Mask assisted fabrication of nanoislands of $BiFeO_3$ by ion beam milling.

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Abstract

We report on a low-damage method for direct and rapid fabrication of arrays of epitaxial $BiFeO_3$ nanoislands. An array of aluminium dots is evaporated through a stencil mask on top of an epitaxial $BiFeO_3$ thin film. Low energy focused ion beam milling of an area several microns wide containing the array-covered film leads to removal of the bismuth ferrite in between the aluminium-masked dots. By chemical etching of the remaining aluminium, nanoscale epitaxial bismuth ferrite islands with diameter ~250 nm were obtained. Piezoresponse force microscopy showed that as-fabricated structures exhibited good piezoelectric and ferroelectric properties, with polarization state retention of several days.

Introduction

Multiferroic $BiFeO_3$ (BFO) holds promise for utilization in device applications, given its ferroelectric and antiferromagnetic ordering at room temperature, with high polarization values (~100 $\mu C/cm^2$)[1]. Due to its rhombohedral structure, the polarization vector lies along the $[111]_{pseudocubic}$ axis and the antiferromagnetic planes orthogonal to it. Thus, given the coupling between the two ferroic orderings, polarization ferroelastic switching leads to rotation of the antiferromagnetic planes [2]. In this regard, it has been reported that this kind of switching is unstable in monodomain BFO thin films, while it is stabilized in micron sized islands [3] due to removal of mechanical constraints. Although the evolution of functional properties in epitaxial BFO thin films has been investigated in relation with film thickness reduction [4], to date there appear to be no studies with respect to the effect of decreasing lateral size. The performance of such work has been hindered by difficulty of fabrication of high quality BFO nanoislands. Fabrication methods based on bottom-up approaches, successfully employed for size effects studies in other ferroelectric materials [5][6][7], are quite challenging in the case of BFO, given the complexity of its phase diagram [8]. Therefore top-down methods have been recently developed for production of nanostructures in BFO, such as use of focused ion beam (FIB) milling followed by double step annealing procedure [9] leading to ferroelectric islands down to a minimum of 250nm in lateral size. Another method is based on differential etching of prepoled polarization patterns [10] giving the possibility of producing islands down to 170nm in diameter but with rounded lateral profile and no complete separation from the surrounding material of the film.

Here we report on a focused ion beam (FIB) milling method to fabricate arrays of nanostructures starting from continuous bismuth ferrite thin films. Using this method we have so far produced BFO islands with flat top surfaces and lateral sizes down to 250nm. These structures preserved ferroelectric properties with switchable polarization and exhibit retention of polarization state at least for several days. With further development of our technique, we expect to be able to produce islands <100nm in size.

Experimental setup

Epitaxial BFO thin films were grown by pulsed laser deposition (PLD) on vicinal $SrTiO_3$(100) substrate, with a layer of $SrRuO_3$ as bottom electrode. The films show good ferroelectricity, with out of plane polarization ~60 $\mu C \cdot cm^{-2}$ [11]. Arrays of 45 nm thick aluminium dots were evaporated on the BFO through stencil masks with aperture diameter of 400 nm (Figs.1a,1b) [12]. A focused ion beam (FEI Nova Nanolab 600) with gallium ions was used to mill large areas of the sample covered by Al dots (Fig. 1c). The FIB process was executed with a 5 kV accelerating voltage and a current of 1.6 pA. Chemical etching of the remaining Al was performed in 10% aqueous solution of potassium hydroxide (KOH), at room temperature for durations up to 90 s (Fig.1d).

The ferroelectric properties of the islands were investigated by piezoresponse force microscopy (PFM), using a commercial atomic force microscope (MFP-3D Asylum Research). The vertical PFM signal (VPFM) was extracted via the in-built lock-in, and the lateral PFM (LPFM) via an external lock-in amplifier (SR830-DSP Stanford Research Systems). PFM imaging was typically performed with a 1 V modulation voltage at a frequency of 25 kHz applied from the atomic force microscope probe, used as a movable top electrode, and with the bottom $SrRuO_3$ electrode grounded. Switching properties were investigated by remanent hysteresis loops detecting the d_{zz} (piezoresponse in the out of plane direction) while ramping the DC voltage applied from the probe [13].

Results and discussion

The results shown here are obtained on islands fabricated on a 35 nm thick BFO film, by use of Al sacrificial dots evaporated through a stencil mask containing an array of holes with diameter ~400 nm. The Al islands that resulted had a height ~45 nm and a rounded profile with diameter ~500 nm at the base reducing to ~250 nm at half height. The 5×5 μm^2 area of BFO film covered by the dot array was then etched by low energy FIB milling. A beam energy of 5keV and current of 1.6pA were selected to minimize the ion implantation damage that might occur during this island definition step, in which the BFO is etched in the regions between the Al dots. The reason for this choice of ion beam parameters is discussed later in this letter. AFM measurements confirmed that after this step, the depth of material that had been etched was 35 nm and the islands of BFO capped with Al had their diameter at half height reduced to 190 nm. Subsequently performed chemical etching of the Al dots produced arrays of BFO islands with 35 nm height and diameter at half height of 250 nm (Figs.2 and 3). All the islands investigated showed piezoresponse right after the removal of the Al sacrificial layer, as shown in Figs.2 and 3 by PFM investigations. Fig.3 shows PFM images of a single dot, from which the top surface of the dot is proved to preserve a low roughness, comparable with the one of the parent film (Figs.3a and 3b). The low roughness is important, because scanning probe techniques applied for characterization of functional properties are sensitive to cross-talk signals from topography. Phase images of the VPFM and LPFM (Figs.3c and 3d) show that the BFO island has domains of different polarization, with prevailing downward direction for the vertical component of the polarization, as for the parent film.

Local piezoresponse hysteresis loops measurements show that the polarization of the islands is switchable (Fig. 4a) proving that ferroelectricity is retained. Comparison with loops measured on the parent film show a change in the sign of the imprint along the voltage axis and the appearance of an offset along the d_{zz} axis for the loop acquired on the islands. Both behaviors may be due to defects at the BFO/SRO interface and on the sidewalls of the islands, shifting the coercive voltage values by modification of the internal bias field [4], and pinning the polarization at the interfaces [14]. This pinning effect is very much reduced compared to that for 250 nm islands obtained by direct FIB milling of BFO at the most commonly used accelerating voltage, 30 keV [9]. This proves that the defective pinned volume of the BFO structures is much reduced by the new developments to our technique, since such volume is not large enough to lead to a complete polarization pinning through all the structure.

In order to investigate retention properties, a scan over the area of a single island was performed while applying from the probe a DC voltage of -3 V. This resulted in reversal of the vertical polarization component leaving un-reversed only a few small areas at the perimeter of the structure, as can be observed from Fig.4c. Investigations performed three days after poling (Fig.4d) showed some partial polarization reversal on the islands propagating from regions that could not be reversed originally. Still this phenomenon is marginal, giving evidence of good retention properties over the islands.

The preservation of ferroelectric properties in FIB processed nanoislands, without the need for post fabrication treatment, and their low surface roughness shows that the developed patterning technique is highly effective in preventing damage to the atomic lattices of the two oxide layers, the BFO and SRO. When using conventional FIB subtractive patterning with 30keV Ga+ ions to nanostructure functional oxides, two main problems arise (a) redeposition of the milled material, in our case upon the island top and side surfaces and (b) material amorphization and Ga penetration both occurring at distances up to 80.4 nm from our island edges in BFO [15]. Our initial investigations showed that the first problem could be addressed by utilizing a sacrificial Al layer on top of the BFO during 30keV direct FIB subtractive patterning to define nanoislands. Etched material that was re-deposited on top of the islands during definition was easily removed afterwards by chemical etching of the Al layer[16]. The second problem was tackled by utilizing lower ion beam energies; modern FIB ion columns can operate in the range from 30keV down to 5keV (or even as low as 2keV). Correspondingly, the penetration depth of Ga+ ions, and damage resulting at the edges of the islands, is predicted to be reduced to 30.6 nm [15]. However in using a low keV beam there is a major drawback. The best spatial resolution available for direct write patterning degrades as the beam diameter increases from ~7nm at 30keV to 100's nm at the lowest keVs, meaning that fine-scale direct patterning is not possible for the latter. In our technique, the ability to define fine-scale features was regained through forming a sacrificial array of Al nano-islands by shadow mask deposition which acts both as an etch mask for the physical sputtering performed by the 5 keV Ga+ ion beam and, as described above, as a protector against redeposition.

Conclusion

In summary, we report on a method to fabricate arrays of ferroelectric BFO nanostructures by employing low energy focused ion beam milling combined with the use of a patterned aluminium sacrificial layer. The obtained islands have a well defined circular shape of 250 nm diameter and 35 nm height, with flat top surface. PFM investigations reveal full preservation of ferroelectric properties, with multidomain polarization pattern over the area of each island. Piezoresponse hysteresis loops demonstrate switchable polarization, though with imprint behavior, deriving from presence of defects located probably at the electrode/BFO interface and on the sidewalls of the islands. However, the defects do not inhibit the overall polarization switching. Moreover, after reversing the polarization in single 250 nm islands, the backswitching observed after several days was minimal, propagating from the initially unswitched areas, attesting good retention properties.

Such a procedure for fabrication of arrays of BFO nanoislands will allow studies of the influence of size effects on the functional properties of BFO. We see opportunities for even more improvement of the presented technique that should further reduce fabrication-induced damage and enable the definition of structures with lateral size smaller than 100 nm and increased aspect ratio.

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Figure captions

FIG. 1 (Color online) Schematic diagram of the procedure performed in order to fabricate BFO nanostructures. (a) Al evaporation through stencil mask over the BFO; (b) mask lift off resulting in an array of Al dots on the film; (c) ion beam milling, yielding BFO islands capped with Al; (d) Al chemical etching resulting in BFO nanoislands

FIG. 2 (Color online) PFM imaging of the array of BFO islands: (a) topography, VPFM (b) phase and (c) amplitude, and LPFM (d) phase and (e) amplitude. Image size is 4.5 μm × 4.5 μm. Color coding for VPFM (LPFM) phase images displays bright contrast meaning vertical (lateral) polarization component pointing outwards (leftwards) the image. PFM modulation voltage with amplitude of 1 V at 25 kHz frequency was applied for imaging.

FIG. 3 (Color online) PFM imaging of one single BFO island: (a) topography, (b) line profile, VPFM (c) phase and (d) amplitude, and LPFM (e) phase and (f) amplitude. Image size is 500 nm × 500 nm. Color coding for VPFM (LPFM) phase images displays bright contrast meaning vertical (lateral) polarization component pointing outwards (leftwards) the image. PFM modulation voltage with amplitude of 1 V at 25 kHz frequency was applied for imaging.

FIG. 4 (Color online) (a) Local remanent piezoresponse hysteresis plots as resulting from measurements performed on an island (triangles) and on an area of the parent film (squares). Retention measurements on an island: (b) topography, (c) VPFM phase after poling a 300 nm × 300 nm area by applying -3V DC from the AFM tip, and (d) VPFM phase three days later. Image size is 500 nm × 500 nm. Color coding for VPFM phase images displays bright contrast meaning vertical polarization component pointing outwards the image. PFM modulation voltage with amplitude of 0.5 V at 25 kHz frequency was applied for imaging.