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FERROELECTRICS

Laser transfer processing for the integration of thin and thick film ferroelectrics

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Abstract Laser transfer processing (LTP) offers the potential to overcome the problems of integrating ferroelectric thin and thick film materials with polymers and other technologically useful substrate materials that cannot sustain the high process temperatures, 600–1,000 °C, required for normal film deposition. The LTP technique involves the fabrication of a ceramic film on a high-temperature substrate material such as sapphire, and subsequent release by application of pulsed ultra-violet laser radiation. Here, the LTP technique is reviewed in the context of ferroelectric thin and thick films, and current developments are presented. Micro- and nanostructural features of the films before and after transfer to a second substrate are revealed using scanning and transmission electron microscopy. The consequences of laser-generated structural changes on ferroelectric properties are illustrated, and measures to mitigate the effects of an amorphous damage-layer are discussed.

Introduction

The integration of ferroelectric ceramics with semiconductor, metal and polymer substrates opens up a range of new device applications. These include system-in-package applications involving light-weight low-cost polymer materials for use in mobile communications. The high temperatures required to produce a dense polycrystalline ferroelectric film make it difficult to maximize integration opportunities due to the thermal instability of the substrates and circuitry. Physical and chemical methods of fabricating ferroelectric thin films generally involve heating the coated substrate at 600–700 °C to form a well-crystallized film with favourable electrical properties. Thin films can be integrated with silicon semiconductor manufacturing processes, but only if the coatings are applied at an early stage, before heat-sensitive circuitry is developed, which limits circuit design options. For thick film ferroelectrics, tens of microns in thickness, the densification of tape-cast or screen printed particulate coatings necessitates sintering at minimum temperatures of 850 °C, if liquid-phase sintering additives are employed, and at $\geq$1,000 °C if no fluxes are present. Upper process temperatures (approximate) for avoiding substrate degradation, or deleterious substrate-film reactions are: blank silicon 725–750 °C, semiconductors 400 °C, polymers 200 °C (specialist polymers, 400 °C).

Laser transfer processing (LTP), or laser lift off, is one promising approach to overcoming the integration problems and enabling the properties of ferroelectrics to be exploited on polymer, metal and semiconductor substrate

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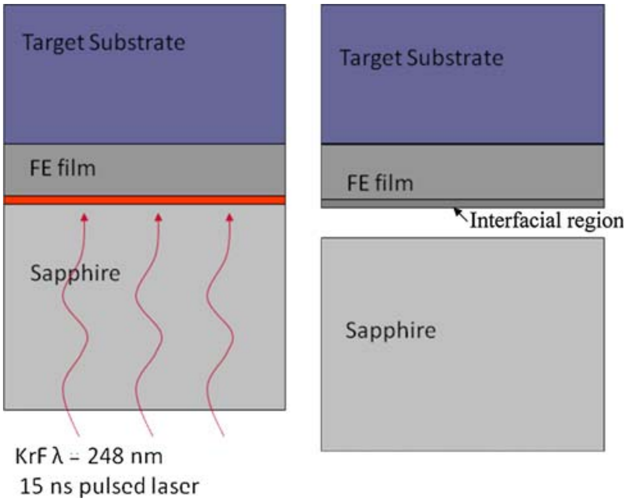


Fig. 1 Schematic of the laser transfer process (LTP)

material [1–7]. The principal steps in laser-transfer processing are summarised in Fig. 1. The ferroelectric film, for example lead zirconate titanate (PZT), is first deposited on a refractory, UV-transparent substrate such as single crystal MgO or Al_2O_3 (sapphire). The coating may then be heated to high temperatures to induce crystallization of thin-films deposited by physical or solution techniques, or to sinter and densify thick film samples deposited by tape casting or screen printing. After cooling, the film is released from the high-temperature fabrication substrate by directing a short pulse of ultra-violet (UV) laser radiation through the UV-transparent substrate onto the absorbing ferroelectric coating. By using a laser pulse duration of around 10–15 ns, the interaction of the laser beam with the film may be restricted to a narrow interfacial region, sufficient to allow the bond between the as-fabricated film and substrate to be weakened and for delamination to occur. The end-use substrate is bonded to the original top surface of the film prior to irradiation. This is usually achieved using a silver-epoxy conductive adhesive (cure temperature ~100 °C) or by transient liquid metal bonding, for example Pd–In (processed at ~200 °C).

There are other approaches to overcoming the integration issue. These include pulsed laser sintering where the goal is to heat the film from above without raising the temperature of the substrate to the point where degradation would occur, and film transfer from a substrate carrying a sacrificial metal or metal oxide layer, which can be etched away to release the ferroelectric film. Additionally, it is possible to deposit dielectrics such as simple metal oxides, which crystallise at low temperatures, ~400 °C, directly onto specialist polymer substrates such as polyimides using sol–gel deposition techniques. Likewise certain pyrochlores for use as a dielectric in integrated capacitors may be deposited directly by pulsed laser deposition at temperatures compatible with polymer substrates. However, ferroelectric and piezoelectric materials require much higher process temperatures and pose a greater integration challenge.

Although LTP has the undoubted advantage of avoiding thermal degradation of the end-use substrate and/or deleterious interfacial reactions at high temperatures, several issues must be addressed for the technique to gain widespread acceptance. The most important of these centres on the formation of a laser-generated damage layer in the region of the ferroelectric exposed to laser beam. Critical variables are: laser fluence, wavelength, pulse duration and repetition rate, as well as the material properties.

The LTP technique has been applied by Tsakalakos et al. [1, 2] to La-modified PZT (PLZT) thin films fabricated by pulsed laser deposition onto 100-orientated single crystal MgO substrates. The 1.4-μm films were transferred to a stainless steel foil (25-μm thickness) using a KrF laser at a fluence of 400 mJ/cm^2. A Pd–In liquid phase bonding technique was used to bond the top surface of the PLZT to the stainless steel substrate prior to laser irradiation. Atomic force microscopy indicated the released surface to have a roughness of the order of 100 nm, and scanning electron microscopy revealed a rough glassy layer at the PLZT interface. The authors postulated that the distinctive microstructure was formed as a result of separation due to melting at the end of the 38-ns radiation pulse. The release fluence (400 mJ/cm^2) was considered to be close to the ablation threshold for PLZT. Ion milling of the surface layer resulted in significant improvements in the ferroelectric and dielectric properties. This is consistent with the removal of a low-permittivity layer generated by the laser interaction. The same research group have also applied LTP to thin PZT films.

Simple calculations based on the heat capacity of PZT, suggest that if the absorption of radiation is assumed to be restricted to a 100-nm interfacial zone, then temperatures of several thousand degrees are possible at the film interface. The affect of heat transfer from this region to other parts of the film, and possible changes in defect structures and properties is uncertain. Other workers assumed a thermal diffusion length in PLZT films to be ~100 nm, and considered that no significant changes to the structure or properties of the film had occurred beyond the interfacial region [1, 2].

Xu and colleagues [3–5] at Palo Alto Research Centre (PARC) have applied LTP to thin and thick film PZT. For thin film samples, they demonstrated that the dielectric constant increased from 650 to 1,000 as a result of using low angle ion milling to remove around 0.1 μm of the exposed surface [3–5]. Again this is consistent with a low-permittivity laser-generated damage layer in electrical series with the ferroelectric component.

In this laboratory, LTP is being applied to PZT and other ferroelectric films both for sol–gel-derived thin films, hybrid particle sol–gel thick films and tape-cast thick films [6, 7]. Examples of this work are reviewed, and results for systems other than PZT, namely bismuth titanate, barium strontium titanate, bismuth ferrite-lead titanate are presented. Structural alterations to the laser-released surface are assessed for thin and thick films, and the consequences on electrical properties illustrated. A polishing technique is introduced for the removal of the damage layer in thick-film samples as a practical alternative to ion beam milling. Finally, the potential of a modified LTP approach for overcoming laser-damage problems in thin-film samples is discussed.

Experimental

Lead zirconate titanate films on sapphire substrates were prepared by tape-casting and by hybrid particle sol–gel thick film deposition techniques. Thin film PZT was prepared by standard sol–gel deposition. The tape-cast 30-μm PZT films were prepared by ball-milling a commercially available PZT powder (TRS610-5H) with added binder and plasticiser. The slurries were then deposited onto sapphire substrates by tape-casting followed by heat treatments to burn-out the organic additives and finally sintered at ~1,100 °C. For the 20-μm PZT film, sol–particle suspensions were deposited by spin coating [8]; heat treatments were carried out at ~700 °C to decompose the gel component. Thin film 1-μm PZT samples were prepared using repetitive sol–gel deposition to build up ~0.1 μm layers [9].

Thick films of 0.7BiFeO3–0.3PT (BFPT) were fabricated by tape casting as described elsewhere [7]. Thin film bismuth titanate [10] and barium strontium titanate films [11] were prepared by repetitive deposition of sols prepared by standard sol–gel routes.

In order to demonstrate laser-transfer, the top surface of a film was bonded to a demonstration Pt/Ti/SiO_2/Si transfer substrate using silver epoxy resin with a curing temperature of 100 °C. To improve electrical contact, a 200-nm gold electrode layer was evaporated onto the top surface of the films prior to epoxy bonding the transfer substrate.

Laser transfer processing of thick film samples was carried out using a GSI Lumnomics pulsed KrF laser ($\lambda = 248$ nm) with a 15-ns pulse duration and operating frequency of 1–100 Hz. Samples were cut to sizes appropriate to the area of the laser beam, in this case approximately 15 mm^2. Threshold fluencies for laser release varied from 250 to 600 mJ/cm^2 dependent on sample composition and fabrication method. LTP of a thin film PZT sample onto Pt/Ti/SiO_2/Si was carried out by Xu and colleagues at Palo Alto Research Centre.

The micro and nanostructural features of the laser-released surfaces of the films were evaluated using scanning electron microscopy (SEM; LEO 1530 FEGSEM, Cambridge, United Kingdom). Thin-film sections for transmission electron microscopy (TEM) analysis were prepared by using a focused ion milling dual beam FIB-SEM system (FEI Nova 200 Nanolab) and analysed using a Philips CM200 TEM instrument. The ferroelectric response of the thick films was measured using a Sawyer Tower circuit at a frequency of 10 Hz and maximum applied fields of ~200–300 kV/cm; thin film samples were analysed using a Radient Technologies RT66a unit. Dielectric measurements were carried using an impedance analyser (Agilent).

Results and discussion

Structural features

Scanning electron microscopy micrographs of the laser-released interfaces of PZT thick films made by hybrid particle sol–gel and tape-casting techniques are shown in

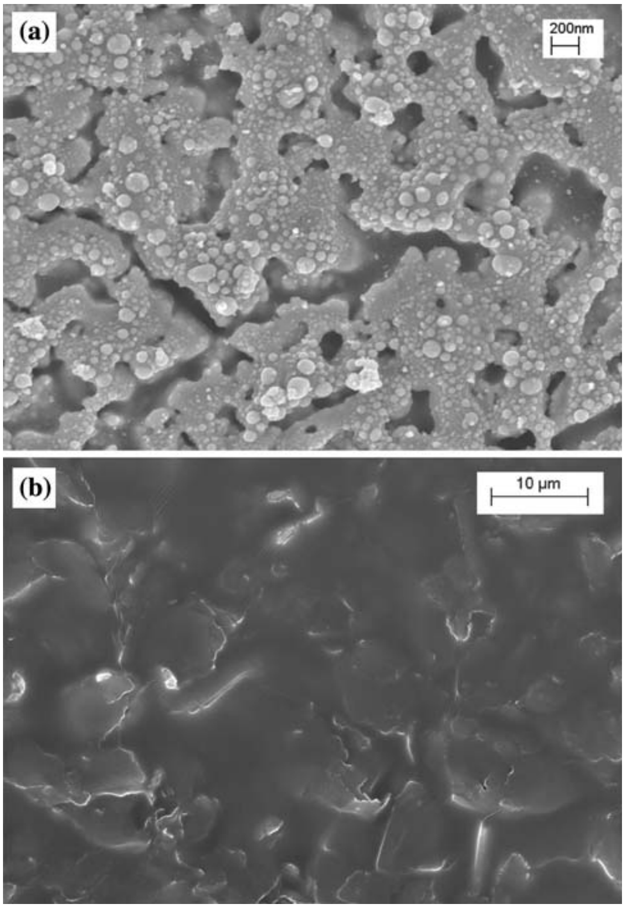


Fig. 2 SEM micrographs of laser-released surfaces: **a** PZT film made from hybrid sol–gel particle route; **b** tape-cast PZT film

Fig. 2a, b, respectively. The physical appearance of the laser-released surface of the hybrid 20-μm film is different to published reports of other PZT films [1, 2] where a continuous molten glassy surface was apparent. Instead the hybrid film shows a porous microstructure with discrete islands of solid material, the shape of which is consistent with some liquid phase having been present during pulse laser treatment. Nanosized spherical deposits can also be observed, Fig. 2a. These sub 100-nm features are too small to be analysed by SEM-EDX and so no reliable elemental analysis could be carried out. However, their light contrast in SEM images is consistent with a lead-rich composition. This could indicate PbO vapour was formed, due to laser ablation or by thermally induced evaporation. On cooling, condensation of the PbO vapour, entrapped within intergranular pores at the PZT-sapphire interface, creates nano particles of PbO (or other Pb-rich phase).

The tape-cast sample, Fig. 2b reveals a continuous glassy type of microstructure similar to that reported by others [1, 2] suggesting that the sample during laser-exposure was in a molten state and formed a continuous glassy phase on cooling. The reasons for the two differing microstructures most likely originate from the different fluences required to achieve release: 250 mJ/cm^2 for the hybrid particle sol–gel film (heat treated at 700 °C), and 400 mJ/cm^2 for the more-dense tape-cast film sintered at higher temperature (1,100 °C). The higher sintering temperature of the tape-cast sample will promote greater adhesion between the film and substrate. There is also a greater contact area because of the film's lower porosity levels. Thus, more laser energy is required to delaminate the tape-cast film than for the hybrid particle sol–gel sample. Consequently, interfacial temperatures are presumed to be higher, resulting in a greater amount of melting.

Examples of the microstructures of laser-released thin-films of lanthanum-modified bismuth titanate and barium strontium titanate (BST) are shown in Figs. 3 and 4, respectively. For bismuth titanate, it appears that surface tension effects have resulted in liquid formed during laser treatment to segregate into islands, 50–500 nm in size, which solidify to a glassy material, Fig. 3. The BST film microstructure by contrast, Fig. 4, is mainly composed of nanosized grains, similar to the original top surface, with only local evidence of melting. The lack of an extensive glass phase is consistent with BST having a much higher melting temperature than PZT or bismuth titanate.

A TEM cross section revealing the nanostructural surface features of a 1-μm PZT thin film sample made by repetitive sol–gel deposition is presented in Fig. 5. An amorphous region varying in thickness from 50–150 nm is located at the interface exposed to laser radiation. This variation in thickness may be because the substrate was released whilst the interfacial region was in a molten state, giving rise to an irregular surface profile [1, 2]. The TEM section shown in Fig. 3 was prepared using a FIB-SEM milling technique. This offers advantages over traditional mechanical preparation techniques in that a specific area of interest may be selected, and specimen preparation times are much shorter. Another advantage for LTP samples arises because the silver-epoxy used to bond the film to the transfer substrate is particularly vulnerable to the dimpling technique used in traditional TEM specimen preparation methods. The use of minimal beam currents during the FIB-SEM final milling stage ensures minimum re-deposition and ion impregnation.

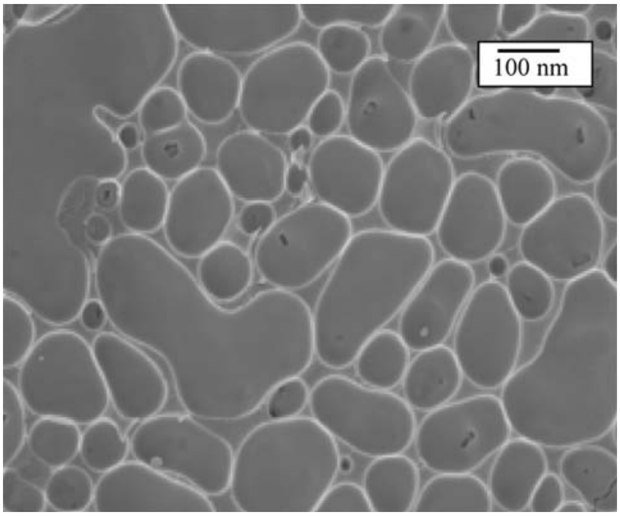


Fig. 3 SEM showing laser-released surface of La-modified bismuth titanate thin film made by sol–gel route

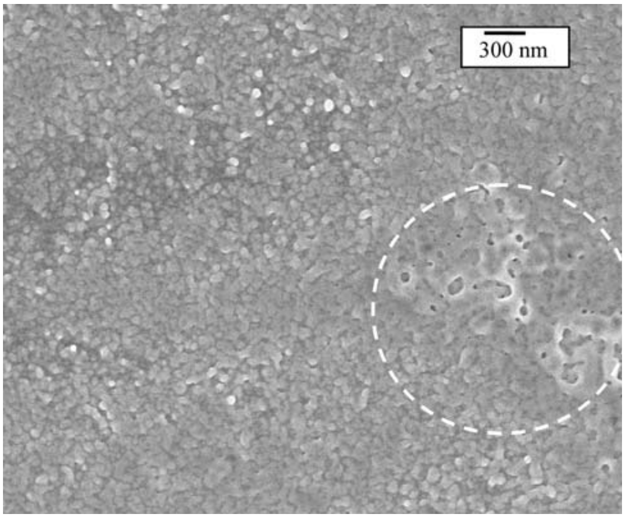
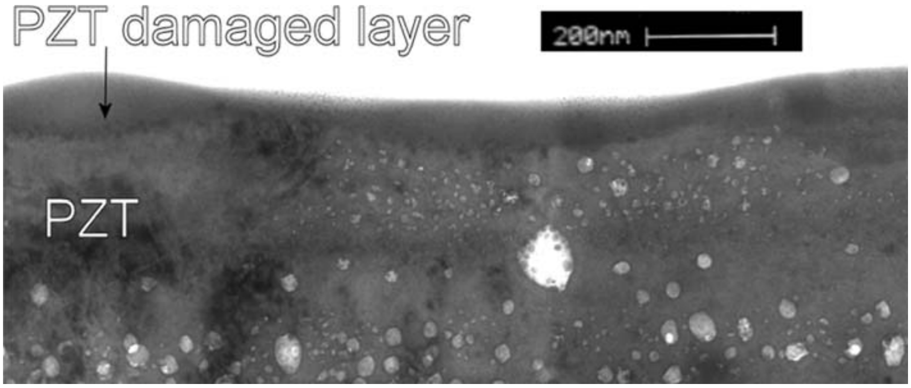


Fig. 4 SEM showing laser-released surface of barium strontium titanate thin film made by sol–gel route. An area of apparent melting is highlighted

The BFPT system is of interest as a high-temperature piezoelectric ceramic and for its multiferroic properties.

Fig. 5 TEM cross section of 1-μm PZT thin film made by sol–gel route after LTP showing laser-generated damage layer



Compositions around 70 mol.% $BiFeO_3$ exhibit high strains at temperatures above the maximum operating temperature of PZT [12–15]. After LTP, tape-cast BFPT samples showed similar microstructures to the tape-cast PZT film in Fig. 2b. Glancing angle XRD analysis of the laser-released surface of a 20-μm BFPT thick-film showed a small amount of crystalline Bi_2O_3 second phase present at depths extending to around 0.5 μm (tilt angle $\psi = 80°$) from the laser-exposed surface, Fig. 6. The formation mechanism of Bi_2O_3 is assumed to involve vaporisation–condensation in a similar manner to PbO formed in PZT films, but in the case of BFPT no crystalline PbO was detected by XRD, nor were any surface nanoparticles observed in SEM images.

The depth of laser-generated alteration to the BFPT structure inferred from glancing angle XRD, 0.5 μm, is much greater than the 100 nm amorphous zone identified by TEM in the thin film sample of PZT (Fig. 5). Thin-film deposition techniques result in highly dense microstructures, whereas the tape-cast BFPT film had a more porous structure [7]. Therefore, in regions where a pore is adjacent to the sapphire, the laser radiation will pass more deeply into the sample than at points where grains interface directly with the sapphire. In addition, metal oxide vapours will percolate along connected porosity and condense at locations deeper into the film also contributing to a greater depth of laser-generated compositional and structural changes.

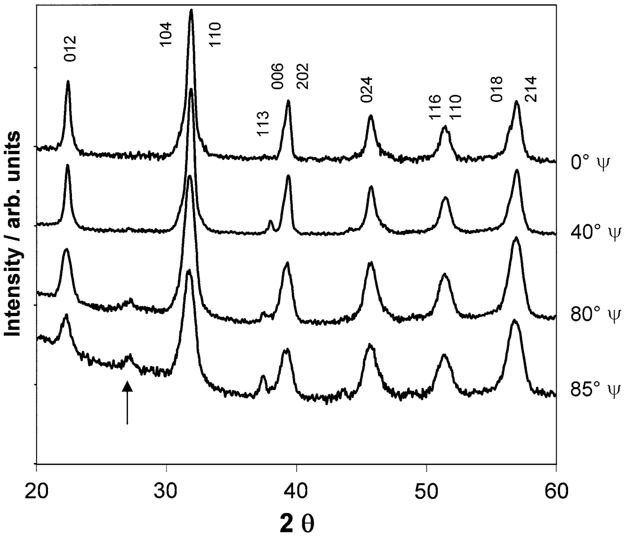


Fig. 6 Glancing angle XRD data for BFPT tape-cast thick film after laser release. *Arrow* indicates secondary Bi_2O_3 phase

Electrical characterisation

The polarisation–electric field, *P–E*, loop of a tape-cast 30-μm PZT film after LTP onto $Pt/Ti/SiO_2/Si$ is shown in Fig. 7a. It confirms that the film exhibits favourable ferroelectric properties after LTP, with $P_r = 22$ μC/cm^2 and $E_c = 50$ kV/cm. These thick films films sintered at 1,100 °C are of higher density than can be achieved by direct hybrid sol–gel coating onto $Pt/Ti/SiO_2/Si$ (at 700 °C). The benefits of this are illustrated by a comparison with the ferroelectric properties of a 20-μm hybrid sol–gel PZT film deposited directly in the normal manner at ~700 °C onto $Pt/Ti/SiO_2/Si$: resultant P_r values were only ~10 μC/cm^2 as opposed to 22 μC/cm^2 for the tape-cast sample; the values of co-ercive field were similar.

Thin films of PZT, ~1 μm in thickness also showed well-saturated hysteresis loops after LTP with $P_r = 24$ μC/cm^2 and $E_c = 150$ kV/cm; the latter value is around three times higher than a normal in situ film on $Pt/Ti/SiO_2/Si$.

For the purpose of evaluating (indirectly) the effects of LTP on ferroelectric properties, the *P–E* response of a hybrid sol–gel film fabricated at 700 °C on sapphire and then transferred to $Pt/Ti/SiO_2/Si$ was compared to a similar film deposited directly at 700 °C on $Pt/Ti/SiO_2/Si$. For the LTP sample, the form of the loop indicates it to be ferroelectric but the P_r value is very low, only 2 μC/cm^2, with an E_c of 50 kV/cm. This represents a 5-fold decrease in polarisation relative to the film deposited directly onto platinised silicon, although E_c values are similar. As well as degradation to properties attributable to the LTP procedure, the microstructure of the film fabricated on sapphire was more porous before LTP than the film deposited directly on $Pt/Ti/SiO_2/Si$.

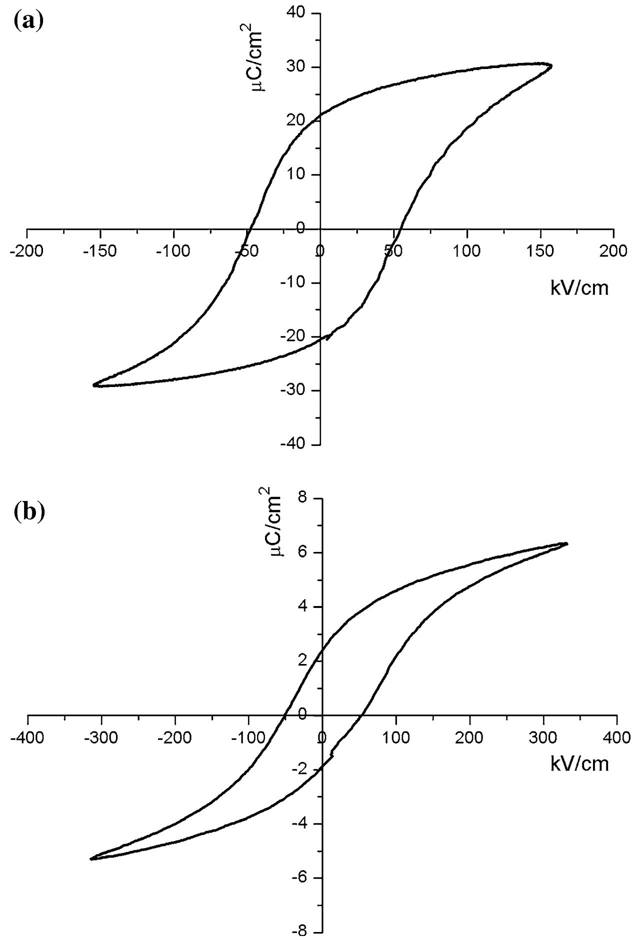


Fig. 7 Polarisation–electric field loop of **a** tape-cast 30-µm PZT film and **b** hybrid particle sol–gel 30-µm PZT film

Ideally in situ measurements of electrical properties on the fabrication substrate would be possible, as this would enable a direct evaluation of changes taking place as a result of LTP. However, present problems of delamination of electrode layers on sapphire at high process temperatures need to be overcome in order to achieve this goal.

We have proceeded to investigate the feasibility of removing the laser-generated damage layer from the tape-cast films through mechanical polishing using nanoparticle media. As a result of removal of the low permittivity damaged layer, there was a decrease in the value of E_c from 50 to 35 kV/cm on removal of approximately 2 µm of the 30-µm film; there was no significant increase in P_r value after polishing. The decrease in the value of E_c for the polished sample reflects the large voltage drop across the low-permittivity damaged region in unpolished samples. The higher porosity of the hybrid sol–gel coatings resulted in the films disintegrating during polishing. The electrical properties of the PZT thick films and a sol–gel derived ~1-µm PZT film after LTP are summarised in Table 1.

Other groups have demonstrated improvements to dielectric properties through the use of low-angle ion milling to remove the laser-affected layer in thin films, but standard ion milling techniques may only abrade a small area of the sample and may not be suited to commercial production runs. Mechanical polishing is potentially a more simple and practical means of mitigating the effects of LTP on dielectric and ferroelectric properties of thick films. The full results of the polishing study will be presented in future, as will measurements of electrical properties of films transferred to polymer substrates.

Conclusions and future trends

Laser transfer processing is demonstrated to have the potential to allow thin and thick films of PZT and other ferroelectric ceramics to be integrated with substrates, which cannot withstand the high processing temperatures associated with normal film fabrication methods. Examination by SEM and TEM revealed microstructural evidence of varying degrees of melting of an interfacial layer during application of pulsed UV laser radiation. Nanoscale particles of a Pb-rich phase were present in PZT films made by a hybrid sol–gel technique. This is consistent with PbO vaporisation during low-energy laser-treatment, and the formation of nanoparticle deposits on subsequent cooling. Higher laser fluencies for tape-cast PZT resulted in full-scale melting and no nanoscale deposits were observed. Glancing angle XRD showed that crystalline Bi_2O_3 was present in a BFPT tape-cast sample after laser transfer.

Favourable ferroelectric properties of thick-film PZT have been demonstrated after transfer. The tape-cast film had a P_r of 22 µC/cm^2 and E_c of 50 kV/cm. For a thin-film sample after LTP, P_r was 24 µC/cm^2 with an E_c of 150 kV/cm. Removal of the damage layer of a tape-cast PZT film by mechanical polishing after LTP lowered the coercive field from 50 kV/cm to 35 kV/cm.

Table 1 Summary of electrical properties of PZT films after laser transfer processing

Film type	Thickness (µm)	Process temperature (°C)	E_c (kV/cm)	P_r (µC/cm^2)
Hybrid LTP	20	700	50	2
Tape cast (polished)	25	1,100	35	20
Thin film LTP PZT	1	700	150	24

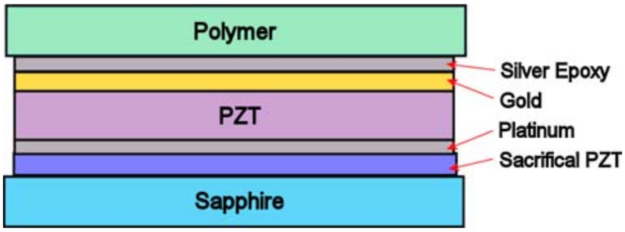


Fig. 8 Schematic of layer stack involving the use of a thin sacrificial layer

Laser transfer processing at the moment is arguably better suited to thick films rather than micron or submicron layers. As total sample thickness decreases, there is an increasing contribution of the low-permittivity damage layer, in electrical series with the ferroelectric, to the total response. Moreover, removal by polishing is not feasible for thin-film samples. We are currently examining a modified architecture prior to laser release which may be advantageous for thin film samples. The approach involves the following: (a) deposit a thin 100–300-nm sacrificial PZT or other UV-absorbing film onto the sapphire substrate; (b) apply metal electrodes by thermal evaporation; (c) deposit the desired ferroelectric sample. The release will be through heating/melting of the very thin sacrificial layer, leaving the sample above the metal electrode undamaged. Any residue of the sacrificial layer may be etched away; amorphous material will be more soluble in acids than the crystalline undamaged layer above the metal electrode. Preliminary trials using the stack sequence shown in Fig. 8 are promising and will be published in future.

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