Hydrothermal deposition of heteroepitaxial lead zirconate titanate nanostructures and thin films

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Abstract

This paper describes the hydrothermal growth of heteroepitaxial PZT nanostructures on single-crystal, $SrTiO_3$ substrates. Short processing times of 30 min led to the nucleation and growth of sporadic, cubic nanoscale PZT islands on the surface of the substrate. In some cases, individual islands coalesced in one direction to form microwires over 1 mm in length. Imperfections in the surface of the substrate introduced during polishing were thought to be responsible for the preferential nucleation. Longer reaction times up to 24 h resulted in the formation of heteroepitaxial PZT films, up to a micron in thickness, that were highly (1 0 0)-oriented. Piezoresponse force microscopy conducted on isolated islands and microwires, grown on conductive Nb:$SrTiO_3$ substrates, gave an indication that the structures were piezoelectric.
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1. Introduction

The production of highly defined and well-controlled metal and oxide nanostructures is an area of research that has been gaining in interest. With the movement from microstructured devices, with associated applications, towards nanostructured devices, at first, in 2D and now increasingly in 3D, there has been an intense research focus on techniques to accommodate the demand for higher resolution tolerances. A variety of techniques and tools have been developed as possible solutions to the generation of nanostructured templates. Among these there has been growing interest in the use of ferroelectric thin films, both in nanostructured devices and as templates for the development of nanostructures, over the past ten, or so, years. Amongst the ferroelectric materials, the use of the solid solution lead–zirconate–titanate (PZT) has become widespread due to its high d_{33} and electromechanical coupling, as well as the ability to control the structure of PZT at small length scales.

The types of devices under consideration range from ferroelectric RAM (FeRAM)[1] to sensors and actuators that utilise either the direct or converse piezoelectric effect.[2] Many techniques have been highlighted as possibilities for the generation of nanostructures of ferroelectric materials. These have varied from the synthesis of thin film materials using sol–gel,[3] pulsed laser deposition (PLD),[4] and photochemical growth on patterned substrates[5] where features such as the crystallography,[6] surface structure and morphology[7,8] of the films are all shown to have an impact on the photochemical behaviour. Such complex interactions with the surface of the ferroelectric material and the electrolyte in which electrochemistry is occurring makes for some fundamental difficulties when using the pattern on the surface of the ferroelectric for the production of nanostructures. These nanostructures have been generated by domain patterning or machining parts of ferroelectric bulk materials. The substrate materials for these applications have traditionally been single crystals or grown via sol–gel synthesis.

An alternative technique for the deposition of ferroelectric thin films on substrates is that of hydrothermal synthesis. This is a technique that uses a combination of high pressures at moderate temperatures to force the equilibrium of a combination of reactants towards the desired product. Initially there

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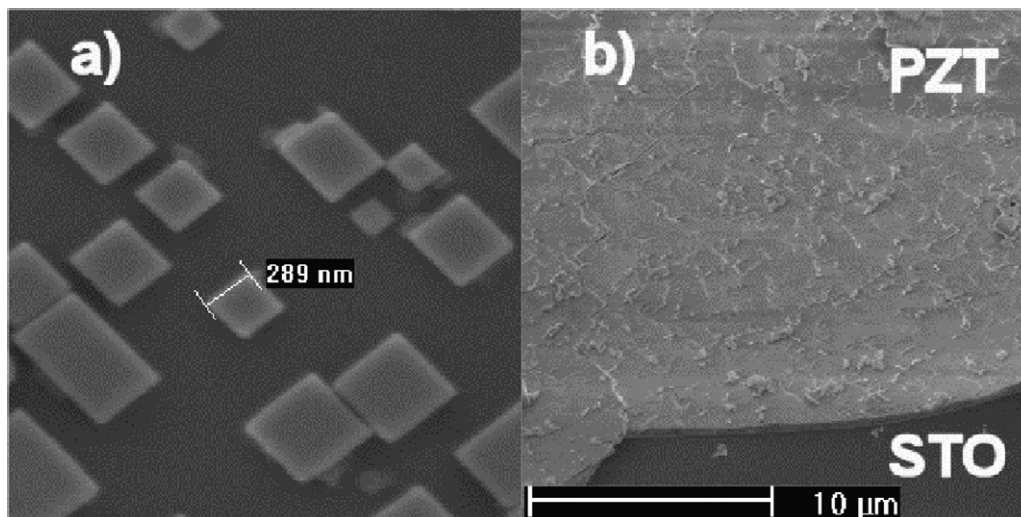   *E-mail address:* s.c.dunn@cranfield.ac.uk (S. Dunn).

Fig. 1. SEM images showing hydrothermal PZT (a) island and (b) film growth on a single-crystal SrTiO$_3$ substrate.

were a number of problems associated with the production of homogeneous nanostructured films of ferroelectric materials, for example.[9] However recent developments have largely solved these problems.[10,11] There are a number of advantages associated with the use of hydrothermal synthesis of PZT over other techniques for producing heteroepitaxial films, such as PLD or sol–gel. One of which is that curved surfaces can be coated.[12–14] It is also possible, due to the lower processing temperatures, to use a wider variety of substrates that would otherwise undergo phase transitions or soften at higher temperatures.[15] Additionally the lower heat of reaction reduces the energy required for the process.

As highlighted above, initial studies showed the difficulty in producing high quality, homogenous PZT films due to segregation and a variation in the reaction rates of the PZT precursors. It is known that the reaction rates of zirconium and titanium compounds differ, as do their diffusion coefficients. It is, however, possible to show that there is a spatial variation in piezoelectric properties of a deposited material with PFM.[16]
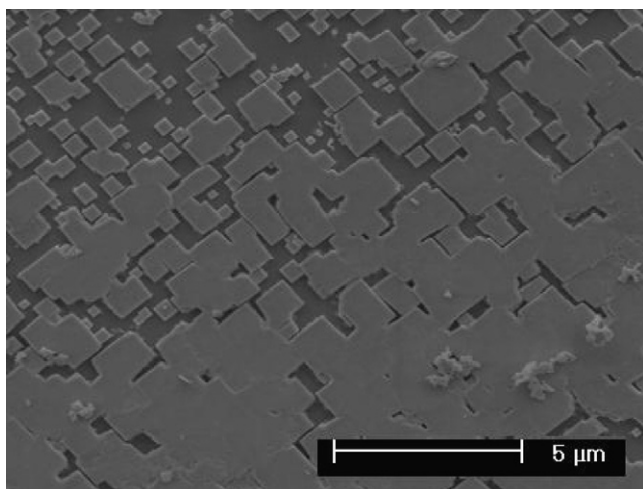

Fig. 2. SEM image showing the coalescence of PZT nanoislands leading to the formation of a film.

This was investigated in a recent paper that showed PZT stoichiometries close to the morphotropic phase boundary have a propensity to crystallise under hydrothermal conditions.[17] During the development of the hydrothermal technique there existed a variety of techniques for the synthesis of PZT with initial studies producing a mixture of lead titanate and lead zirconate. Choi et al. showed that a simple 'one-stage' process could be used[18] which led to the development of processes for the hydrothermal synthesis of PZT films and increasingly as nanoparticles. There are a number of advantages to the hydrothermal technique, prime of these are that it is not necessary to use excess heat and so delicate substrates can be used.

A variety of substrates have been investigated for the growth of ferroelectric nanostructured films. The main substrates of interest have been those based on single-crystal oxides, such as Nb-doped SrTiO$_3$, as when incorporated into a device such substrates produce a film with a good fatigue lifetime. Such substrates are both conducting and match well to the crystal lattice of PZT so tend to produce a heteroepitaxial film. Ahn et al. showed, in 2005, that it was possible to produce epitaxial nanoislands of PZT on Nb–SrTiO$_3$.[19] The growth of nanoislands on the substrate was also observed for PbTiO$_3$ by Szafraniak and Alexe,[20] and so this process of the nucleation of discrete nanoislands followed by coalescence to form a complete surface layer appears to be a common one.

In this work we show that there are influences governing the growth of a ferroelectric film that range from the ratios of precursor materials used to, most interestingly, an opportunity to use the initial growth of nanoislands for the templated growth of ferroelectric nanostructures.

2. Methodology

To accommodate the high pressures involved in hydrothermal synthesis a commercially available (Parr Instrument Co.), oven heated, acid digestion bomb was used (Model 4744). The device consists of a 45 ml PFTE liner, into which the precursor mate-
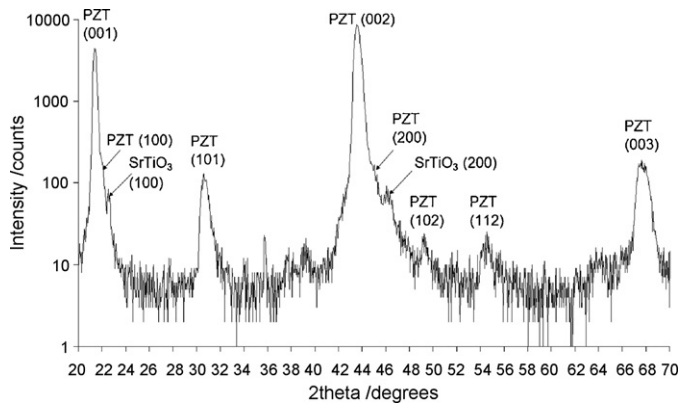
Fig. 3. XRD data for PZT grown on a (1 0 0) SrTiO$_3$ single-crystal substrate via the hydrothermal method (indexed peaks correspond to the accepted values for 52:48 PZT, PDF card no. 33-0784 and SrTiO$_3$, PDF card no. 35-0734).

rials are inserted, surrounded by a screw top steel casing. The absolute maximum rated temperature of the bomb is 250 °C, although when used at temperatures above 200 °C the Teflon liner degrades rapidly. This is because Teflon has a tendency to creep at high pressures making it hard to attain a tight seal. For this reason experiments were restricted to temperatures at or below 200 °C.

A thermostatically controlled laboratory oven (Memmert) was used to heat the bomb. The oven was pre-heated to the reaction temperature before the start of each experiment. The temperature of the bomb was taken at the surface of the steel casing using a K-type thermocouple and meter accurate to ±0.05 °C. Timing started when the meter recorded the desired reaction temperature. At the end of each experiment the oven was switched off and the door left open to increase the cooling rate of the bomb.

The basic hydrothermal technique used in this work is an adapted procedure first proposed by Deng et al. for the synthesis of freestanding PZT crystals.[21] It is a relatively simple one-step technique that utilises the following precursors in powdered form:

- lead nitrate, Pb(NO$_3$)$_2$;
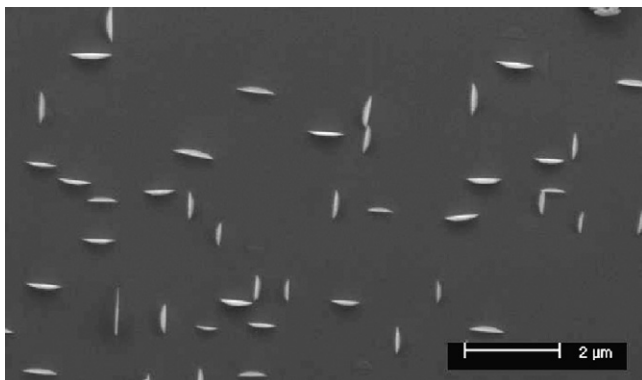- zirconyl oxychloride, ZrOCl$_2$·8H$_2$O;
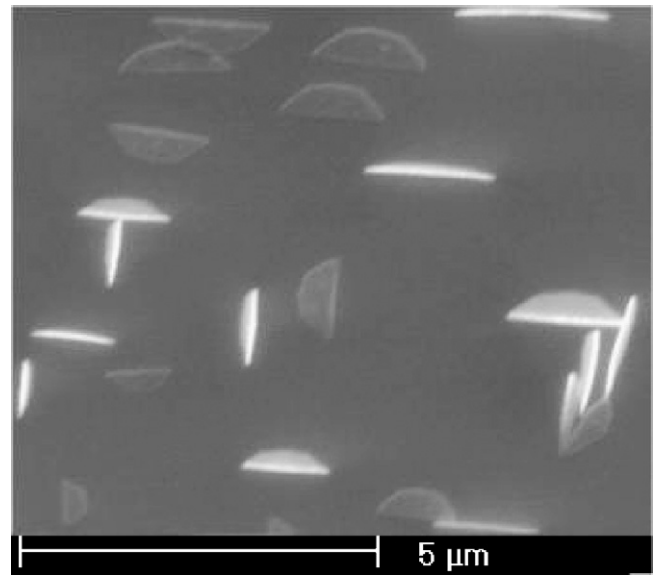- titanium dioxide (anatase), TiO$_2$.

Fig. 5. SEM image showing the semi-circular morphology of the platelets.

To start with, an as received, single-side polished (1 0 0) SrTiO$_3$ or Nb:SrTiO$_3$ crystal (MTI Corporation, USA) was placed, polished side up, on the bottom of the Teflon liner. Stoichiometric quantities of the three powder precursors were then added, to give a desired 52:48 Zr/Ti ratio. In some cases the effect of adding a 100% excess of the Pb(NO$_3$)$_2$ precursor, was tested. Next, 25 ml of deionised water were added and the mixture stirred vigorously. Finally, potassium hydroxide flakes were added slowly, with continuous stirring, to give an initial mineraliser concentration of 5 mol/l. All chemicals were analytical grade and obtained from Sigma–Aldrich, UK (TiO$_2$ and KOH) or Fisher Scientific, UK (ZrOCl$_2$·8H$_2$O and Pb(NO$_3$)$_2$). Processing times were varied from 0.5 to 24 h while the processing temperature was fixed at 160 °C. After the substrates were removed from the bomb they were gently rinsed by dipping in deionised water.

A Siemens D5005 diffractometer was used for all the XRD experiments. The x-ray tube emitted Cu Kα ($\lambda = 1.5406$ Å) radiation at 40 kV and 30 mA. In general, θ–2θ scans were conducted between 20° and 70° in increments of 0.04° with a dwell time of 1 s per increment. All measurements were made at room

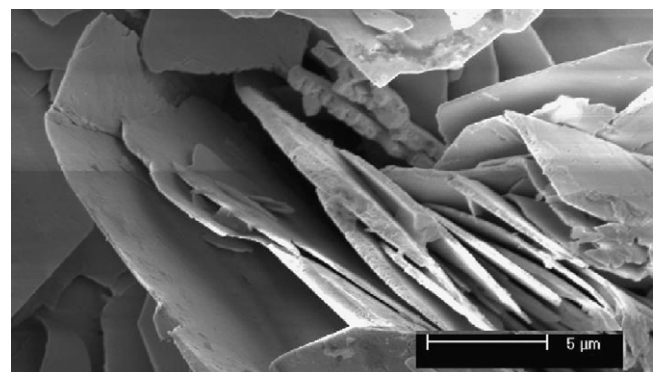Fig. 4. SEM image of platelets oriented to the crystallographic axes of the substrate.

Fig. 6. SEM image of PbO platelets produced after the reaction between Pb(NO$_3$)$_2$ and KOH.
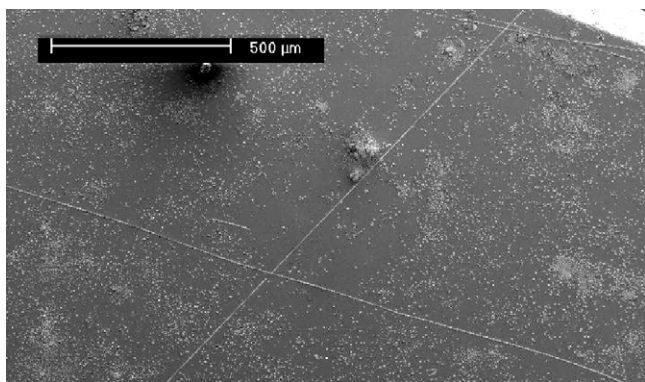
Fig. 7. SEM image showing the extent of PZT coverage on a Nb:SrTiO$_3$ substrate after 30 min processing at 160 °C.

Fig. 9. SEM image showing the misalignment between the epitaxial PZT islands and the axial direction of the microwire. Scratches in the substrate exert an influence over the location of islands whilst the crystallographic orientation of the substrate affects their growth.

temperature. Phase identification involved matching peaks from a given scan with the accepted values for compounds found in the Powder Diffraction File (PDF-2) database, produced by the International Centre for Diffraction Data (ICDD). The morphology and size distribution of the deposited structures were analysed using an FEI Sirion S-FEG SEM. Piezoresponse images were acquired from a Veeco 3000 instrument by applying an AC voltage with a magnitude of 1.5 V and frequency of 62 kHz between a conductive PtIr$_5$-coated Si tip and the bottom electrode of the sample. The tip had a nominal resonant frequency and spring constant of 14 kHz and 0.2 N/m, respectively.

3. Results and discussion

The first experiment reported involved observing the growth mechanism of PZT on undoped SrTiO$_3$ substrates under hydrothermal conditions. Long processing times, on the order of 24 h, were used together with a 100% Pb-precursor excess. The PZT coverage across the surface of the substrate, after 24 h at 160 °C, was inhomogeneous. Some areas remained relatively bare, but for the occasional well faceted, rectangular-shaped nanoisland, see Fig. 1(a). Other parts were covered in a dense film, up to a micron in thickness as shown in Fig. 1(b). The films appeared to grow in stages that began with the coalescence of nanoislands, Fig. 2. After the coalescence stage, film thickness increased through the nucleation and growth of fresh layers on
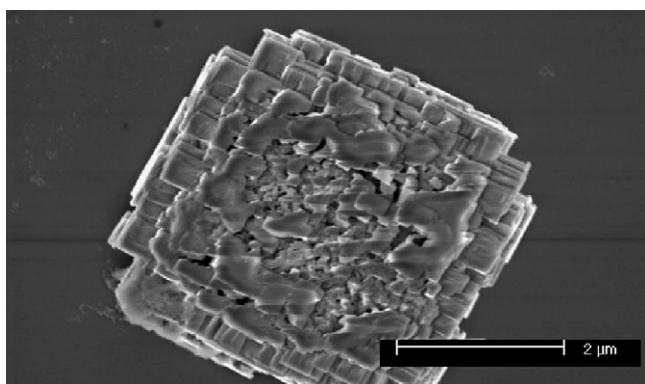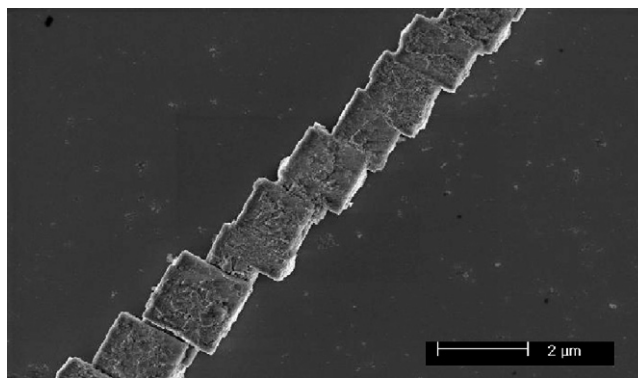
top of the original film. In this study we are investigating the effect of growing PZT direct from the precursor material, but a similar growth mechanism[20] has been reported for PbTiO$_3$ films on SrTiO$_3$ substrates. The similarity in the growth mechanisms for materials with differing precursors shows that the growth of the cubic platelets is not dependent on diffusion of the titania or zirconia precursor material. It seems likely that the growth of cubic islands is a feature of the crystallography of the material being generated. No pattern was seen in the coverage of the PZT in the bottom of the reaction vessel when comparisons were made between experimental runs. There are a number of possible explanations for the inhomogeneous coverage of the film. Variations in concentration of the precursor material, density of nucleation sites and temperature fluctuations could all account for the distribution of the product. In our case, the inhomogeneous film coverage was most probably due to local variations in all of the above at the bottom of the hydrothermal bomb during reaction. However, as we shall later show, the concentration of surface defects on the substrate has a very large influence on the location at which PZT islands are deposited.

The pseudo-epitaxial nature of the nanoislands and thin films was confirmed through XRD analysis. Strong preferential orientation in the [0 0 1] direction was a clear indication that the (1 0 0) SrTiO$_3$ substrate had influenced PZT growth, Fig. 3. Peaks corresponding to three alternative PZT orientations were also visible, but their intensities were over an order of magnitude

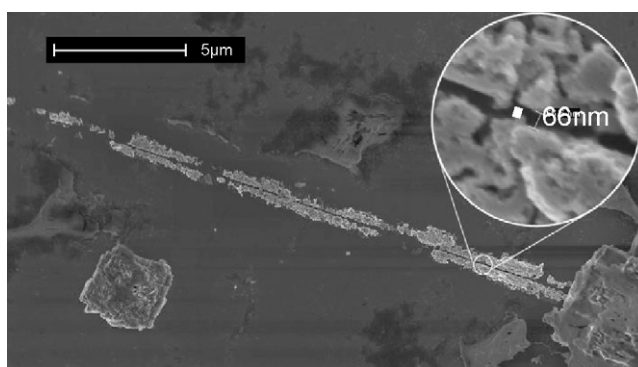Fig. 8. SEM image of a PZT island grown on Nb:SrTiO$_3$ without a Pb-excess.

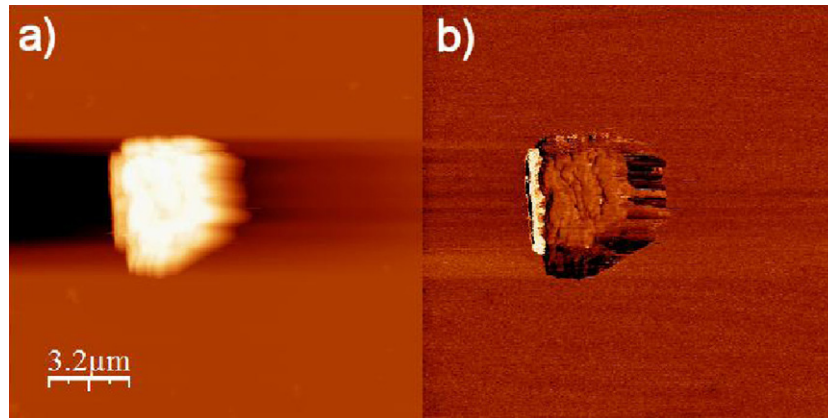Fig. 10. SEM showing the remnants of a microwire after mechanical removal.

Fig. 11. AFM image showing the (a) topography and associated (b) out-of-plane piezoresponse of a PZT island.

less than that of the preferred orientation. These reflections can be attributed to stray PZT particles that had formed in solution before coming to rest arbitrarily on the surface of the substrate. The positions of the peaks in the XRD data for the PZT film matched particularly well to the accepted values for the 52:48 composition of PZT (PDF card no. 33-0784). As the *a*-axis lattice parameters of PZT and SrTiO$_3$ are different there will be a degree of epitaxial strain within the film, which can be expressed as:

$$\frac{\Delta a}{a} = \frac{a_s - a_f}{a_s}$$

where a_s and a_f are the *a*-axis lattice parameters for the substrate and film, respectively. The stress within a given film is compressive for $\Delta a/a < 0$ and tensile for $\Delta a/a > 0$. Inserting the accepted values for 52:48 PZT and SrTiO$_3$ into the equation gives a lattice mismatch equal to -2.2%. This figure is sufficient to account for the island growth mode observed during the initial stages of hydrothermal PZT film formation.

An unusual crystal morphology was observed in one small area of a (1 0 0) SrTiO$_3$ substrate that was processed for 24 h at 160 °C. Platelets were found that grew perpendicular to the substrate surface and were orientated parallel to the SrTiO$_3$ crystallographic axes, Fig. 4. They possessed a semi-circular morphology and grew with their curved surfaces in contact with the substrate, see Fig. 5. Quantitative compositional analysis of the platelets via EDAX proved difficult due to a combination of the small interaction volume and an abundance of contaminant species across the surface of the substrate following the hydrothermal reaction. However, the data suggested a large quantity of Pb was present indicating the possibility that the platelets were in fact composed of lead oxide. Prior hydrothermal tests that involved reacting the Pb(NO$_3$)$_2$ precursor alone with KOH produced platelet particles of PbO with a similar morphology, Fig. 6. If the structures found on the SrTiO$_3$ substrate are indeed composed of PbO their location is puzzling. They were found in a region that separated to two large areas of well-crystallised PZT film. What's more, no sign of island growth was present in the vicinity, which would appear to rule out the possibility that the platelets act as a template to PZT island growth. Instead, it is more likely that the area in question was exposed to a particularly high concentration of Pb ions leading to the nucleation and growth of PbO, that has formed as a result of the reaction of the precursor materials and the mineraliser, on the substrate surface. This finding emphasizes the significance of concentration of precursors across the reaction volume. Furthermore, the well-crystallised PZT film found close to the platelets is con-
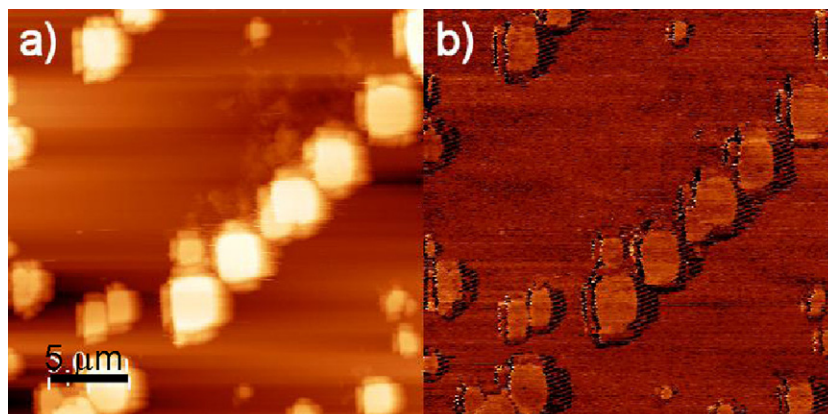

Fig. 12. AFM image showing the (a) topography and associated (b) out-of-plane piezoresponse of a collection of PZT islands and amorphous material. Note the apparent lack of piezoresponse from the amorphous material.

sistent with a large excess of Pb ions. It is possible that the platelets of PbO formed after the zirconia and titania precursors had been used in the production of PZT, remember that there is a 100% excess of Pb precursors. The growth of half-moon platelets of silver has recently been described by Sun and Weiderrecht.[22] The differences in the orientation of the half-moon are interesting and are related to the growth mechanism of the platelet. In the case of the PbO there is a distinct nucleation site and then this allows growth of the PbO via reaction of precursors. In the case of the silver the reverse geometry is seen and there is an equal probability of the electrochemical reaction occurring across the length of the silver face.

After establishing the mechanism involved in the growth of hydrothermal PZT on (1 0 0) SrTiO$_3$, further investigations where performed to determine if it was possible to control the size of the nanoislands by reducing the reaction times. Conductive Nb-doped (1 0 0) SrTiO$_3$ substrates were used in place of pure (1 0 0) SrTiO$_3$ so that the electrical properties of the resultant nanoislands could be assessed.

Fig. 7 shows a large area of a Nb:SrTiO$_3$ substrate processed for 30 min at 160 °C without any Pb excess. No continuous film coverage was visible; instead the PZT structures consisted of isolated and partially coalesced cubic islands as well as lines of interconnected islands that formed unbroken "microwires", sometimes over a millimetre in length. The rough morphology of the islands, Fig. 8, was similar to that witnessed during the hydrothermal synthesis of freestanding PZT cubes without a Pb-excess.[17] Furthermore, in contrast to the Pb-excess experiments, the islands appeared to display a layered structure. The size of the islands did not scale with reaction time, which suggests growth rates for PZT crystals on the SrTiO$_3$ substrates and in solution (freestanding) were comparable.[17]

The origin of the PZT microwires across the substrate is unclear, however certain attributes of the lines favour one explanation in particular. Firstly, their length, sometimes in excess of 1 mm, would appear to rule out crystallographic defects such as step edges, which persist over much shorter lengthscales in SrTiO$_3$ substrates, even after etching.[23] Secondly, the individual islands, of which the microwires are composed, aligned themselves to the crystallographic directions of the substrate surface, even if the microwire itself followed a different path (Fig. 9). These observations point to the existence of preferred nucleation sites on the surface of the substrate, which are independent of the underlying crystal structure. Single-crystal substrates are subjected to a chemical–mechanical polishing process during their fabrication that introduces scratches into the surface. Particles from the polishing paste (often diamond-based) can become embedded in these scratches and later act as potential nucleation sites during the hydrothermal treatment. After nucleation, the PZT islands grow heteroepitaxially and coalesce with neighbouring crystals to form a continuous wire. Fig. 10 shows the remnants of a PZT microwire that detached from the substrate through mechanical contact. The outline of the scratch can clearly be seen, bounded by the remaining crystalline material.

The limited adhesion of the microwires to the SrTiO$_3$ surface opens up the exciting possibility of using intentionally scratched
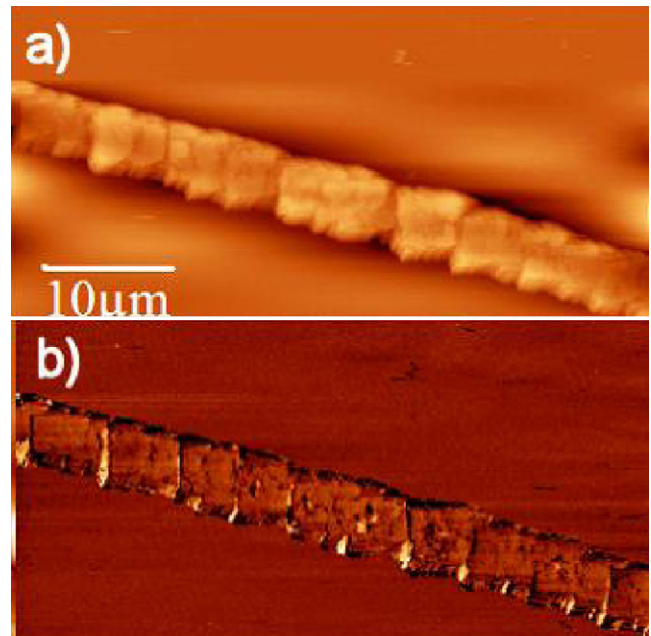

Fig. 13. AFM image showing the (a) topography and associated (b) out-of-plane piezoresponse of a PZT microwire.

substrates as a templated growth mechanism for generating ferroelectric structures via the hydrothermal method.

PFM was used to produce piezoresponse images of the structures found on the surface of the Nb:SrTiO$_3$ substrates after a 30 min hydrothermal treatment without Pb-excess. Fig. 11 shows the topography and associated out-of-plane piezoresponse of an isolated, cubic PZT island, scanned using AFM. No domain patterns are seen; instead the cube displays a uniform, weak piezoresponse as evidenced by the low contrast. Greater piezoresponse is detected around the edges of the cube; however this is most likely due to topographic cross-talk of the type encountered by Tiruvalem et al. during their PFM analysis of relaxor nanocrystals.[24] They found an apparent dipolar ordering of the piezoresponse along the cantilever axis, which was attributed to the interaction between the tip and the sloping sides of the nanocrystals. The net effect being that positive slopes produced a strong in-phase response while negative slopes gave an out-of-phase signal. This behaviour is replicated to an extent in Fig. 11, whereby the left-hand and right-hand edges of the cube show strong in-phase and out-of-phase response, respectively. It has been reported that the use of stiffer cantilevers can diminish this effect, however the limited adhesion of islands to the substrate surface precluded this option.

We show further evidence that the PZT islands were indeed ferroelectric when a larger area of the sample was scanned, Fig. 12. In the piezoresponse image we can see that the cubic crystals display a response, whilst adjacent regions, containing non-piezoelectric material, do not.

Acquiring piezoresponse images of microwires proved challenging because of their aforementioned relatively weak adhesion to the substrate. Consequently, during a scan the AFM tip had a tendency to remove them. However, in a limited number of cases it was possible to acquire images, Fig. 13, it can

be seen that the detected piezoresponse is consistent with the theory that the microwires formed through the coalescence of individual islands, each bearing their own piezoresponse.

4. Conclusions

We have shown that it is possible to use a hydrothermal technique to deposit isolated, PZT islands on SrTiO$_3$ substrates after just 30 min processing at 160 °C. The initial Pb precursor concentration was shown to have an intimate impact on the morphology and coverage of the PZT islands that are produced. Higher concentrations led to well-faceted islands and longer processing times (24 h) resulted in the coalescence of islands into dense films up to a micron in thickness. XRD analysis revealed the PZT to be highly (1 0 0)-oriented, indicating a degree of epitaxy with the substrate was attained.

We also show that imperfections on the substrate, most probably introduced during polishing, can impact the nucleation and subsequent growth of the PZT islands. Several lines composed of coalesced cubic PZT islands were observed, over a millimetre in length, with the individual islands aligning along the crystallographic axes of the substrate. Finally, PFM undertaken on a variety of the adhered PZT structures showed them to possess a weak piezoresponse.

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