MICROSTRUCTURE OF PULSED-LASER DEPOSITED PZT ON POLISHED AND ANNEALED MGO SUBSTRATES

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ABSTRACT

Thin films of Lead-Zirconate-Titanate (PZT) have been grown by pulsed-laser-deposition (PLD) onto polished MgO substrates both with and without pre-annealing.

The surface morphology of polished MgO substrates, which are widely used for deposition, is examined by AFM. Commercially available, mechanically-polished substrates are shown to be microscopically very rough and seem unlikely to present a surface suitable for the growth of the highest quality thin films. Annealed MgO substrates, on the other hand, comprise atomically flat terraces. The use of annealed substrates is found to enhance considerably the crystalline quality of PZT films deposited thereon.

INTRODUCTION

The MgO (100) surface is in widespread use as a substrate for thin films grown by a variety of deposition techniques, including pulsed-laser deposition (PLD). These films include numerous ceramic metal oxides, such as TiO_2, ferroelectrics and, notably, superconductors, such as $YBa_2Cu_3O_{7-d}$ (YBCO).

The importance of substrate surface morphology has been demonstrated in observations of grapho-epitaxy, in which island growth is initiated at surface steps [1], whilst, for titania deposition, the microscopic surface morphology can bring about, as well as inhibit, localised phase changes [2,3]. In a recent publication, YBCO was deposited by PLD onto bulk MgO (100) substrates, and annealing of the substrate prior to deposition shown to lead to a dramatic reduction in the density of outgrowths - a phenomenon of serious technological concern in the production of multi-layered, superconducting devices - as compared with deposition onto unannealed substrates [4].

Commercially available (100) MgO substrates have a quoted root-mean-square (RMS) roughness only of the order of a few angstroms. The vast majority of thin film growth onto MgO substrates is performed onto these surfaces, either as-received or after washing in solvents. Given the known importance of substrate surface morphology, surprisingly little information is available about the detailed microstructure of such optically-polished MgO substrates.

The importance of substrate pre-annealing is demonstrated for the growth of PZT thin films deposited onto MgO, via a considerable enhancement in crystalline quality. For piezoelectric applications, such as in micropumps and force sensors, optimum film crystallinity is required. Crystalline quality may also play a role in ferroelectric applications, such as in non-volatile memories, although the choice of electrode material appears most significant [5,6].

EXPERIMENTAL

MgO (100) substrates, 8 x 8 mm, were cleaved from a block of 4N purity MgO. These substrates were then ground to remove cleavage steps prior to various polishing stages ending with 1 micrometre diamond. Annealing is performed for times between 0 and 90 minutes at 1350°C in air.

A Topometrix TMX2010 AFM at the Department of Physics, UCL, was used for characterisation of the substrate surfaces. In order to enhance topographical contrast, and best show the surface morphology, AFM images are shaded along the scan direction and then recoloured using the Topometrix "2D Colour" option.

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The deposition of PZT thin films was performed using a frequency quadrupled (266nm) Nd-YAG laser operating at 10Hz. Substrates were cleaned by baking in flowing oxygen at 700°C for 30 minutes prior to deposition. A target-substrate distance of 38mm and fluence of 4J/cm^2 was employed. Depositions were carried out in 0.25 mbar of flowing oxygen and at a substrate temperature of 560°C for 5 minutes, leading to films with an average thickness of 70nm. The substrate heater was switched off immediately after deposition, and the chamber allowed to reach room temperature in 50mbar of oxygen. These are not the ideal growth conditions presented in an earlier paper [7], owing to experimental constraints, and the absolute quality of these films is poorer than would otherwise be achievable.

RESULTS

As-polished MgO (100) substrates are examined in figures 1-3. These specimens are shown after cleaning in 1 mbar of flowing oxygen at 700°C and before deposition. The AFM image of figure 1 shows a 5 x 5 µm area of a commercially-polished MgO substrate.

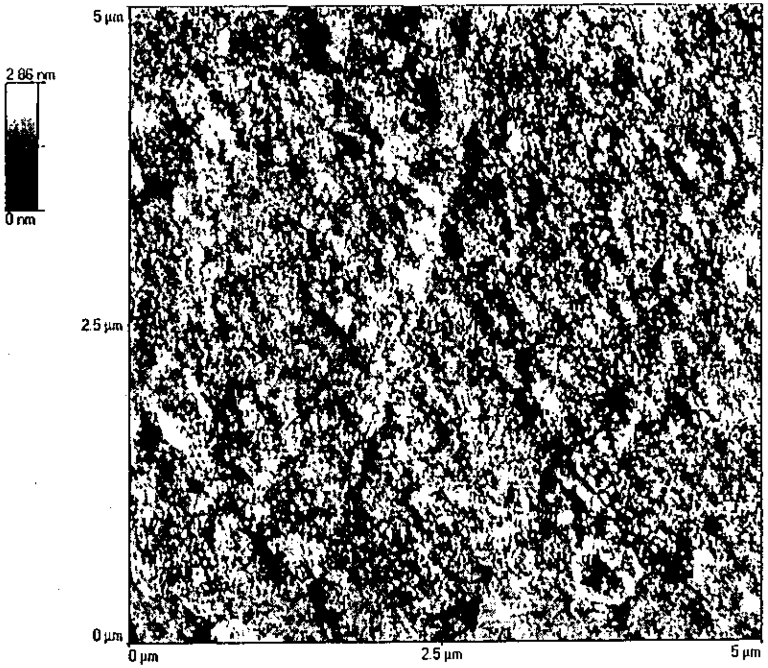

Figure 1: 5 x 5 µm AFM image of commercially-polished susbstrate.

As is evidenced by the vertical scale bar, this surface is macroscopically flat, with a total height differential across all regions of the image only of the order of 3 nm. The RMS roughness for 5 x 5 micrometre areas of these commercially-polished substrates varies between 0.25 and 0.4 nm. It should be noted that after processing of the AFM images, the contrast exhibited by each pixel of the image does not necessarily match that indicated by the vertical scale bar. However, the vertical scale bar is accurate in its measure of the total height differential within each image.

A line trace across the specimen of figure 1 is shown in figure 2. Employing such line analyses on higher magnification images, features are seen to range between atomic dimensions (0.2nm) and three unit cells (1.2nm) in height. A very similar result is found for UHV-cleaved MgO [8]. A striking feature clearly in these line traces is the constantly undulating (microscopically rough) nature of this substrate surface. A similar morphology is displayed by polished $SrTiO_3$ substrates [9]

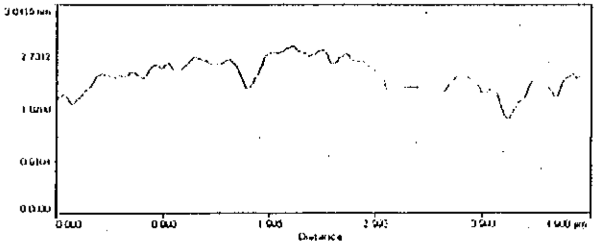

Figure 2: 5µm Line scan across AFM image of figure 1

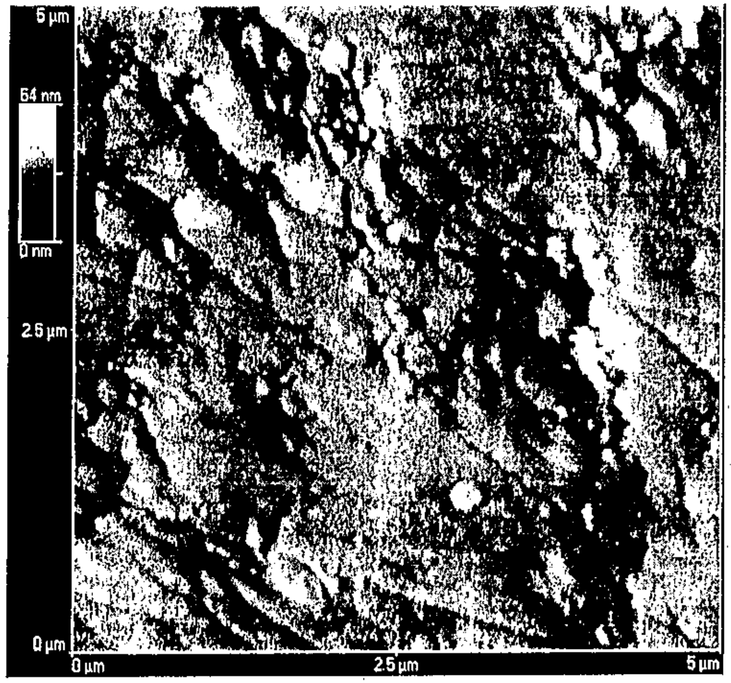

Figure 3: AFM image of cleaved MgO polished with 1µm diamond

The constantly undulating surface morphology is duplicated in the image of Figure 3, which shows a cleaved substrate polished with 1 micrometre diamond. Further similarities are apparent between the differently-polished surfaces of figures 1 and 3, in that both specimens exhibit scratches and a heterogeneous distribution of regions of greater and lesser roughness. These figures indicate that, although the amplitude of the undulation is lessened or increased by the use of different final polishes, the basic morphology is representative of all mechanically polished MgO substrates. In fact, if the vertical scale bar were omitted from these figures, the surfaces would be qualitatively indistinguishable.

A specimen annealed for 90 minutes at 1350°C in air is shown in figure 4. During annealing at high temperature, surface diffusion is accelerated sufficiently to allow facetting onto the low energy (100) surface [10]. After a 90 minute annealing time, the surface consists of very wide terraces, which may be seen from the line trace of figure 5 to be atomically flat.

The evolution of this surface with increasing annealing time is examined using AFM in reference [11].

In figure 6, Cu-Kα XRD patterns of the (001) perovskite peaks from thin PZT films deposited onto 1 micrometre polished and polished and annealed substrates are shown. Both depositions were identical within experimental error, and both films are apparently single-phase perovskite. The dramatic improvement in crystalline quality of the thin film deposited onto the annealed substrate over that deposited onto the polished substrate is readily apparent.

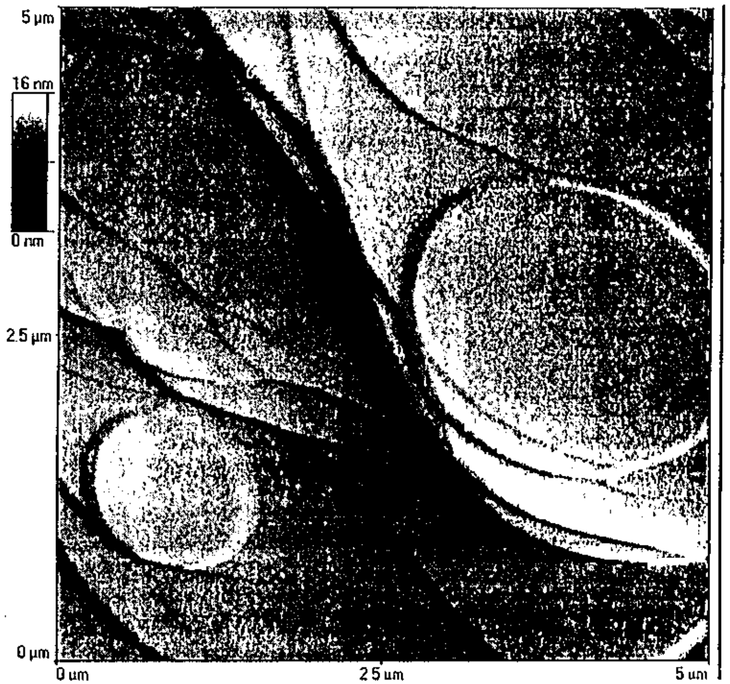

Figure 4: AFM image (5 x 5µm) of polished MgO substrate annealed for 90mins.

DISCUSSION

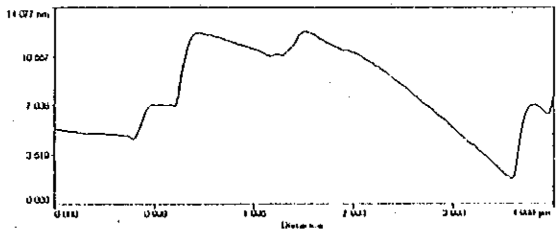

Figure 5: Line trace across figure 4

The improvement in film crystalline quality achieved by deposition onto pre-annealed substrates is similar to that seen for $PbTiO_3$ deposition by rf sputtering onto vicinal MgO substrates [11]. It is also reminiscent of YBCO de-positions, onto both vicinal and annealed MgO substrates [1, 4, 13], in which the use of these substrates is shown to be beneficial to film quality and properties.

Kim et al [12], via XRD analysis, suggest that epitaxy is established between their $PbTiO_3$ film and MgO substrate, with growth proceeding normal to the (100) substrate direction and not to the macroscopic substrate plane. Selected-area diffraction TEM observations [14] appear to confirm the establishment of two primary epitaxial relationships for $PbTiO_3$ growth onto MgO (45° rotation between the two). However, our experiments suggest that growth may be proceeding relative to, or at least strongly affected by, the local substrate normal. Films are markedly less well aligned for growth onto polished MgO substrates, which present almost no (100) surface to the incoming laser plume, perhaps leading to numerous crystallites inclined towards local substrate normals. Without detailed surface morphological information from the vicinal MgO surfaces employed by Kim et al [12], it is difficult to determine the role played by (100) terraces between steps in growth thereon. It is possible that the vicinally-polished MgO presented (100) terraces to the growing species, whilst the polished MgO employed either did not, or presented very few.

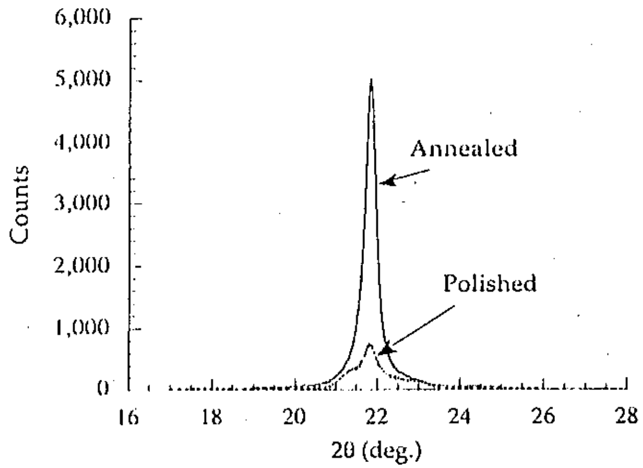

Figure 6: XRD Scans of perovskite (001) peaks from PZT films on polished and annealed MgO substrates.

For YBCO, the improvement in thin film quality on deposition onto vicinal or annealed MgO is likely to be related to the phenomenon of grapho-epitaxy, whereby island nucleation occurs on inclined surface step faces [1,15]. Such growth may not be said to be epitaxial Whilst a detailed structural explanation has yet to be advanced, the observed nucleation behaviour dictates that this improvement is most likely to be related to the formation of well-defined surface steps rather than of the (100) terraces between them (although both will be important).

Lastly, AFM images (not shown) of these PZT thin films suggest an island growth mechanism similar to YBCO. These islands have been imaged by cross-sectional TEM in $PbTiO_3$ [14]. The marked similarities between observations in PZT and YBCO (a much better characterised system), may indicate that very similar growth mechanisms are operating; namely that the formation of large, well-defined, surface steps (through annealing or through the use of vicinal substrates) is a dominant factor, and that growth is affected by the local substrate normal. Separation of these effects is not straightforward, but should be elucidated by further experimentation.

CONCLUSIONS

Polished MgO substrates present very little (100) surface for growth. These surfaces are shown to be microscopically very rough and unsuited for most thin film growth..
Annealing of MgO substrates leads to the formation of large, atomically flat, terraces separated by well-defined surface steps.

The use of annealed substrates leads to a significant improvement in film crystallinity (and likely also film properties) for as-deposited PZT thin films grown by pulsed-laser deposition.

ACKNOWLEDGEMENTS

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EFFECT OF ELECT
PROPERTIES OF F
MAGNETRON SPUTT

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ABSTRACT

The electrical propertie
grown by rf magnetron spu
and polycrystalline RuO_x/S
thin film, processed by rapic
700°C. It is pointed out tha
such films: TEM analysis r
show that an oriented (111
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depend strongly on the dep
PZT deposited on Pt or R
with high values of Ps and
leakage current about 10^{-11}

INTRODUCTION

Ferroelectric thin films h
electro-optic and piezoelec
based devices (1).
Lead zirconate-titanate
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(4), and thermal processing
has been shown that the
transformation to perovsk
transformed to perovskyte,
(3).
Compatibility with electr
chemical and thermal stabili
key roles in the preparation
systems to date are Pt/Ti/Si
post-deposition annealing of
(5) and the degree of orienta
on it.
In the present work, w
$RuO_2/SiO_2/Si$ substrates by
to reach the target stoic
postdeposition RTA on crys

EXPERIMENT

Sputtering apparatus c
800nm boro-phospho-silicat
magnetron rf-sputter deposit
stoichiometry of about TiN
deposited, from a Ru target,