**Influence of the substrate surface on the self-assembly of
ferroelectric PbTiO₃ nanostructures obtained by
microemulsion assisted Chemical Solution Deposition**

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Abstract

The achievement of long range periodicity of ferroelectric nanostructures on substrates remains as a challenge in the processing of devices by the relatively inexpensive self-assembly methods. To this aim, here we make the proposal of processing strategies involving commercial single-crystal SrTiO₃(100) substrate surface treatment. The topography, global ordering and crystal symmetry of the surface of the treated substrates as well as the near surface layer composition were analysed by Scanning Force Microscopy, Low Energy Electron Diffraction and Auger Electron Spectroscopy, respectively. The study shows that a combination of chemical etching and thermal annealing in air produces smooth and well terraced surfaces which have steps of few unit cells height and a nearly complete TiO₂ termination, while keeping the 1x1 bulk structure. Preliminary results shows that PbTiO₃ nanostructures, obtained by a novel microemulsion assisted Chemical Solution Deposition method onto such substrates, grow at regular distances and preferentially located at the edges of the substrate surface terraces. Thus, long range order of these nanostructures is envisaged when deposited onto substrates that are treated by the procedure here studied.

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1. Introduction

The potential use of ferroelectrics in ultra-high density ($>1\text{Tb/inch}^2$) non-volatile random access memories [1,2] needs of innovative strategies for reproducible and low cost production of isolated ferroelectric particles with a uniform size down to the few tens of nanometer range and periodically distributed on the substrates surface.

“Top-down” (lithography based techniques) [3] and “bottom-up” (self-assembly methods) [4] approaches have been reported in the literature for the fabrication of structures in this size range. Within the latter class, a novel microemulsion assisted Chemical Solution Deposition (CSD) method has been recently developed for the processing of PbTiO_3 perovskite nanostructures on single-crystal $\text{SrTiO}_3(100)$ (STO) substrates [5].

The use of microemulsions in the fabrication of nano-size powder particles has been extensively used in many fields including the processing of ferroelectric powders [6] and nanostructured ferroelectric ceramics [7]. However, microemulsion aided methods to produce ferroelectrics onto substrates [8, 9, 10], mainly thin films, are scarcely found in the literature. One of the advantages of the microemulsion assisted method is that the soft built up of the nanostructures preserves their crystal structure, as determined by Synchrotron X-ray diffraction analysis at grazing incidence, and, consequently, their ferroelectric properties [5], making realizable their application in devices.

Here, transparent micellar solutions are prepared by mixing an emulsion containing reverse micelles and a PbTiO_3 precursor sol [11]. In the resulting solutions, sol drops will be placed in the core of the micelles. Deposition of the solution onto a substrate, controlled drying and thermal treatment lead to the formation of isolated oxide particles, given that highly diluted solutions are used, as explained in detail elsewhere [5]. This method provides mechanisms of self-assembly, since both the size of the nanostructures and the distance between them are determined by the chemistry of the microemulsion. Lack of order in the nanostructures

obtained by the microemulsion-aided CSD method onto polycrystalline substrates was observed [12]. Fluid streamrings are formed during the deposition of the solution when nanostructures were deposited onto commercial, as received, single-crystal STO substrates, mainly due to an irregular wetting of the micellar solution and, consequently, irregular evaporation of the solvent during the spin-coating and drying steps. Despite of the non-homogeneous coating, in some areas a one-dimensional short range periodicity of the nanostructures was found [5]. Long range order is greatly determined by the nature of the substrate surface onto which the micellar solution is deposited and the nanostructure nucleation and crystallization take place.

The achievement of long range periodicity of the ferroelectric nanostructures remains as a great challenge in the processing of devices by the relatively inexpensive “bottom-up” methods. For this purpose, here we propose processing strategies involving commercial single-crystal STO substrate treatments. The obtained surfaces were analysed by Auger Electron Spectroscopy (AES), Low Energy Electron Diffraction (LEED) and Scanning Force Microscopy (SFM). Among the numerous works that have been published on the surface treatment of STO substrates, we focus here on treatments that take advantage of the difference in physical and chemical properties (e.g., solubility in acids) of the A- and B-site cations of the perovskite-type structure of SrTiO_3 , in order to achieve nearly perfect and single terminated surfaces, which promote epitaxial growth of defect-free thin films [13-16]. PbTiO_3 nanostructures were deposited onto optimized STO substrates and the occurrence of self-assembly also studied by SFM.

2. Experimental

Two types of chemical etching of commercial 10x10x1mm STO substrates were carried out, both with an NH_4F buffered HF solution (BHF). The first (hereinafter referred to as etching-1) was carried out at $\text{pH} = 4.3$, within the range reported [13] as adequate to avoid extensive

surface damage. The second (hereinafter referred to as etching-2) was carried out with a pH=5.56 solution, and was preceded by an immersion in deionized water in ultrasonic bath for 10 minutes. This immersion aims to produce an intermediate, acidic soluble, Sr-hydroxide complex when reacting with the SrO layers of the surface, while keeping intact the more stable TiO₂ layers of the substrate [16]. Etching times were in the range from 10 to 30 seconds. After etching, the substrates were rinsed in water, dried in N₂ stream and annealed. Two types of thermal treatment were also carried out. Some of the substrates were annealed in Ultra-High Vacuum (UHV) by using a radiative heater facing the sample backside [17], without oxygen gas flow. Other substrates were annealed in air, using a Thermal Processor for the microelectronic industry (RTP Jetstar 100T. Jipelec) located in a clean room. Both heating and cooling ramps were kept below 10°C/min. Annealing was carried out between 900°C and 1050°C for 1 or 2 hours.

A substrate was also annealed for the sake of comparison after Ar⁺ ion bombardment (60min, 3μA, 0.6-1kV), instead of chemical etching. Both processes took place in the UHV chamber. A rear view LEED optics, also adapted for AES measurements, available in the same UHV chamber utilized for substrate treatment, was used in the surface characterization. Auger spectra in the 20 to 550 eV energy range were taken in the first derivative mode (dN/dE), using a 2 KeV incident electron beam and the same measurement parameters for all the surfaces under study. Information on the relative changes of composition produced in the near surface layers is achieved by comparing the intensity ratios of the Sr, Ti and oxygen peaks. A few selected results of this study will be shown here, whereas the complete study will be reported separately.

Nanostructures were prepared onto the optimised STO substrate surfaces with advantageous characteristics for the matching of the SrTiO₃ substrate ($a=b=3.905\text{\AA}$) and PbTiO₃ ferroelectric ($a=b=3.895\text{\AA}$) crystal structures, aiming to the growth of defect-free self-

assembled nanostructures. They were obtained by the microemulsion aided CSD procedure reported elsewhere [5] using 0.01 M micellar solutions (equivalent moles of PbTiO_3 per litre of solution) and Rapid Thermal Processing at 650°C for 50s. A commercial Scanning Force Microscope (SFM) (Nanotec® Electronica) was used to observe the topography of the substrate surfaces and deposited nanostructures. Silicon tip cantilevers with a force constant of 42 N/m and resonance frequency of 320 kHz, working in dynamic mode, were used to get the topographic images.

3. Results and Discussion

Figure 1(a) shows the SFM topographic image of the surface of a STO substrate after etching-1 and thermal treatment at 950°C for 2h in UHV. Big etch pits of lateral size higher than $1\text{ }\mu\text{m}$ and some island-like residues can be observed. It has been already discussed [16] that the reproducibility of the BHF etching is critically dependent on the previous polishing or annealing of the surface, which affects the 50/50 surface ratio of occupancy of SrO/TiO_2 terminations expected by cleaving or cutting STO single crystals. Figure 1(b) shows the SFM topographic image of a substrate surface after etching-2 and annealing in air in clean room at 950°C for 1h. In contrast with the severely damaged surface of Figure 1(a), substrates show in this case a smooth surface, with a scarce number of small etch pits of lateral size below 200 nm. Figure 1(b) shows clear terraces of few unit cells height (1.2 nm) and a few hundreds of nm width.

Figure 2 displays the AES spectrum and LEED pattern of a clean STO surface prepared by Ar^+ ion bombardment followed by UHV annealing at 900°C -1h. This reference surface exhibits excellent 1×1 LEED patterns (i.e., keeps crystal bulk structure without additional reconstructions) and the measured O-to-Ti Auger ratios are also in agreement with previous reports [18]. Figure 3 shows the AES spectra of the surface of two STO substrates treated by BHF etching-2 for 10 seconds and subsequently annealed, one of them in UHV at 900°C -1h

and the other annealed in air in clean room at 1050°C-1h. A comparative study of the Sr-to-Ti and O-to-Ti intensity ratios (for the Auger transitions marked by arrows in Figure 2) achieved for the surfaces of our STO treated substrates indicates that those processed by both BHF etching protocols and UHV annealing are Ti-deficient in the near surface layers. This study also shows that the highest Ti content of the series here analyzed corresponds to substrates prepared by the BHF etching 2 and annealing in air, whose AES spectrum is shown in Figure 3. Moreover, the latter surface may have occupancy fraction of the TiO₂ termination in the 80 to 100% range, since their Sr-to-Ti and O-to-Ti Auger ratios are lower than those we measured on as received (polished) commercial substrates. A 75 to 95% occupancy fraction of TiO₂ termination has been reported for as polished substrates [14, 15]. SFM experiments performed in Lateral Force (LF) mode, not shown here, on this type of substrate also support a nearly perfect TiO₂ termination, since lack of contrast was obtained at both sides of the terrace edges. Figure 3 also shows the LEED pattern of a STO substrate right after BHF etching-2. This pattern is not as clear as the one in Figure 2 for the reference STO substrate due to some post-etching atmospheric contamination (C) that AES analysis reveals. However, the low background and sharp 1x1 spots observed in the LEED pattern of Figure 3 reveal the good crystal quality of the top substrate layers already at this stage (before any thermal treatment) for etching-2. A similar LEED pattern is observed after subsequent annealing in air in clean room at 1050°C-1h, whereas UHV annealing at 900°C-1h gives place to a surface reconstruction.

For their smooth and well terraced surfaces, good crystal quality, 1x1 LEED pattern and nearly complete TiO₂ termination, the STO substrates after BHF etching-2 followed by annealing in air at 1050°C-1h were chosen for the ferroelectric nanostructure self-assembly tests. Preliminary results of these tests show that nanostructures obtained by the microemulsion assisted CSD method grow, homogeneously throughout such substrates, at

regular distances and preferentially located at the edges of the surface terraces, as it is shown in the SFM topographic image of Figure 4(a). For the sake of comparison, Figure 4(b) also shows an example of the disordered particles grown on certain areas of the as-received STO substrates, in which wetting problems prevent to obtain a homogeneous coating [5, 12].

Conclusions

A number of treatments of commercial single-crystal $\text{SrTiO}_3(100)$ substrates were analysed in order to obtain a surface amenable to produce ferroelectric nanostructures for use as high-density computer memories. Chemical etching with an NH_4F buffered HF solution (BHF) of $\text{pH}= 5.56$ for 10 seconds, preceded by ultrasonic soaking in deionized water, and followed by annealing in a clean room Thermal Processor in air at 1050°C -1h, results in smooth surfaces that keep the crystal bulk structure, without additional reconstructions, and present a Ti content consistent with a 80 to 100% occupancy of the surface of TiO_2 terminations. They are advantageous for the matching of the SrTiO_3 substrate and PbTiO_3 ferroelectric perovskite-type crystal structures needed for the growth of defect-free nanostructures. These surfaces also have clear terraces of few unit cells height and hundreds of nanometers width. It was observed that PbTiO_3 nanostructures obtained by this microemulsion assisted CSD tend to grow at regular distances at the edges of the surface terraces. Thus, long range order of such nanostructure distribution is envisaged on the optimized STO substrates.

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References

- [1] R. Waser and A. Rüdiger “Ferroelectrics: Pushing towards the digital storage limit”. *Nature Mater.*, **3**(2), 81 (2004)
- [2] W. Lee, H. Han, A. Lotnyk, M.A. Schubert, S. Senz, M. Alexe, D. Hesse, S. Baik and U. Gösselle. “Individually addressable epitaxial ferroelectric nanocapacitor arrays near 10^{12} cm⁻² density”. *Nature Nanotechnology* **3**(7), 402 (2008)
- [3] M. Alexe, C. Harnagea, D. Hesse and U. Gösselle. “Patterning and switching of nanosize ferroelectric memory cells”. *Appl. Phys. Lett.* **75**(12), 1793 (1999)
- [4] M. Alexe and D. Hesse. “Self-assembled nanoscale ferroelectrics”. *J. Mater. Sci.*, **41**, 1 (2006)
- [5] M.L. Calzada, M. Torres, L.E. Fuentes-Cobas, A. Mehta, J. Ricote and L. Pardo. “Ferroelectric self-assembled PbTiO₃ perovskite nanostructures onto (100)SrTiO₃ substrates from a novel microemulsion aided sol-gel preparation method”. *Nanotechnology*, **18**(37), 375603 (2007)
- [6] C. Beck, W. Härtl, R. Hempelmann. “Size-controlled synthesis of nanocrystalline BaTiO₃ by a sol-gel type hydrolysis in microemulsion-provided nanoreactors”. *Journal of Materials Research* **13** (11), 3174 (1998)
- [7] C. Pithan, Y. Shiratori, R. Waser, J. Dornseiffer and F.-H. Haegel. “Preparation, Processing, and Characterization of Nano-Crystalline BaTiO₃ Powders and Ceramics Derived from Microemulsion-Mediated Synthesis”. *J. Am. Cer. Soc.* **89** (9), 2908 (2006)
- [8] S. Bhattacharyya, S. Chattopadhyay and M. Alexe. “Fabrication of isolated ferroelectric nanostructures”. *Mat. Res. Soc. Symp. Proc.* **740**, 333 (2003)

- [9] S.S.Kim, E.K.Choi, J.K.Kim, J.S.Kim, T.K.Song and J.Kim. “Effects of surfactant on surface morphology and orientation of Nb-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films”. J.Korean Phys.Soc. **42**, S1126 (2003)
- [10] M.L.Calzada and. “Photo-sensitive sol-gel solutions for the low-temperature UV-assisted rapid thermal processing of PbTiO_3 based ferroelectric thin films”. J.Mater.Chem. **13**(6), 1451 (2003)
- [11] Y. Yamashita, H. Yamamoto and Y. Sakabe. “Dielectric Properties of BaTiO_3 Thin Films Derived from Clear Emulsion of Well-Dispersed Nanosized BaTiO_3 Particles”. Jap.J. Appl.Phys. (2004) **43**, No. 9B, 6521–6524 (2004)
- [12] M. Torres, J. Ricote, L. Pardo and M.L. Calzada. “Nanosize Ferroelectric PbTiO_3 Structures onto Substrates. Preparation by a Novel Bottom-Up Method and Nanoscopic Characterisation”. Integrated Ferroelectrics **99**, 95 (2008)
- [13] M. Kawasaki, K. Takahashi, T. Maeda, R. Tsuchiya, M. Shinohara, O. Ishiyama, T. Yonezawa, M. Yoshimoto, and H. Koinuma. “Atomic control of the SrTiO_3 crystal surface”. Science **226**, 1540 (1994)
- [14] M. Kawasaki, A. Ohtomo, T. Arakane, K. Takahashi, M. Yoshimoto, and H. Koinuma. “Atomic control of the SrTiO_3 surface for perfect epitaxy of perovskite oxides”. Appl. Surf. Sci. **107** 102 (1996)
- [15] T. Ohnishi, K. Shibuya, M. Lippmaa, D. Kobayashi, H. Kumigashira, M. Oshima and H. Koinuma. “Preparation of thermally stable TiO_2 -terminated SrTiO_3 substrate surfaces”. Appl. Phys. Lett. **85** 272 (2004)
- [16] G. Koster, B. L. Kropman, G. J. H. M. Rijnders, D. H. A. Blank and H. Rogalla. “Quasi-ideal strontium titanate crystal surfaces through formation of strontium hydroxide”. Appl. Phys. Lett., **73** (20), 2920 (1998).

- [17] N. Galiana, P.P. Matin, C. Munuera, M. Varela, F. Soria, C.Ocal, A. Ruiz and M. Alonso. “MBE fabrication of self assembled Si and metal nanostructures on Si surfaces”. Surface Sci. **600**, 3956 (2006).
- [18] Y-W Chung and W.B. Weissbard. “Surface spectroscopy studies of the SrTiO₃(100) surface and the platinum-SrTiO₃(100) interface”. Phys. Rev. B **20**, 3456 (1979).

Figure 1. SFM images of STO substrate surfaces: (a) after BHF etching-1 and UHV annealing at 950°C-2h.and (b) after BHF etching-2 and RTP annealing at 950°C-1h.

Figure 2. AES spectrum and LEED diagram of the clean surface of a STO substrate after Ar⁺ ion bombardment followed by annealing in UHV.

Figure 3. AES spectra of the surface of two STO substrates after BHF etching-2 for 10 seconds followed by annealing in UHV at 900°C-1h and in air at 1050°C-1h. The LEED diagram of the surface of a STO substrate right after BHF etching-2 is also displayed.

Figure 4. SFM images ($1,5\ \mu\text{m} \times 1,5\ \mu\text{m}$) of PbTiO_3 particles prepared from 0.01M micellar solutions, crystallized by RTP at 650°C for 50s on two STO substrates: (a) treated with BHF etching-2 during 10 seconds followed by annealing in a Thermal Processor in air at 1050°C for 2h (particle size $< 40\text{nm}$) and (b) as-received substrate (maximum particle width $\sim 100\text{nm}$).