Epitaxial Lead Zirconate Titanate Nanocrystals Obtained by a Self-Patterning Method

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Epitaxial lead zirconate titanate nanoislands were obtained by a self-patterning method using 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. Nanostructures, as small as 20 nm lateral size with a height of 9 nm, were epitaxially grown on Nb-doped (001) SrTiO₃ substrates. The formation of nanostructures was investigated as a function of the initial film thickness and crystallisation condition. Single-crystal nanoislands were studied by scanning and high-resolution transmission electron microscopy, atomic force microscopy and X-ray diffraction. Ferroelectric switching of several individual islands was investigated by piezoresponse force microscopy.

Keywords: PZT; ferroelectric epitaxial nanosize crystals; self-assembly; piezoresponse-AFM

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INTRODUCTION

Multifunctional ferroelectric materials offer a wide range of useful properties from switchable polarisation that can be applied in memory devices, to piezoelectric and pyroelectric properties used in actuators, transducers and thermal sensors [1, 2]. However they can not be applied to nanometer scale devices before the influence of the lateral size on physical properties

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will be clarified. In real system it is difficult to distinguish between the intrinsic and extrinsic size effects caused by crystal imperfections or by surface effects. Therefore, to investigate the true size effect there is a need to have single-crystalline structures with a lateral size that can be tuned in the nanometer range. Recently, there were a few attempts to fabricate ferroelectric nanostructures. However, the lead titanate nanograins obtained by a solution-based dilution technique on platinum-coated silicon had completely random orientation [3–5]. 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 [6]. A different approach to study nanostructures is based on investigating thin films at their initial growth stage when islands develop [7–9]. A detailed analysis of PbTiO_3 and PZT nanostructures on Pt coated Si wafers has shown that they do not possess single crystal quality (viz. twin boundaries were observed by TEM) [7, 10], making the investigation of the size effects on those samples even more complicated. Therefore, the best way to study size effects in ferroelectrics is to produce single-crystal, defect-free, mono-domain nanostructures with controlled size and orientation.

In order to fabricate uniform, single-crystal nanosize ferroelectric structures we have applied a self-patterning method based on the instability of ultrathin films during high-temperature treatment. It was previously observed that the preparation of ultrathin epitaxial films by chemical solution deposition (CSD) is hindered by a microstructural instability, i.e. thin films with a thickness below a critical value break up into islands with a narrow size distribution after a high-temperature annealing [11, 12]. The aim of the present paper is to investigate the influence of the initial film thickness and thermal treatment on island formation. The island morphology and properties were studied by electron microscopy, atomic force microscopy and X-ray diffraction. The ferroelectric behaviour, viz. local switching of polarization by an external field, was verified for individual nanostructures using piezoresponse force microscopy.

EXPERIMENTAL

$\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) ultra-thin films of different thickness were obtained by spin-coating a commercial precursor (PZT9906, *Chemat Technology, INC.*) onto single crystalline niobium doped SrTiO_3 (STO:Nb) (001)-oriented substrates with a Nb concentration of 0.5% (*CrysTec GmbH, Berlin*). The initial film thickness was set by dilution of the raw precursor in its solvent (butanol), which ranged from 1:10–1:40, and by adjusting the

spinning speed from 3000 to 6000 rpm. The obtained gel film was dried on a hot plate at 80°C for 5 min, pyrolyzed at 300°C for 5 min, and finally crystallised in a lead oxide atmosphere. To study the growth mechanism the crystallisation process was performed by annealing for 5 min—10 h at different temperatures between 650°C and 800°C. The obtained nanostructures were studied by high-resolution transmission electron microscopy (HRTEM) (JEOL 4010 at 400 kV), atomic force microscopy (AFM) (Dimension 5000, Digital Instruments), and by X-ray diffraction (XRD) (Philips X'Pert Diffractometer). Piezoresponse force microscopy measurements were performed using an Autoprobe CP Research AFM and a lock-in amplifier (EG&G Instruments, Model 7260) as described previously [13, 14]. The ac voltage was applied to the tip mounted on medium-stiff cantilevers of type CSC11b (Micromasch) coated with the hard semiconductor W₂C. The dc voltage for polarisation switching was applied to the bottom electrode of the sample using a computer-controlled Keithley 2400 Source Meter.

RESULTS AND DISCUSSIONS

The growth of nanostructures was investigated as a function of the initial film thickness. Figure 1(a–c) shows the AFM morphology of the structures obtained after crystallisation at 800°C for 1 h of films with different initial thicknesses. As expected, the microstructural instability generates small single-crystal islands after thermal treatment. If the initial film thickness is just below a critical value, relatively large islands of irregular shape form, as shown in Fig. 1a. Islands have an average height of 15 nm and a wide distribution in lateral sizes up to a few hundreds nanometers. Thinner layers create more regular islands that are both larger and higher (Fig. 1b). Their height increases up to about 25 nm due to the contraction in the lateral size, and the conservation of the total volume. The distance between close neighbours increases as well, resulting in a low areal density of the islands. When the initial layers are even thinner the height of islands decreases and their areal density increases (Fig. 1c). The smallest islands obtained from the most diluted precursor have a height of about 9 nm and lateral dimensions of about 50 nm with a relatively narrow distribution in size (Fig. 1d). The islands are distributed on the substrate with a high density of about 150 crystals on an area of 1 μm^2 .

XRD analysis (Fig. 2) and HRTEM investigations (Fig. 3) were performed to get structural information on the nanocrystals. An epitaxial relationship between the substrate and top structures was proved. No secondary phase

FIGURE 1 AFM images of PZT nanoislands obtained after deposition of (a) 1:20, (b) 1:25, (c) 1:30 and (d) 1:40 diluted PZT precursor.

peak was detected in XRD pattern, confirming the formation of a good quality perovskite phase. Moreover, HRTEM images show that all islands have uniform heights and truncated pyramidal shape with relatively sharp facets that preferably consist of $\{111\}$ and $\{110\}$ planes as lateral surfaces and $\{001\}$ planes as top surfaces [15]. All PZT islands appear as single crystalline with single c -domain orientation. The crystals are free from volume defects, and the only defects are dislocations concentrated along the interface, caused by relaxing the stress induced by lattice mismatch between the substrate and PZT islands.

To investigate the growth mechanism of PZT nanoislands two series of samples were prepared by varying the crystallisation temperature (650–800°C for 1 h) and time (5 min–10 h at 800°C). This experiment was done using the initial layers that give 9 nm high islands after 800°C treatment. HRTEM images, shown in Fig. 3, suggest that in the early stage of nucleation

FIGURE 2 X-ray diffraction pattern of PZT nanocrystals. The peaks labelled with circles indicate the substrate peaks originating from the remaining $\text{CuK}\beta$ radiation.

the pre-existing holes penetrate down to the substrate surface and during longer heat treatments (650°C for 1 h, see Fig. 3a) the nanoislands migrate on the substrate surface and coalesce into larger irregular structures. Nanostructures crystallised at higher temperatures (e.g., at 800°C for 5 min, see Fig. 3b) have better thickness uniformity. However, annealing as long as 1 h at 800°C is needed to form the equilibrium shape and distribution of islands (Fig. 3c). Treatments longer than 1 h do not lead to significant changes in island morphology, shape and distribution. As it was previously shown, the nanostructure formation is connected with the lowering of the interfacial energy of the film by breaking up the film into islands, which lowers the interface area and consequently the interface energy [11]. However, longer thermal treatments at higher temperature are needed to reach the equilibrium state in which well-defined facets appear.

The ferroelectric properties of individual crystal islands were probed by piezoresponse force microscopy [16]. The islands having a large volume (either with a small lateral size and heights above 25 nm or thinner with a larger lateral size) show well-developed piezoelectric hysteresis loops [17]. Figure 4 shows the topography and piezoresponse images proving switching

FIGURE 3 Cross section transmission electron microscope image of PZT nanostructures grown on STO:Nb substrate and annealed for (a) 1 h at 650°C, (b) 5 min at 800°C and (c) 1 h at 800°C.

of polarisation in crystals with a height of 15 nm. The grain marked by the dashed contour was successively polarised negatively (polarisation pointing into the sample, Fig. 4b) then positively (Fig. 4c) by the biased AFM tip. Investigations of the smallest self-assembled structures are under progress in order to establish the minimum size of the epitaxial nano-size crystals that can still be switched.

FIGURE 4 Switching of an individual nanocrystal by PFM: (a) topography (z-scale 25 nm) and piezoresponse images after applying (b) a negative and (c) a positive dc voltage.

CONCLUSIONS

Epitaxial nanostructures of ferroelectric PZT have been successfully fabricated onto Nb doped (001) SrTiO_3 single crystals by a self-assembly route that exploits microstructural instability developed in ultrathin films at high-temperatures. 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 the post-deposition thermal treatment. If the crystallisation process happens at high enough temperatures for sufficiently long times, than all the nanoislands have a well-defined shape with relatively sharp facets that preferably consist of $\{111\}$ and $\{110\}$ planes as lateral surfaces and $\{001\}$ planes as top surfaces. X-ray and TEM confirmed good quality of the epitaxial nanostructures. They are single crystalline, epitaxial, uniform in height and free from any volume defects. Islands of relatively large volume and a height above 15 nm show ferroelectric properties.

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