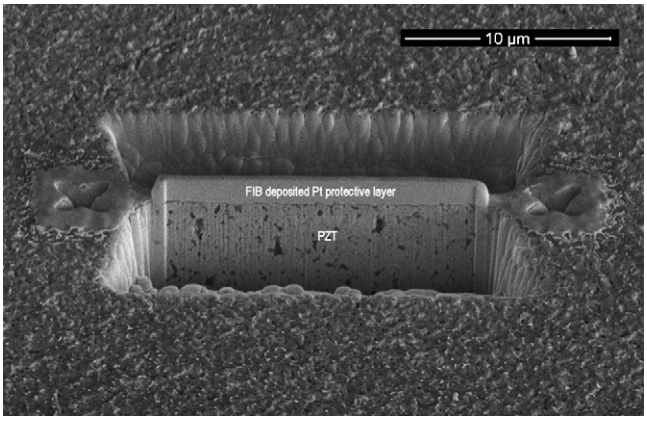

Fig. 5. SEM image of a focussed ion beam (FIB) milled cross-section of a PZT film.

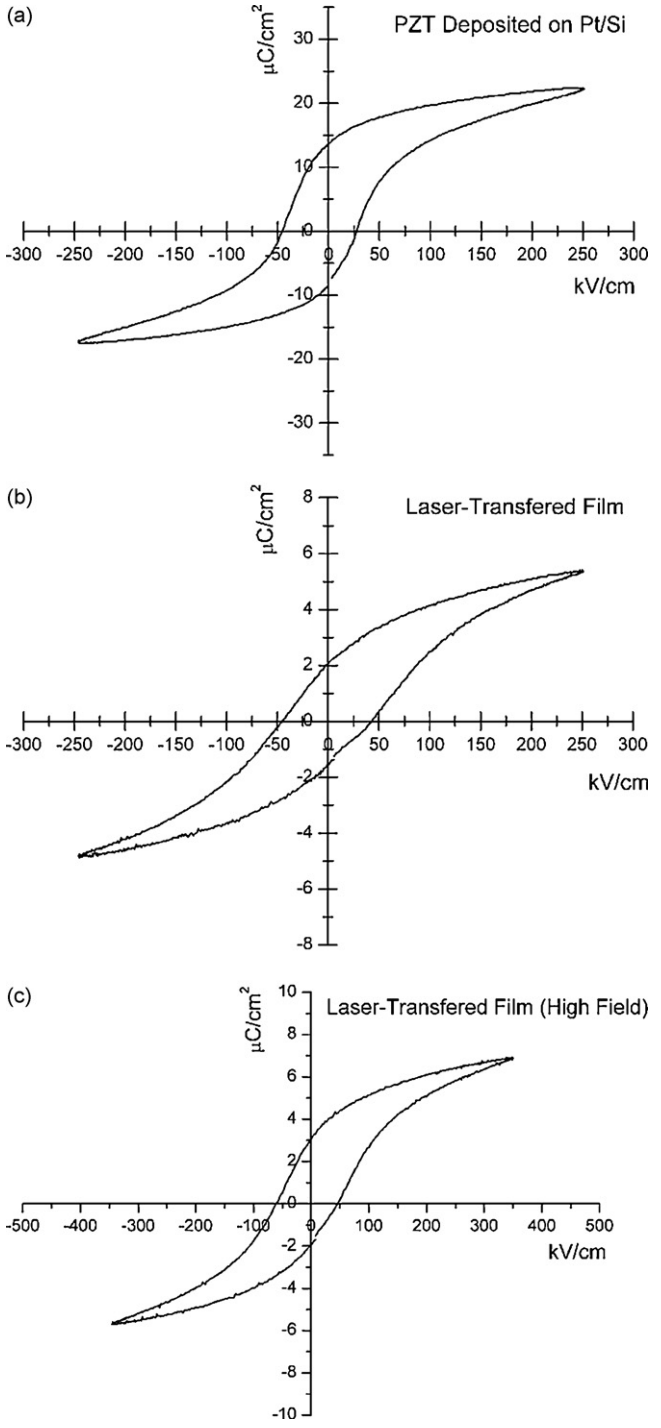

Fig. 6. Polarisation–electric field hysteresis loops for: (a) the as-deposited PZT film on Pt/Si; (b) a laser-transferred PZT film originally deposited on sapphire (note differing polarisation scales in (a) and (b)); (c) the same laser-transferred film at higher applied fields.

(248–308 nm), it is more likely due to higher levels of porosity at the film/substrate interface, consequently decreasing total surface bonding (and also affecting laser penetration depth). As a result a lower laser power is needed to separate the film from its growth substrate. Deposition of the particle-sol suspension on sapphire, as opposed to the more common platinised silicon substrate, may give rise to higher levels of porosity within the film due to less favourable wetting associated with depositing onto sapphire.

Polarisation–electric field (P–E) hysteresis loops were obtained for the films deposited directly onto Pt/Si and laser-transferred PZT films (Fig. 6). From Fig. 6 it is apparent that there is a significant degradation of electrical properties in the laser-transferred films compared to the film deposited directly on Pt/Si. The coercive field, E_c, for the film directly deposited directly onto Pt/Si is approximately 36 kV/cm (Fig. 6a) increasing to 50 kV/cm for the laser-transferred film (Fig. 6b). For values of remnant polarisation, P_r, there is a significant decrease from a modest value of 10 $\mu C/cm^2$ in the 'standard' film to 2 $\mu C/cm^2$ for the laser-transferred film (for an applied field of 250 kV/cm). This reduction in remnant polarisation, and increase in coercive field, is considered to arise from a low-permittivity laser-generated damage layer in electrical series with the ferroelectric layer. The damage layer differs in structure and most probably composition from the remainder of the film, as has been demonstrated experimentally in related experiments for $BiFeO_3$–$PbTiO_3$ thick films.[9] The laser-generated damaged layer in PZT thin films has been reported to be of the order of 100 nm[7]; however, in the present porous films it is conceivable that laser penetration depth and damage is of greater magnitude.

The same laser-transferred PZT film was tested again but with a higher maximum applied field, 350 kV/cm (Fig. 6c). Here we can see that this has led to an increase in P_r from 2 to 3 $\mu C/cm^2$ with E_c remaining at 50 kV/cm. This P_r value is around one third of that for a PZT film deposited directly from the hybrid sol–gel mixture onto Pt/Si and heat-treated at 700 °C. The non-ferroelectric damaged layer reduces the effective field across the ferroelectric film. This increases the applied field required to switch ferroelectric domains. Physical or chemical removal of the damage layer may be possible in order to 'recover' the ferroelectric properties.

PZT films were also transferred to a variety of polymer substrates, including Duroid (PTFE) and PMMA. Transfer was completed successfully; however, values of electrical property measurements were inferior to the films transferred to Pt/Si. This is thought to relate to the use of a non-metal bottom electrode, silver epoxy, in the Duroid and PMMA samples. Work is in progress to employ highly conductive Pt/Pd intermetallic bonding and bottom electrode layer in place of the silver epoxy.

In future the PZT/sapphire samples will be heated to higher temperatures than those used in this preliminary study. This should produce a higher density sample with improved ferroelectric properties.

4. Conclusions

PZT thick films deposited onto a single crystal Al_2O_3 (sapphire) substrate by a hybrid particle sol–gel route have been successfully transferred to a second substrate, Pt/Si, via a laser-transfer process. Laser irradiation of the interface between the PZT film and sapphire fabrication substrate appears to cause localised melting of the interface, and the segregation of PbO due to a vaporisation–condensation mechanism. The laser-generated damaged layer causes degradation in ferroelectric properties of the film, namely in terms of the retained remnant polarisation values, decreasing in this study to approximately 20–30% of the original values depending on applied field. Coercive fields show a twofold increase. An explanation of the lower laser energy density used in this work for delamination as compared to past authors, may be related to higher levels of porosity in the hybrid films.

Acknowledgments

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