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Fabrication of high-density BiFeO₃ nanodot and anti-nanodot arrays by anodic alumina template-assisted ion beam etching

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Abstract
Efficient and cost-competitive fabrication of high-quality ferroelectric and multiferroic nanostructures is of general interest. In this work, a top-down nano-patterning technique is developed by the Ar⁺ ion beam etching in combination with the sacrificed ultrathin anodic alumina (AAO) mask. This technique is demonstrated by preparation of the epitaxial BiFeO₃ (BFO) nanostructures of various geometries, including nanodot and anti-nanodot arrays. The lateral dot size is as small as ~60 nm and an ultrahigh dot density of ~60 Gbit/inch² is achieved. It is revealed that the etching process involves sequential shape evolution of both the AAO mask and the underlying BFO film, resulting in the nanodots and anti-nanodots arrays of various geometries. The as-etched BFO nanodots array exhibits well-established ferroelectric domain structures and reversible polarization switching, as examined by piezoresponse force microscopy (PFM). It is suggested that this technique is extendable to fabrication of a wide range of functional oxide nanostructures for potential nanoelectronic applications.

Keywords: nano-patterning, ferroelectrics and multiferroics, nanodots array

1. Introduction

Ferroelectrics and multiferroics have been extensively investigated due to their rich physical properties and a number of application potentials in high-density memory, electromechanical sensors/actuators, spintronic devices, etc [1–8]. The high stability of ferroelectric polarization against spatial scale-down to ~5 nm allows the possibility for achieving ultrahigh data storage density of 30 Tb/inch² using ferroelectric memory [9]. This is far beyond the storage limit of conventional ferromagnetic media and one order of magnitude higher than that of commercial solid-state random access memory. Ferroelectric/multiferroic memory exhibits the advantages of non-volatility and ultra-low energy consumption, motivating substantial efforts in fabricating ferroelectric/multiferroic nanostructures, in particular the nanoscale ordered arrays. Along this line, the prominent size and surface effects often result in unique physical properties

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unavailable in the film or bulk counterparts, further adding to the interest of nanostructured ferroelectrics/multiferroics. For instance, BiFeO$_3$ (BFO) nanoparticles show strongly size-dependent photocatalytic, magnetic, and magnetoelectric properties [10–12]. Hence, it will be of both scientific and technological interest to fabricate high-quality nanostructures with the novel physical properties and functional performances.

A wide variety of fabrication techniques for nanostructures have been developed in the past decade, as summarized by Han et al [13]. Among them, the top-down approaches like focused ion beam (FIB) milling and electron beam direct writing (EBDW) [14–16], enable good control of the shape and size of nanostructures but their efficiencies are typically low. The bottom-up approaches like the self-assembly method have also been attempted. While epitaxial structures can be obtained, large-area and high-density ordered features are not easily accessible [17–20]. In this sense, modified bottom-up approaches (mask-assisted film deposition) such as anodic alumina (AAO) membrane mask or copolymer template methods combine the advantages of both top-down and bottom-up techniques, and thus they can produce well-ordered nanostructures [21–28]. In particular, the AAO template technique has been widely applied in the fabrications of ferroelectric nanodots. For instance, Hyun et al modified the AAO template method and obtained well-ordered and large-area epitaxial BiFeO$_3$ nanodots [29]. Nevertheless, these AAO template-based approaches usually require a narrow deposition parameter window or a post-annealing process at high temperature in order to improve the materials’ crystallinity, making it difficult to achieve good epitaxy and to avoid undesired shape variations. Besides, it is also very difficult for this method to achieve geometric shapes other than nanodots, e.g., nanorings or anti-nanodots. Therefore, an effective approach of fabricating geometrically controllable, structurally epitaxial, and ultra-high density ferroelectric/multiferroic nanostructures remains to be developed.

In this work, we propose an efficient top-down strategy for patterning well-ordered oxide nanostructures by Ar$^+$ ion beam etching in combination with AAO membranes of controlled thickness (~250 nm). Here, the well-patterned AAO membrane acts as the sacrificing mask stacked onto the epitaxial oxide thin film. Then the Ar$^+$ ion beam etching is performed onto the stacked structure to fabricate the nanoarrays. Although there have been some efforts combining the mask and etching techniques [30, 31], a similar approach has never been reported so far. By properly choosing the etching time and beam dose, one is able to prepare a series of nanodots or anti-nanodots arrays with good shape and dimension controllability. As an example to demonstrate this strategy, multiferroic BiFeO$_3$ (BFO) is used and its nanodots and anti-nanodots arrays have been successfully synthesized. The reason to choose BFO is because it is a well-known room temperature multiferroic offering the excellent ferroelectric, optoelectronic, and magnetoelectric properties among many others [32, 33]. We then present a series of characterizations on the morphologies and structures of as-prepared BFO nanodots and anti-nanodots arrays, and their ferroelectric properties including domain structures and polarization reversal behaviors. It will be suggested that this efficient, well-controlled, and cost-competitive technique is certainly extendable to fabricate other functional oxide nanostructures as a complimentary to the conventional lithography techniques.

2. Experimental details

The fabrication procedure of BFO nanostructures using the top-down method is illustrated in figure 1, which involves three main steps: (i) deposition of thin films by pulsed laser deposition (PLD) on SrTiO$_3$ (STO) substrates (figure 1(a)), (ii) transfer of the AAO mask to the film surface (figure 2(a)), and (iii) ion beam etching (figure 3(a)). In the first step (figure 1(a)), the epitaxial BFO thin films of ~40 nm in thickness together with ~10 nm thick epitaxial SrRuO$_3$ (SRO) layers were deposited on the (001)-oriented STO substrates. Then the thin AAO membrane masks of ~250 nm in thickness with periodically ordered pores of ~60 nm in pore size were smoothly transferred onto the film surfaces in a liquid environment. The details of the AAO mask fabrication can be found in earlier literature [34] as well as the online supplementary data.
Subsequently, both the AAO membrane and the films underneath were etched by the Ar\(^+\) ion beam for various etching durations. Finally, the AAO membranes were mechanically removed by using adhesive tape, leaving the as-prepared BFO nanostructures.

The as-prepared BFO thin films and nanostructures were examined by atomic force microscopy (Asylum Cypher AFM) and scanning electron microscopy (SEM, Zeiss Ultra 55). To characterize the epitaxy and crystallinity of the as-prepared nanostructures, high resolution transmission electron microscopy (HRTEM, JOEL-2011) and x-ray diffraction (XRD, PANalytical X’Pert PRO) were also performed. The ferroelectric domains and polarization reversal behaviors were characterized by piezoresponse force microscopy (PFM, Asylum Cypher).

3. Results and discussion

Figure 2 shows the AFM and SEM morphologic images for the as-etched BFO nanostructure arrays produced for different etching durations: 5 min (a), 10 min (b), 20 min (c), and 25 min (d).

![Figure 2](image)

**Figure 2.** AFM and SEM topographic images for the respective BFO nanostructure arrays produced for different etching durations: 5 min (a), 10 min (b), 20 min (c), and 25 min (d).

![Figure 3](image)

**Figure 3.** SEM images and schematic diagrams illustrating the morphology evolution of AAO mask for different etching durations: 5 min (a), (e), 10 min (b), (f), 20 min (c), (g), and 25 min (d), (h). The dark contrast in the above figures stands for pores or empty space.

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identical AAO masks were used. In order to explore the underlying mechanisms, we look into the morphologies of the AAO masks after etching for different durations, as shown in figures 3(a)–(d). It turns out that the AAO surface evolves in sequence from well-ordered holes array to ordered dots array. At the initial stage of etching (5 min), it seems that the Ar⁺ ion beam passes through the holes of the mask and creates holes on the BFO surface, which leads simultaneously to the re-deposition of the ablated BFO on the rings surrounding these holes (see figures 3(a), (e)). As the etching goes on (10 min), the ion beam makes the holes in both the mask and the BFO film larger, and concurrently removes the re-deposited BFO rings. As a result, the holes arrays (antidots array) are generated (see figures 3(b), (f)). At the etching stage after 20 min, the circular holes are further enlarged, leading to gradual collapse of the ordered holes array via the AAO wall disintegration, thus reshaping the holes array into nanodot chains (see figures 3(c), (g)). In this stage, the BFO film underneath the AAO mask evolves into the nanodot chains or nanodots array (see figure 2(c)). When the etching time extends to 25 min, the AAO mask eventually evolves into the nanodots array (see figures 3(d), (h)). This sequence offers us

Figure 4. TEM cross-section image and XRD diffraction pattern for a BFO nanodot sample. (a) Cross-section TEM images, (b) magnified cross-section image for a selected area (the square region in (a)), inset images shows the selected area FFT transformation patterns for both the BFO layer and STO substrate (the square regions in (b)), and (c) the XRD diffraction pattern for the whole specimen of the BFO nanodots.

Figure 5. PFM images for a BFO nanodot array: (a)–(c) The PFM amplitude and phase images superimposed with their corresponding 3D topographic image before (a), and after applying the first (b) and second (c) pulsed bias voltages via AFM probe on selected nanodots; (d), (e) local piezoresponse hysteresis loops acquired on a single BFO nanodot: the amplitude-voltage (d) and phase-voltage (e) piezoresponse hysteresis loops.
opportunities to obtain various BFO nanostructures whose geometries and sizes can be controlled by varying the etching duration if the dose is pre-assigned.

The microstructure of the BFO nanodots is examined carefully using the high-resolution TEM (HRTEM) technique and the typical images are shown in figures 4(a)–(b). First, the BFO and SRO layers in each nanodot show well-developed single crystal structures, and the STO/SRO and SRO/BFO interfaces are sufficiently sharp, as shown in figure 4(b). The fast Fourier transformation (FFT) patterns using the selected area HRTEM data (square area), as shown in figure 4(b), reveals a good epitaxy of the nanodot. The epitaxial structure can be further confirmed by the XRD θ-2θ pattern (figure 4(d)) where the (00l) reflections from the BFO, SRO and STO are detected. From our FFT pattern and XRD results, the average a-axis and c-axis lattice constants of the BFO layer are ~0.39 nm (similar to that of STO), and ~0.402 nm, respectively, indicating that BFO is compressively strained.

The ferroelectric domain structures of the as-prepared BFO nanodots and anti-nanodots can be evaluated by the PFM images. The 3D topographic image for a nanodot array superimposed onto its vertical amplitude and phase maps, as well as piezoresponse phase-voltage and amplitude-voltage loops are given in figure 5. It is identified that most nanodots exhibit uniformly bright contrast in the phase image and the rests show uniformly dark contrast or mixed contrasts. The dark contrast in the phase image implies the upward polarization and the bright contrast corresponds to the opposite orientation. This indicates that the as-fabricated samples prefer a downward
polarization. To study the domain switching behaviors of the nanodomain structures, we apply local pulsed voltages on the individual nanodots (cycled nanodot) via the PFM probe. It is revealed that the nanoscale domain of the nanodots can be partially switched from downward polarization to upward at an applied pulsed voltage of $-7$ V (figure 5(b)). Once the voltage reaches to $-8.5$ V, the domains can be completely switched upwards, and the switching is reversible at $\pm 8.5$ V.

The local piezoresponse hysteresis loops measured on this nanodot are plotted in figures 5(d), (e), where a square piezoresponse phase-voltage loop and a butterfly like amplitude curve are obtained, which confirms the typical polarization reversal behavior. The loops also exhibit an asymmetric shape to some extent, characterized by a horizontal shift. This suggests a preferred polarization orientation or an imprint behavior, which may arise from the possible built-in-voltages originating from different work functions of the probe tip (Pt) and the bottom electrode (SRO).

In additional, the PFM study is also conducted for a region of the anti-dot array to check the spatial homogeneity of the polarization reversal. The results are summarized in figure 6. The topography image of a randomly selected region is presented in figure 6(a) where the black contrast marks the holes. The region is divided into two columns. The left and right columns are written by electric voltages of $+6$ V and $-6$ V, respectively. After the electric writing, the as-generated amplitude and phase images are shown in figures 6(b) and (c), respectively, while the measured amplitude and phase loops are plotted in figure 6(d). It is clearly shown that the electric writing/poling makes the phase image in the left column bright (downward polarization) and that in the right column dim (upward polarization), indicating that all the anti-dots can be homogeneously switched.

To this stage, the template-assisted ion beam etching strategy reported in this work has been demonstrated to be effective to fabricate BFO nanostructures with various shapes and preserved ferroelectricity. The advantages of this strategy are summarized as follows. First, the nanodots/anti-nanodots arrays are directly patterned from high quality epitaxial films, and one has the reason to believe that the arrays are of high crystallinity quality as well. Second, the Ar$^+$ beam is a clean etching source, avoiding impurity doping during the etching process, different from the FIB method [31]. Third, this technique enables tailoring the geometric parameters of nanodots by properly adjusting the processing parameters, such as thin film thickness, hole size of AAO template, and etching duration and dose. These ferroelectric nanostructures may allow us to further explore their unique functional properties, including topological domain structures, resistive switching, and magnetoelectric couplings. With no doubt, this technique does not show much selectivity of materials and properties and it should be quite a general approach to be expanded to fabrications of a wide range of oxide materials for various applications.

4. Summary

In summary, an AAO template-assisted ion beam etching technique for fabricating large-area well-ordered ferroelectric/multiferroic nanodots and anti-nanodots arrays have been developed and successfully employed to prepare a series of BFO nanostructures. This technique makes use of the AAO membrane masks stacked onto the pre-etched BFO thin films, allowing a controllable synthesis of BFO nanostructures including nano-ring like structure, nano-antidots array, nanodot chains, and nanodots array, by adjusting the Ar$^+$ ion beam etching duration. The as-etched BFO nanostructures and anti-nanodots arrays are demonstrated to exhibit well-oriented epitaxial structures and sharp interfaces with the bottom SRO electrode layers. In addition, well-developed ferroelectric domains and reversible polarization switching are revealed. This technique is expected to be applicable to fabricate a wide range of functional oxide nanostructures with adjustable shape, size, pixel density, and functional properties.

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