Preparation of PZT nanodots on Nano-Templated Substrates

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ABSTRACT

There is considerable interest in creation of nanoscale capacitor arrays. For example, in FeRAM technology, which has great potential, significant capacitor cell size reduction and transition to 3D structures, can be achieved within existing CMOS procedures. However, cheap and simple methods to create nanoscale capacitors would be attractive. Lead zirconate titanate (PZT) films were deposited on alumina substrates using a solution deposition method involving dip-coating. The method was based on the pre-calcination of oxides, which were then dissolved in nitric acid. XRD θ–2θ scans showed that deposition improved with higher concentrations of PZT solution. AFM roughness analysis of the as-deposited films gave an r.m.s. roughness of approximately 39 nm, which was found to improve to approximately 6 nm on post-annealing. TEM imaging and EDX elemental analysis confirmed the presence of PZT on the deposited samples. Having found the optimum conditions for solution deposition, nano-dots were prepared by deposition on porous anodic alumina substrate templates. Further TEM imaging and EDX elemental analysis showed the presence of the PZT nano-dots aligned with the pores.

Keywords: ferroelectric, nanodot, porous-alumina, substrates, template.

1 INTRODUCTION

The smooth operation and growth of modern economies is increasingly dependant on memory and data storage. Consequently, technological advancement in this area is of great significance [1], and a variety of possible future memory technologies are now being driven forward [2]. Amongst these are systems based on ferroelectric thin films (FeRAM), where the difference between two polarisation states allows binary data storage [3]. FeRAM is attractive: read and write times are comparable to conventional DRAM and much faster than Flash; significantly, storage is non-volatile and write-cycle endurance (fatigue resistance) has been improved to the extent that now it is orders of magnitude better than Flash [2]. However, FeRAM is a still-maturing technology. Despite 2002 being seen as "a coming of age" [4], it will need further development if it is to supplant the mainstream established Si-based systems. In particular the following issues remain: materials integration (perovskites integrated with CMOS); storage densities (capacitor cell/footprint sizes must be reduced and moved into 3D configurations, by 2007); and, in common with all microelectronics, reduction of production costs is a major motivation [2].

To address this latter challenge it may well be necessary to explore alternative process and fabrication methodologies. There has already been preliminary work in this area [5] by examining the self-assembly of top electrode material on a continuous film of ferroelectric (see also [6]), but other approaches included creation of islands of ferroelectric material on a continuous lower layer [7]. The field is, however, only in infancy.

A particularly promising route that may be explored is that due to the work of Masuda et al. [8] who developed a two-stage anodisation process that produces an alumina film with a regular distribution of pores on an aluminum substrate. Due to their spatially periodic index of refraction, these porous alumina structures display a stop band in their electromagnetic transmission properties and therefore have been investigated as photonic crystals [9]. However, they also offer a nanoscale template that could be used with a range of nanotechnology applications such as magnetic storage, solar cells, carbon nanotubes, catalysts and metal nanowires.

We have already successfully prepared porous alumina substrate templates [10]. We have also extended the procedure to create arrays of nano-magnetic Co elements [11].

A particular challenge is to find a process that can prepare ferroelectric media, for example lead-zirconate-titanate (PZT), which can be incorporated easily into a self-assembly methodology. Conventional vapour deposition techniques such as sputtering or pulsed laser [12] are perhaps not so promising. A solution deposition technique may be more appropriate.

The most frequently used solution preparation methods for ferroelectric thin films are; Sol-gel processes, using alkoxide compounds as starting precursors, hybrid processes, which use chelating agents such as acetic acid and metalorganic decomposition (MOD), which uses carboxylate compounds [13]. An alternative solution-deposition method has been developed recently, based on the pre-calcination of oxides or carbonates to be used as the precursor material for the solution. This method is based on the fact that not all precursor oxides (e.g. PbO, TiO_2, ZrO_2, Bi_2O_3) are soluble in acid media, but a reacted oxide may be soluble [14]. The method has been used to prepare

PZT and bismuth titanate (BIT) thin films with good quality, homogeneity and the desired stoichiometry [14].

In this paper we describe preliminary work in the creation of a basic element of a self-assembled capacitor structure by combining a porous alumina substrate template process with solution-deposition. The porous alumina films were coated with the ferroelectric PZT using a solution deposition method. X-ray diffraction was used to determine the crystallographic orientation of the PZT films. Transmission electron microscopy was used to investigate the formation of ferroelectric films over the alumina pores.

Potential advantages of this technique are that the resulting capacitor structures could be electrically isolated from each other, and that their architectures may well made to be reminiscent of those familiar to industry.

2 EXPERIMENTAL METHODS

2.1 Solution deposition of lead zirconate titanate

In the present work, PZT powder was prepared from oxides and dissolved in nitric acid (HNO_3) to produce a PZT solution for dip-coating substrates.

The preparation of the PZT solution for deposition was carried out as follows. Lead oxide, titanium oxide and zirconium oxide were mixed at a ratio of Zr/Ti = 53/47. This mixed powder was then calcined in an electric furnace at 850^{o}C for 3.5 hours in air ambient. The result was approximately 20 g of $PbZr_{0.53}Ti_{0.47}O_x$ powder.

Then 2g of this powder was dissolved in 60mL of diluted acid solution (10% HNO_3, 90% distilled water) for 1 hour at 80^{o}C. The solution was allowed to cool to room temperature and then further diluted with distilled water to complete a PZT stock solution with concentration 12.5gL^{-1}.

This stock solution was then diluted further to produce solutions with concentrations of 6.25gL^{-1} and 3.125gL^{-1}; this would allow investigation of how the film properties varied with the concentration of solution.

The films were initially deposited on r-plane Al_2O_3 substrates to determine the optimum conditions for deposition and anneal. The substrate was heated on a hotplate in air to approximately 200^{o}C for 15 minutes. It was then immediately dipped in the solution and removed.

The films were also deposited onto porous alumina templates prepared by anodisation of thin film aluminium as described elsewhere [15]

2.2 Characterization

The films were characterized by a range of techniques; including X-ray diffraction (XRD), atomic force microscopy (AFM), transmission electron microscopy (TEM), and energy dispersive X-ray analysis (EDX). XRD θ-2θ scans were performed on a Bruker-AXS D8, the surface roughness and topography was determined using a Digital Instruments D3000 AFM in tapping mode. The microstructure was revealed by TEM on a FEI Tecnai F20, scanning mode (STEM) was also used. The TEM cross-sectional samples were prepared on a FEI FIB200TEM focused ion beam microscope.

3 RESULTS

3.1 Dip coating of PZT on alumina substrates

Various anneal protocols were investigated; including immediate post-deposition high temperature annealing or being allowed to dry in air for approximately 3 hours before the annealing. An as-deposited film showed presence randomly oriented PZT in (100), (110) and (111) orientations (Fig. 1). The (110) and (111) peaks are not as clearly visible in scans of films where the solution was cold during dip-coating.

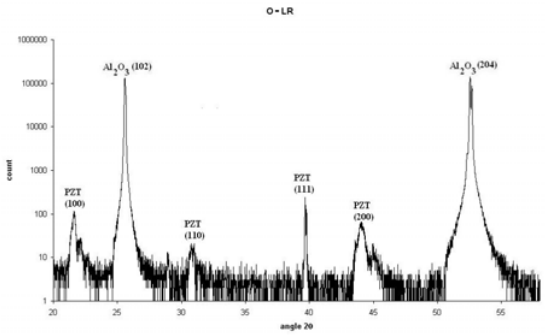

Figure 1: A θ-2θ scan of an as-deposited PZT film.

The various PZT XRD reflections were lost if the substrate and the as-dipped film were immediately transferred on to a hotplate until the coating dried. This suggesting that the immediate anneal on the hotplate after dip-coating does not encourage the growth of PZT. Also it was observed that as the concentration of the PZT solution decreased, the various PZT XRD peak intensities decrease, until a film made with a concentration 3.125gL^{-1} showed no PZT fingerprints..

A series of high temperature anneals following the room temperature drying indicated that optimum results were obtained at around 500^{o}C for 2.5 hours in air. A XRD trace of a film prepared with a 12.5gL^{-1} solution is illustrated in Fig. 2.

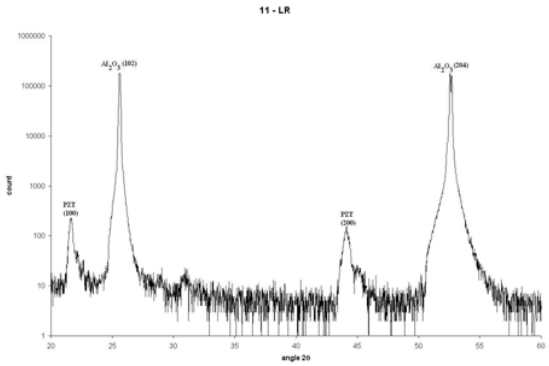

Figure 2: A θ-2θ scan of a 12.45gL^{-1} solution PZT film after the 500^{o}C anneal.

AFM roughness analysis on films prior to annealing showed a very coarse surface topography, with r.m.s. roughness of order 39nm. This was improved by introduction of the high temperature anneal. In Fig. 3 an image and data are presented illustrating an r.m.s. roughness of 6nm. This film was prepared from a 12.5gL^{-1} solution and subject to the 500^{o}C anneal described above. The AFM images show the presence of large crystallites on the film surface. It is not clear if the thin PZT film extends, uniformly, over the whole of the substrate surface, or if the peaks on the XRD scans are due only to isolated, oriented crystals.

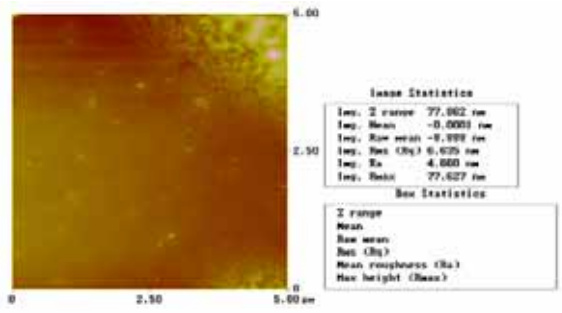

Figure 3: AFM topography of the 12.45gL^{-1} solution PZT film after the 500^{o}C anneal.

A film annealed for 30 minutes on a hotplate was imaged by TEM and no PZT coating was observed at any point on the sample. A STEM image is shown in Fig 4. EDX analysis at a point between the substrate and the protective gold layer also failed to produce evidence of a PZT film. This again would suggest that such film is certainly not uniform, and may exist only as isolated crystals on the substrate surface as suggested by AFM.

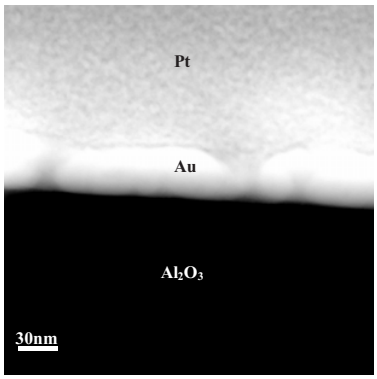

Figure 4: STEM image showing absence of PZT at interface with Al_2O_3 substrate. The Au and Pt layers are to protect the sample and provide contrast.

3.2 Dip-coating on porous alumina

Having established the behavior of dip-coating PZT on Al_2O_3 substrates the process was then transferred to the coating of the porous anodic alumina (Section 2.2). Conditions used included the 12.5gL^{-1} PZT solution in combination with high temperature annealing around 500^{o}C.

In Fig. 5 the XRD θ-2θ scan of a PZT film on a porous anodic alumina substrate is shown. It confirms the presence of PZT, with (100), (110) and (111) orientations visible.

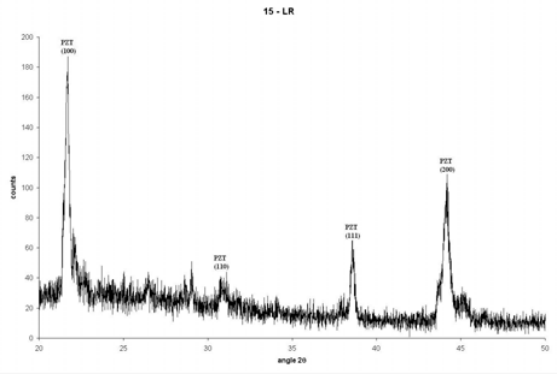

Figure 5: A θ-2θ scan of the 12.5gL^{-1} solution PZT film on porous anodic alumina substrate following anneal at 500^{o}C.

Cross-sectional TEM imaging of the sample reveals some interesting features. In Fig 6. the pores in the alumina may be clearly seen, with PZT nano-dots visible just below the darker gold layer. At lower magnification we see a similar distribution of PZT adjacent to the nano-pores. An EDX spectrum was obtained at a point in one of the pores and small peaks are visible for Zr and Ti, indicating the presence of PZT nano-dots.

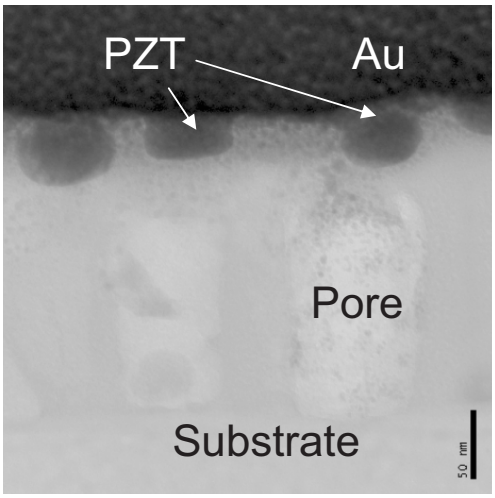

Figure 6: A cross-sectional TEM image showing the presence of PZT nano-dots aligning with the pores on the porous anodic alumina substrate.

4 DISCUSSION

A solution deposition method was implemented for the preparation of $PbZr_{0.3}Ti_{0.7}O_3$ thin films. This approach was based on the pre-calcination of oxides which were then dissolved in nitric acid. Using XRD, it was observed that higher concentrations of solution resulted in the best deposited films and that optimum anneal temperature was 500^{o}C. AFM roughness analysis showed that the surface roughness was greatly improved by annealing the films. TEM imaging and EDX analysis confirmed the presence of PZT on the deposited samples.

The PZT was solution deposited on anodic porous alumina substrates. TEM imaging and EDX analysis were used to examine the formation of the film over the porous structure, and PZT nano-dots were confirmed to be present.

Future, and ongoing, work involves deposition of metals for plugs, and both lower and upper electrodes to provide electrical contacts. The hexagonal symmetry of the anodic pores makes registry an interesting avenue to explore.

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