Ferroelectric mesoscopic structures by room-temperature PLD

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Abstract. Usually ferroelectric thin films are deposited by pulsed laser deposition (PLD) at elevated substrate temperatures, in order to obtain a good crystalline quality. Here we report the fabrication of ferroelectric BaTiO$_3$ and BiFeO$_3$ structures by room-temperature PLD combined with post-deposition annealing, and their ferroelectric characterization. A method to control the position of the deposited structures is also presented.

1. Introduction

Pulsed Laser Deposition (PLD) is a versatile deposition technique widely used to prepare various complex oxide materials. In particular, ferroelectric materials, which are promising functional materials for applications in pyroelectric sensors, MEMS and various electronic devices, have been grown by PLD in order to study their properties in the thin film or structured form. The establishment of the optimal deposition parameters that results in films with highest crystallographic quality and best electrical properties is still a challenging task and a semi-empirical process. Among the deposition parameters, the optimal substrate temperature usually falls in a narrow window and was found to be difficult to establish but of crucial importance, because it governs both the nucleation and the growth of the deposited film.

Here we report the fabrication of ferroelectric mesostructures by PLD at room temperature, thus eliminating the need to determine this difficult-to-control growth parameter. We have succeeded in growing mesoscopic BaTiO$_3$ and BiFeO$_3$ ferroelectric structures (30 nm to 3000 nm in lateral size) with good properties by combining room temperature PLD with a post-deposition annealing at high temperature (800 - 900°C).

2. Experiment

2.1. Pulsed laser deposition

A KrF excimer laser (λ = 248 nm, pulse duration = 14 ns) was employed for ablation with an incidence angle of the laser beam on the target of 45° and laser fluence set at 2 J/cm$^2$. Deposition was carried out in vacuum at 5×10$^{-5}$ mbar at room temperature, with a laser repetition rate of 5 Hz.

For the deposition, we have used stoichiometric Barium titanate (BaTiO$_3$), and Bismuth ferrite (BiFeO$_3$) ceramic targets from Praxair Surface Technologies. Firstly we estimated the deposition rate by depositing continuous thin films with thicknesses in the range 100 – 500 nm. The values we found are approximately 0.5 Å/pulse for BaTiO$_3$ and 0.2 Å/pulse for BiFeO$_3$. The films deposited at room temperature were amorphous and a thermal treatment was performed afterwards in order to crystallize them into the ferroelectric phase. The films and structures were deposited on SrTiO$_3$, (100)- and (111)-
oriented substrates. After optimization of the deposition parameters, we used Nb-doped substrates in order to apply the voltage needed to perform the piezoresponse measurements.

2.2. Controlling the position of the deposited structures
In order to control the position of these islands or mesostructures, we have performed the deposition through a miniature shadow-mask (nanostencil), an approach directly applicable to the deposition of arbitrary materials [1]. Here we present the successful transfer of a pattern drawn in the nanostencil directly onto the substrate surface in the form of complex-oxide ferroelectric nanostructures. The miniature shadow-masks were made of 500 nm thick silicon nitride nanosieves with hexagonal arrays of circular holes having a diameter of 300 nm. The masks were temporarily fixed onto the substrate prior to the PLD process and removed afterwards.

2.3. Structural and electromechanical characterization
The films were investigated by Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) after annealing. To prove the ferroelectricity of the mesoscopic structures, we used piezoresponse force microscopy (PFM), a method which allows the detection and switching of ferroelectric domains at the nanoscale [2]. The measurements were performed using a commercial atomic force microscope, AFM, (DI-EnviroScope, Veeco Instruments) and a computer-controlled lock-in amplifier (Signal Recovery Model 7265) connected to the AFM via a Signal Access Module. To apply the voltage to the sample, we used the conductive cantilevers from Micromash with a spring constant of 0.06 - 0.6 N/m coated with semiconductor W2C. An ac testing voltage of 0.5 V was applied between the tip and the conductive substrate on which the structures were deposited. Hysteresis measurements were obtained using an auxiliary digital to analog converter of the lock-in amplifier, by sweeping the voltage between the chosen maximum and minimum values.

3. Results and discussion
To obtain separated structures, we deposited very thin amorphous films with a reduced number of laser pulses. The number of laser shots was estimated as follows: We observed that the surface of relatively thick films (100 – 500 nm thick) becomes rough upon annealing at temperatures 700 – 900°C for 1h in O2 flow. This is caused by the transformation into the crystalline phase. If the thickness of the amorphous layer is thin enough, then the annealing treatment will result in separated grains of 35 - 50 nm for BaTiO3 and 300 - 500 nm for BiFeO3. This is consistent with the known fact that the annealing favors the minimization of the free energy of the film-substrate system by breaking up the continuous films into islands [3]. Additionally, we also observed that there is little or no volume change of the film material upon thermal treatment. Therefore, for the deposition of the ferroelectric isolated mesoscopic structures we used a reduced number of laser pulses, assuming a linear dependence of mass of the deposited films on the number of shots.

3.1. Barium titanate structures
We deposited amorphous BaTiO3 films with an estimated thickness of 2 nm (shooting 50 pulses into the target), corresponding - after crystallization - to one grain (assumed to be one half of a sphere) of 35 nm diameter over a square with a lateral size of ~211 nm, (i.e. a density of ~22 grains/μm²). Figure 1 shows a piezoresponse measurement performed on BaTiO3 structures deposited on Nb-doped SrTiO3(111). The topography, Figure 1a shows crystallites with laterals sizes in the range of 50 – 100 nm, somewhat larger than the expected range of 35 - 50 nm. This is due to the finite radius of the AFM tip apex, estimated to be about 20-30 nm, a well-known artifact in AFM measurements. The corresponding piezoresponse images (acquired simultaneously with the topography) in Figure 1b and 1c prove that most of the grains exhibit a piezoelectric response, proving the ferroelectric nature of the structures. It is important to note that the crystallites do not show a domain structure, each of them having only one polarization orientation, consistent with previous results on fine-grained barium
titanate ceramics [4]. Analysing the out-of-plane and the in-plane piezoresponse images we can deduce that the structures are not epitaxially formed on the substrate. If the structures were (111)-oriented, then the z-contrast of all grains should have only two level of contrast, one positive (white, corresponding to a z-component of polarization upward) and one negative (black). Instead, we observe grains like the one circled which shows a weaker, intermediate z-contrast, and therefore a different crystallographic orientation.

![Figure 1](image1.png)

**Figure 1.** Piezoresponse characterization of BaTiO₃ structures: (a) topography, z-scale 20 nm. (b) z-piezoresponse image showing the ferroelectric domains with a component out-of-plane. (c) x-piezoresponse image showing the domains with a component along the long edge of the figure.

3.2. Bismuth ferrite structures

BiFeO₃ is a multiferroic material which has recently attracted attention due to its large ferroelectric polarization (up to 1C/m²) in the thin film form [5].

![Figure 2](image2.png)

**Figure 2.** Piezoresponse characterization of BiFeO₃ structures: (a) topography, z-scale 700 nm. (b) z-piezoresponse image showing the ferroelectric domains with a component out-of-plane. (c) x-piezoresponse image showing the domains with a component along the long edge of the figure. (d) piezoelectric hysteresis loop obtained from one of the structures.

Because there are several stable compounds of Bi, Fe and O it is quite difficult to obtain the desired ferroelectric-antiferromagnetic phase. PLD, however, because it allows a stoichiometric material transfer from a target to a substrate, seems to have a greater rate of success than other deposition techniques. We succeeded in preparing BiFeO₃ structures with a lateral size in the range 500 nm – 3 μm (as seen in Figure 3a), in a similar way as the BaTiO₃ structures. However, very thin amorphous films did not result in ferroelectric structures upon annealing. We believe that this is due to the volatility of Bi, which lead to the formation of a Bi-deficient phase, enhanced by the fact that the surface-to-volume ratio increases with decreasing the structure size.
Figure 2b and 2c show a ferroelectric characterization of BiFeO$_3$ mesoscopic structures deposited on Nb-doped SrTiO$_3$(100). In contrast to the BaTiO$_3$ islands, a complex domain structure with lateral sizes in the 100 nm range is present within the structures, as expected for rhombohedral ferroelectrics, with spontaneous polarization along the [111] direction. An analysis of the as-grown domain structure reveals the presence of both 180° and 90° domain walls. The piezoelectric hysteresis (Figure 2d) obtained from one of the structures shows the strong ferroelectric character of BiFeO$_3$ mesoscopic structures.

3.3. The nanostencil approach for controlling the structure location

Using a stencil with circular holes, ordered hexagonal arrays of BaTiO$_3$ dot-like structures were grown uniformly throughout sieve areas (1 mm × 0.1 mm) [6]. Figure 3a shows the topography of the well-ordered structures observed by AFM. The as–deposited BaTiO$_3$ nanostructures grown on SrTiO$_3$(100) have a lateral size (FWHM) of 400 nm and a height of 50 nm. Upon annealing, the structures crystallized into grains, 35-50 nm lateral size, similarly to the crystallization in the thin film form. The piezoresponse image (Figure 3b) proves that the structures deposited in a controlled manner are also ferroelectric and exhibit piezoelectric hysteresis (not shown here).

![Figure 3. Piezoresponse characterization of BaTiO$_3$ structures: (a) topography, z-scale 100 nm. (b) z-piezoresponse image showing the ferroelectric domains with a component out-of-plane.](image)

4. Conclusion

We have deposited the ferroelectric materials BaTiO$_3$ and BiFeO$_3$ in the form of mesoscopic (sub-micron size) structures by room-temperature PLD. Upon a thermal treatment the structures crystallized into the ferroelectric phase, as demonstrated by piezoresponse force microscopy. Formation of structures at desired location was also achieved, by using a nanostencil mask.

References

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