Focussed ion beam etching of the interfacial region of lead zirconate titanate thin film after laser-release from sapphire fabrication substrate

T Chakraborty[*], B Xu[+], J Harrington[*], S Chakraborty[*], Q Zhang[++], R E Miles[*], R Dorey [++], S J Milne[*]

[*]University of Leeds, Leeds LS2 9JT, UK
[+]Palo Alto Research Center Inc,. 3333 Coyote Hill Road, Paulo Alto CA 94304, USA,
[++]University of Cranfield, Bedford MK 43 0L, UK

ABSTRACT

Although many lead zirconate titanate (PZT) based MEMS have been demonstrated, the thermal incompatibility problems associated with in-situ fabrication of PZT films on the device substrate remain a major challenge. Process temperatures of 600–700 ºC are common for PZT on silicon, however these temperatures can degrade silicon microelectronics and metal interconnects. By depositing the film on a separate fabrication substrate, such as sapphire, and then using a pulsed UV laser to aid its transfer to the device substrate the problems of thermal incompatibility are avoided [1]. In order to gain a better understanding of the effects of the laser radiation on the interfacial region of the film originally adjacent to the sapphire substrate, we are examining the merits of dual-beam SEM focussed-ion- beam etching (FIBSEM, Nova 200 Nanolab, FEI UK Ltd). Microstructural information from SEM, together with preliminary results using FIBSEM are presented.

Keywords: laser lift off, microstructure, focused ion beam etching

1 INTRODUCTION

Thin and thick films of lead zirconate titanate (PZT) have been widely studied for sensor and actuator applications in a variety of microsystem applications [2, 3, 4]. Deposition techniques for 100 nm - 1μm thin films fall into two broad categories - vacuum deposition techniques such as sputtering or CVD, and chemical solution deposition (sol-gel) techniques. In order to develop piezoelectric and ferroelectric thin film properties, thermal processing at ~ 550-700 ºC is required. These temperatures are problematic for integration with silicon microelectronic circuit manufacturing processes. The use of thermal diffusion barriers or rapid thermal processing does not fully solve the integration difficulties. Chemical interdiffusion at the film-substrate interface can degrade film properties, and damage may also occur to metal interconnects. Device integration problems are more severe where thicker films a few tens of microns or more in thickness are required. Tape-casting and screen printing of particle suspensions are well established thick-film fabrication techniques, but even with additive fluxes, sintering temperatures are > 800 ºC which is beyond the range of silicon compatibility. Combined particle and sol-gel processing has been considered as an alternative thick-film processing technique, with minimum PZT process temperatures of ~ 720 C.

For full integration with semiconductor devices, it would be necessary to limit substrate and circuit temperatures to ~ 400 ºC , and although many workers have sought to achieve this through for example changes to sol-gel chemistry the in-situ fabrication at temperatures below 450-480 ºC has not been achieved for piezoelectric PZT thin films. The enormous potential of ferroelectric films in new microsystems is a strong driver for solving the present integration and device fabrication problems. Moreover if substrate temperatures could be restricted to < 200 ºC it would open up new opportunities for integration with polymeric substrates.

As a solution to these device integration difficulties researchers at Palo Alto Research Centre [5] and researchers at University of California have recently demonstrated the merits of a laser-assisted film transfer process in which the ceramic film is fabricated on a thermally-stable substrate such as sapphire. The end-use semiconductor substrate, or a temporary transfer substrate, is then bonded to the top surface of the film and the growth substrate released by exposure of pulsed UV laser through the sapphire. The technique has similarities with laser transfer processing well known in semiconductor optoelectronics, as applied for example to GaN-based films.

Laser transfer processing has been applied to PZT and La-modified PZT (PLZT) films ranging in thickness from 100 μm to 1 μm. The mechanism for film release is believed to involve local heating and melting of the film in the region adjacent to the interface with sapphire. We have now demonstrated that other ferroelectric thin and thick films may also be treated in this way. Table 1 indicates the different ferroelectric thin film materials which we been released and transferred to either semiconductor or polymer target substrates. In this paper we concentrate on the characteristics of laser-released PZT films, and illustrate the merits of using a dual beam focuussed ion beam-SEM etching technique to disclose micro and nanostructural

details of the laser-affected region of PZT films after their removal from the sapphire fabrication substrate.

Film	Thickness (μm)	Sintering temperature ºC	End-use substrate
PZT	1	650	Pt/Si
PZT	20	950	Pt/Si, PTFE
BST	2	950	Pt/Si, PTFE
BST	50	1200	Pt/Si
BiT	2	650	Pt/Si, PTFE
BiT	50	1100	Pt/Si
La-BiT	50	1100	Pt/Si
BFPT	10	1400	Pt/Si

2 EXPERIMENTAL PROCEDURE

PZT films with a Zr/Ti ratio of 30/70 were prepared by a hybrid particle-sol-gel technique.

The thick PZT film was deposited onto a sapphire substrate using a composite sol-gel deposition process whereby a PZT powder (PZ26 Ferroperm, Denmark) was mixed with a PZT producing sol, of nominally identical composition, and ball milled under nitrogen for 24 hours to produce a slurry. The sol fabrication was based on the 2-methoxyethanol route using lead acetate, zirconium propoxide and titanium propoxide with 2-Methoxy ethanol as the solvent [6].

PZT thick films were built up using a repeated layering process. The sapphire substrate was first coated with the PZT composite slurry and then spun at 2000 rpm for 30s. The system was then dried at 200ºC for 1 minute and pyrolysed at 450ºC for 30 seconds. To increase the density of the film, a 0.5M sol was infiltrated into the structure. The excess sol was spun off at 2000 rpm and the system dried and pyrolysed as before. The sol infiltration process was repeated 4 times for each composite layer. The film thickness was increased by depositing multiple composite/infiltration layers. Once the required film thickness was achieved the film was crystallised at 720ºC for 20 minutes. Films were further sintered at 950 ºC for thirty minutes to promote grain growth.

In another experiment a 1μm PZT (70/30) thin film was deposited by a standard sol-gel method onto a sapphire substrate by spin coating. The full thickness was built up by multiple coatings, each ~ 0.1μm in thickness. The final film was sintered at 650 ºC for 30 minutes.

The process of laser transfer is schematically shown in Fig 1. The top of the PZT film (on sapphire) was first coated with Cr/Ag by thermal evaporation and then bonded to a Pt/Si substrate using silver epoxy cured at room temperature. The film-sapphire interface was irradiated with a KrF 248 nm excimer laser of fluence ~ 400 mJ/cm^2. This allowed the PZT film to be released from the sapphire.

For electrical measurements top dot electrodes were formed on the PZT film, which was now attached solely to the Pt/Si substrate, by Cr/Au thermal evaporation using a shadow mask; the electrode diameter was about 0.5 mm. Polarisation-electric field hysteresis was recorded using a Radiant Technology ferroelectric tester.

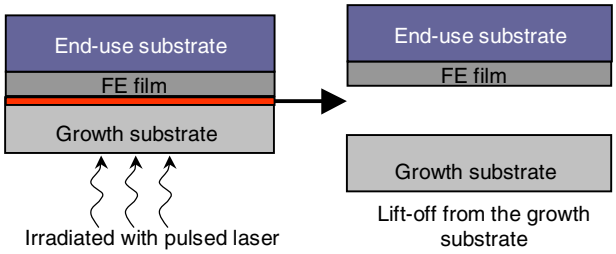

Fig.1 Schematic representation of laser transfer

3 RESULTS AND DISCUSSIONS

Figure 2 shows a plan view of the laser-affected region of the PZT thick film made by the hybrid particle sol-gel route after exposure to a beam of fluence ≥ 600 mJ/cm^2. The porosity levels are higher than at the top-surface and are considered to have formed during the laser-treatment step. The as-fabricated PZT thick films (before laser release) contained microcracks which increased in size during the final heat-treatment at 950 ºC, Fig 3. Hence the crack running vertically toward the left-hand side of the micrograph in Fig 2 is not directly associated with the laser treatment process. The general appearance of the laser-affected region, which had received the ≥ 600 mJ/cm^2 laser beam exposure, suggests it is amorphous and formed by localised melting during laser treatment. At higher magnification nanoscale rounded features became evident, Fig 4, these could be Pb-rich deposits formed by volatilisation and subsequent condensation of PbO during melting and cooling.

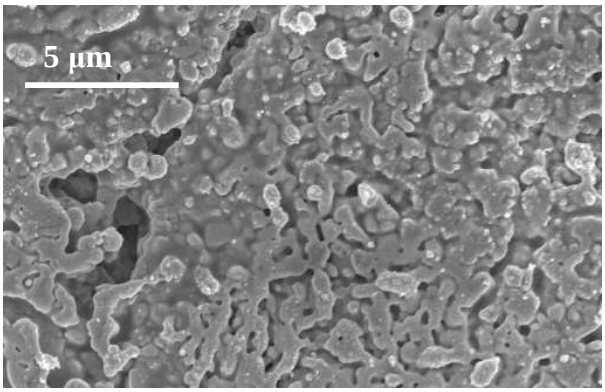

Fig.2 FEGSEM image of the laser-transferred 20μm film; surface adjacent to sapphire

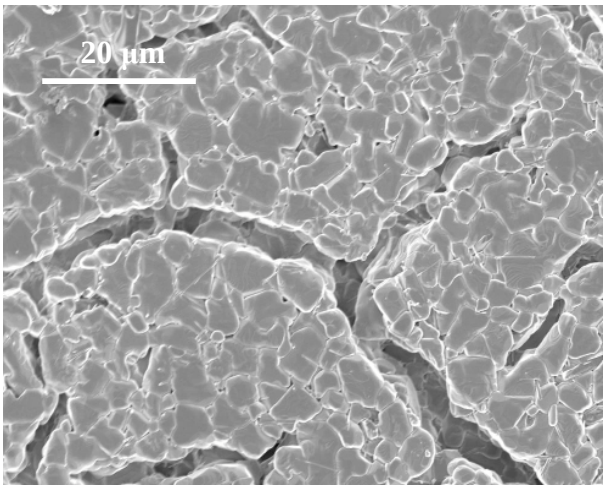

Fig.3 FEGSEM image of the top surface of original 20μm film on sapphire, sintered at 950 ºC.

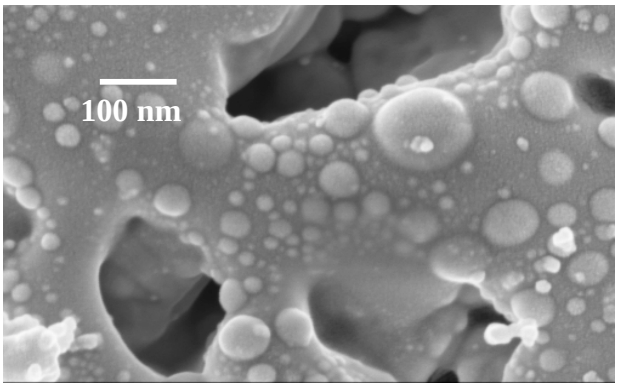

Fig.4 High resolution FEGSEM of the lifted off 20μm film; surface adjacent to sapphire

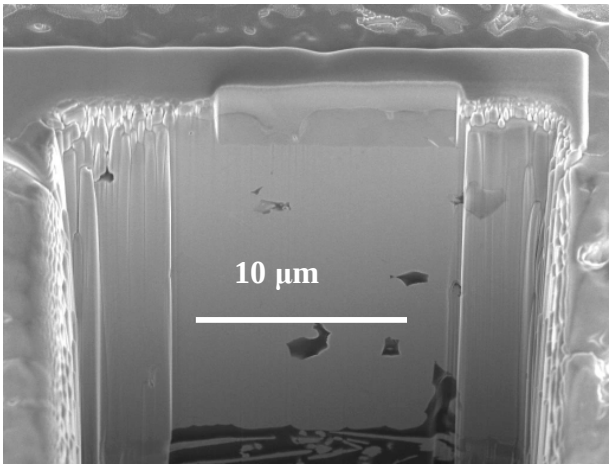

Fig.5 Cross-section revealed by FIB etching

The laser-affected zone was investigated further using FIBSEM. The technique requires that a trench is first removed (at high current density), each wall of the trench offers an opportunity for further etching (at low current densities) to expose cross-sectional features in nanoscale increments by etching at progressively lower current densities.

The first features to emerge were pores within the interior of the film, which were up to 2-3 μm in diameter Fig 5. These pores are not unexpected for this type of film made by a hybrid particle-sol-gel route.

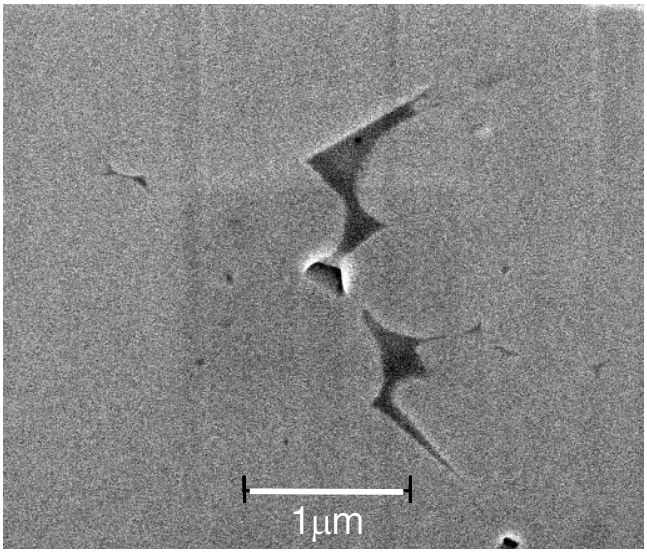

Fig.6 Higher magnification view of section

There was also some evidence of grain boundary features immediately adjacent to the pores, Fig 6. However there was no structural evidence using FIBSEM under these conditions to indicate the extent of laser-affected zone. From the appearance in SEM plan view Fig 2, a distinction in nano and microstructural features would be expected at increasing depth from the interface originally in contact with the sapphire. However this was not clearly visible, although there was some evidence of a band of different contrast, Fig 7 but at this time its origin is uncertain.

Although beam damage, and re-deposition of evaporated material is reduced by moving to pA currents, it is unclear whether structural information on microstructure in these fine-grained films, and the necessary topographical information can be resolved in sufficient detail from in-situ FIBSEM analysis. In future work PZT film lamellae will be transferred by nano-manipulation to TEM grids for conventional ion milling and TEM analysis.

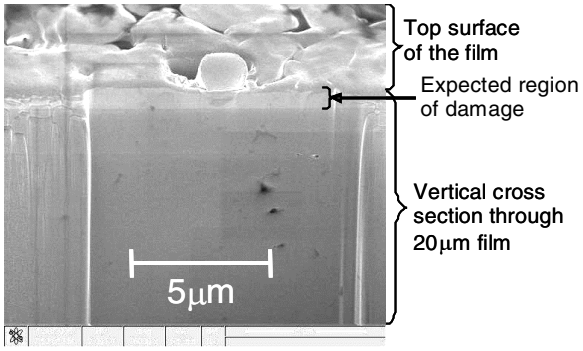

Fig.7 SEM image of FIB-etched trench PZT 20μm film (950 ºC) after laser-release.

By using a lower laser fluence, ~400 mJ/cm^2 compared to the ≥ 600 mJ/cm^2 used to transfer the thick PZT film described above, and by optimising the translational control of the beam, it has been possible to transfer films of only 1 μm in thickness. SEM of the laser-released surface showed minimal damage, Fig 8. Moreover polarisation-electric field hysteresis loops have been obtained for a film crystallised at 650 ºC, Fig 9, which confirm that any non-ferroelectric interfacial layer had little effect. In previous work electrical measurements for a range of films of different thickness, to which a blocking layer model of two capacitors in series was applied, gave results consistent with an interfacial layer thickness of ≤ 100nm.

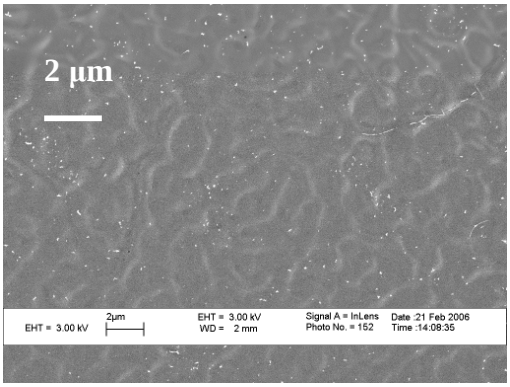

Fig.8 SEM of 1 μm PZT film after laser release using ~ 400 mJ/cm^2 laser beam

4 CONCLUSIONS

Thick film PZT and thin film PZT samples have been separated by pulsed laser treatment from a sapphire high-temperature fabrication substrate and transferred to a platinised silicon substrate. SEM analysis of the laser-affected region revealed a porous microstructure with no evidence of grain structure. This is consistent with localised melting at the PZT-sapphire interface during laser-treatment. The extent of laser-damage was reduced considerably by reducing the laser fluence. This permitted thin films, of thickness 1 μm, to be transferred. These exhibited P-E hysteresis loops typical of a good quality PZT thin film, confirming that minimal damage had occurred during release. Applying FIBSEM for abstracting lamellae suitable for TEM cross-sectional analysis is in progress and results will be reported .

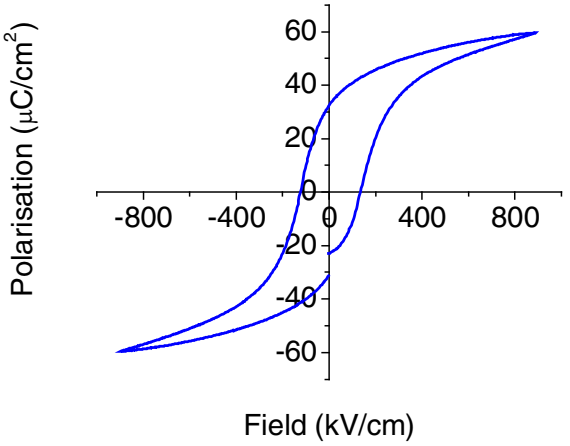

Fig.9 P-E loop of 1 μm PZT film transferred from sapphire (heat-treated at 650 ºC) onto platinised silicon substrate

5 REFERENCES

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