Ferroelectric epitaxial nanocrystals obtained by a self-patterning method

I. Szafraniak,[a] C. Harnagea,[b] R. Scholz, S. Bhattacharyya,[c] D. Hesse, and M. Alexe
Max Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle, Germany

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Lead zirconate titanate nanoislands were obtained by a self-patterning method making use of the instability of ultrathin films during high-temperature treatments. After high-temperature annealing, the as-deposited film breaks into islands with a narrow size distribution. The single-crystal nanoislands were studied by scanning and high-resolution transmission electron microscopy, atomic force microscopy, and x-ray diffraction. They show an epitaxial relationship with the Nb-doped (001) $SrTiO_3$ substrate. The ferroelectric switching of several individual islands was investigated by piezoresponse force microscopy. © *2003 American Institute of Physics.*
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Ferroelectric materials offer a wide range of useful properties such as spontaneous polarization, pyroelectric, piezoelectric, and electro-optic effects that can be applied in nonvolatile memories, actuators, transducers, and thermal sensors.[1] At the nanometer scale, i.e., 10–100 nm, material properties are expected to be different from those of the bulk counterpart. It is a challenge to fabricate structures in this range using both lithography (''top-down'' approach) and self-assembling and self-patterning methods (''bottom-up'' approach). Whereas conventional lithographic systems work usually with a resolution of about 100 nm, bottom-up approaches offer fabrication methods of nanostructures with lateral sizes below 50 nm. It was previously observed that the preparation of ultrathin epitaxial films by chemical solution deposition (CSD) is hindered by a microstructural instability.[2] Oxide thin films with a thickness below a critical value are breaking up after a high-temperature annealing. The driving force of this process is an excess of the total free energy of the continuous film compared with a film partially covering the substrate. The free energy is minimized by (i) formation of islands, which lowers the interface area and consequently the interface energy and (ii) appearance of free surfaces with lower free energy by breaking up the films.[2–4] Up to now, this effect has been regarded mainly as an undesirable effect occurring during the preparation of ultrathin epitaxial films.[5] Recently this approach was used to fabricate lead titanate nanograins on platinum-coated silicon.[6–8] However, the obtained grains have completely random orientation[7] and the analysis of the size effect can be rather complicated without any information on the crystal orientation of each grain since ferroelectric and piezoelectric properties are closely connected with crystallographic orientation.[9] A different approach to study nanostructures is based on investigating thin films at initial growth stage when islands develop.[10–12] A detailed analysis of $PbTiO_3$ and ferroelectric lead zirconate titanate (PZT) nanostructures on Pt coated Si wafers has shown that they do not posses single crystal quality [viz. twin boundaries were observed by transmission electron microscopy (TEM)].[9,13] Therefore, it can be difficult to distinguish between the intrinsic and extrinsic size effects associated with crystal imperfections. The best way to investigate size effects in ferroelectrics is to produce single-crystal, defect-free, monodomain nanostructures with controlled size and orientation. The present letter shows preparation and properties of single-crystal ferroelectric nanostructures obtained by a self-patterning method based on the instability of ultrathin films. Nanosize lead zirconate titanate epitaxial crystals were prepared in a simple way by depositing ultrathin films onto single-crystal substrates followed by a high-temperature crystallization.

$PbZr_{0.52}Ti_{0.48}O_3$ (PZT) ultrathin films of different thickness were obtained by CSD, spin-coating a commercial polymeric precursor (PZT9906, Chemat Technology, Inc.) onto (001)-oriented single crystal niobium-doped $SrTiO_3$ (STO:Nb) substrates with a Nb concentration of 0.5% (CrysTec GmbH, Berlin). The initial film thickness was set by diluting of the raw precursor in its solvent (butanol) within the range from 1:10 to 1:40, and by adjusting the spinning speed from 3000 to 6000 rpm. The obtained gel film was

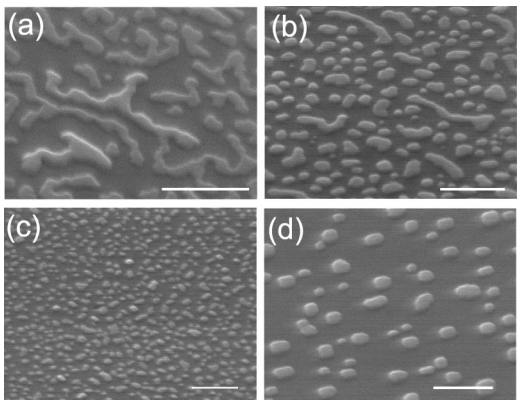

FIG. 1. Scanning electron micrographs of PZT nanoislands obtained after deposition of (a) 1:20, (b) 1:25, (c)–(d) 1:40 diluted PZT precursor and after 1 h of crystallization at 800 °C (a)–(c) and 1100 °C (d). Scale bar represents 400 nm.

[a]Present address: Institute of Materials Science and Engineering, Poznan University of Technology, M. Sklodowska Curie 5 Sq., 60-965 Poznan, Poland; electronic mail: jza@mpi-halle.de
[b]Present address: INRS-Énergie et Matériaux, 1650 boul. Lionel-Boulet, Varennes QC J3X 1S2, Canada.
[c]Present address: Materials Research Center, Indian Institute of Science, Bangalore 560012, India.

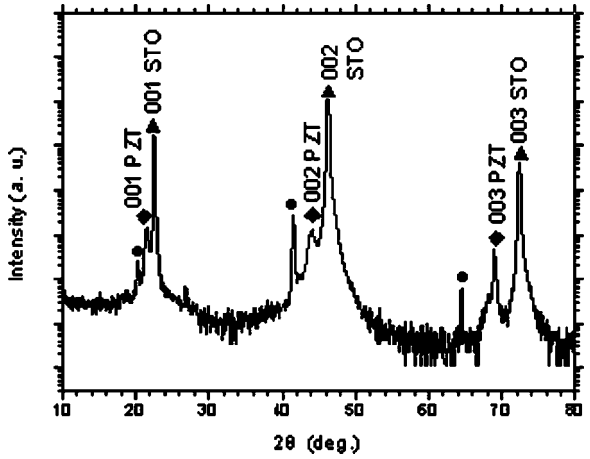

FIG. 2. X-ray diffraction pattern of PZT nanocrystals annealed at 800 °C. Triangles indicate substrate peaks, squares correspond to island peaks. The peaks labeled with circles indicate substrate peaks originating from the remaining Cu K_β radiation.

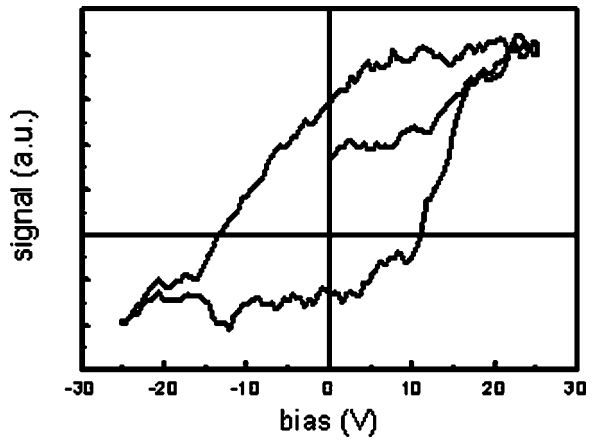

FIG. 4. Piezoresponse hysteresis loop of an individual nanoisland with a height of 15 nm and an area of 8×10^4 nm^2.

dried on a hot plate at 80 °C for 5 min, pyrolized at 300 °C for 5 min, and finally crystallized at 800–1100 °C for 1 h in a lead oxide atmosphere. During the high-temperature treatment, the ultrathin films break up into islands of 20–200 nm lateral size depending on the initial film thickness. The obtained nanostructures were studied by scanning electron microscopy, high-resolution TEM, atomic force microscopy, piezoresponse force microscopy (PFM), and by x-ray diffraction.

The growth of nanostructures was investigated as a function of the initial film thickness and the crystallization temperature. As expected, thicker films transform into films with faceted holes after 1 h of crystallization at 800 °C. A deposition using a higher dilution results in ultrathin films, which after the high-temperature crystallization break up into small single-crystal islands, as shown in Fig. 1. For the highest dilution (1:40) the resulting islands have a height of about 9 nm and lateral dimensions of 40–90 nm with a relatively narrow distribution in size [Fig. 1(c)]. The islands are distributed on the substrate with a high density of about 150 crystals on an area of 1 μm^2. Thicker layers obtained with lower dilution (1:25) create islands that are both larger and higher [Fig. 1(b)]. Their height increases up to about 25 nm and the distance between close neighbors increases as well, resulting in a low areal density of the islands of about $30/\mu$m^2. If the initial film thickness is just below a critical value, larger islands of irregular shape form, as is shown in Fig. 1(a).

The crystallization temperature plays an important role in the morphology of the final structures. The films annealed at higher temperature result in islands with pyramidal shape and increased height. For instance, the height of nanocrystals obtained from the 1:40 diluted precursor increases from 9 nm after a treatment at 800 °C up to 20 nm after a 1100 °C annealing. The area density decreases drastically down to 15–20 islands per 1 μm^2. We assume that at higher temperature the mobility and surface diffusion are enhanced and that this allows the deposited material to migrate and to coalesce into larger islands. As a result the PZT nanoislands are higher and more separated. The mechanism of nanoisland formation was shown to be similar[14] to that used to produce semiconductor quantum nanostructures in materials as Ge on Si in which the shape and distribution obeys the Shchukin–Williams theory.[15,16]

In order to investigate the structure of the PZT islands, x-ray diffraction was performed. Figure 2 shows the 00*l* reflections from the STO:Nb substrate (cubic), and 00*l* reflections of tetragonal PZT revealing the epitaxial growth of the PZT islands. The TEM analysis of the nanocrystals revealed a well-defined shape with relatively sharp facets that prefer-

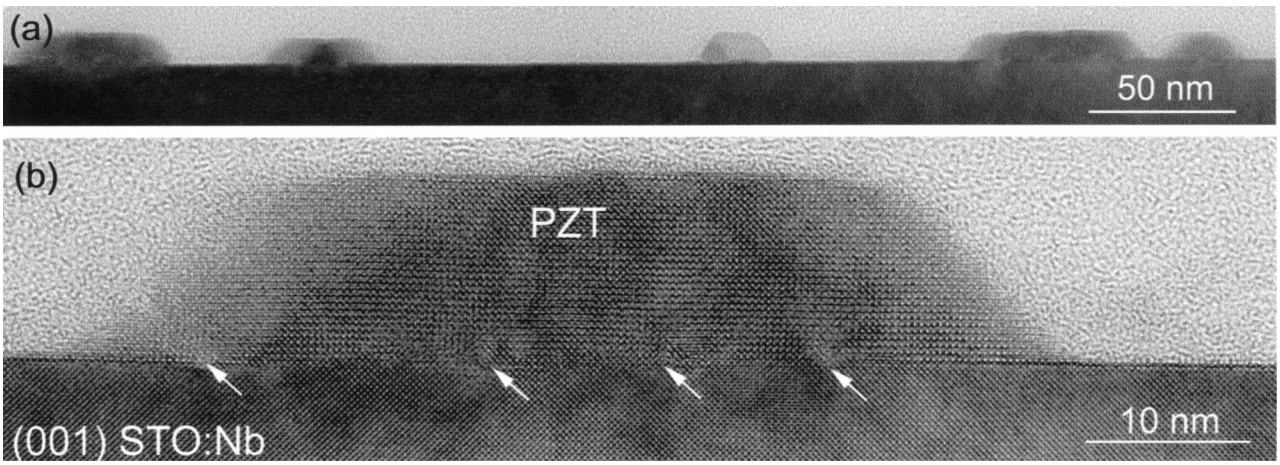

FIG. 3. Cross-section transmission electron micrographs of small PZT islands grown on STO:Nb substrate. Arrows point to misfit dislocations.

ably consist of {111} or {110} and {100} faces (Fig. 3). The lattice mismatch strain between the nanocrystals and the substrate relaxes by formation of misfit dislocations. Results of a detailed structural analysis will be published elsewhere.[17]

The ferroelectric properties of individual islands were probed by piezoresponse force microscopy.[6–9,18] Islands with heights above 25 nm or a large lateral size show a well-developed piezoelectric hysteresis loop. Figure 4 presents a loop obtained on an island of irregular shape as shown in Fig. 1(a). Similar loops were obtained for islands with heights above 25 nm and smaller lateral size. For smaller structures (low height and low lateral size) there were problems to obtain a hysteresis loop. We assume that for such structures defects such as dislocations and stacking faults, which are located near the PZT/STO:Nb interface, have a negative influence on the ferroelectric properties of the crystal around them by inducing stresses that can pin the polarization. Further investigations are under way in order to establish the minimum size of the epitaxial nanosize crystals that are still switching, also taking into account the sensitivity of the PFM measurement setup. Nevertheless, our first experiments suggest that the ferroelectric properties are related rather to the volume than to the lateral size of the structures.

In conclusion, we have presented a simple bottom-up approach to fabricate epitaxial single-crystal nanosize structures. The lateral size as well as the height of the nanocrystals can be tuned in a certain range by adjusting the initial thickness of the deposited films and by the postdeposition thermal treatment. PZT nanoislands with heights as small as 9 nm and with average lateral sizes of about 50 nm were prepared. They show an epitaxial orientation relationship to the substrate. Islands of relatively large volume and a height above 15 nm show ferroelectric properties.

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