Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Fabrication of epitaxial ferroelectric $BiFeO_3$ nanoring structures by a two-step nano-patterning method

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ARTICLE INFO

Keywords:
$BiFeO_3$
Ferroelectric
Nanodot
Nanoring
Ion-beam etching

ABSTRACT

A novel two-step nano-patterning method is proposed to fabricate epitaxial ferroelectric $BiFeO_3$ (BFO) nanoring array, which maintains well-epitaxial structure and possesses strong ferroelectricity demonstrated by X-ray diffraction (XRD) and piezoresponse force microscopy (PFM). The ferroelectric polarizations were examined by PFM, revealing the reversible switching behavior under an electric field. This novel method could also be extended to other oxide material systems. The fabrication of high quality ferroelectric nanoring structure provides the possibility to explore novel functionalities (e.g., ferroelectric vortices) and offers application potentials for the high-density non-volatile memory devices.

1. Introduction

In 1994, Gorbatsevich [1] and Grimmer [2] reported the possible existence of a unique domain structure called vortices or toroidal ordering in ferroelectrics. In recent years, ferroelectric vortices are attracting much attention both for the study of the emerging fundamental physical phenomena as a new state of matter and due to potential applications in ultra-high density memory "bits" applications [3–8]. So far, there is tantalizing experimental evidence for vortices (or closure structure) in ferroelectric nanodots [9–11], paraelectric/ferroelectric superlattices [6] or as a transient state during switching in thin films [4,9,12,13]. However, it is difficult to observe static ferroelectric vortices due to the tremendous disclination strain in the core [5,14]. The theory study [3] predicted that the ferroelectric vortices could be stabilized in the nanoring structure as the release of the strain energy in the core, which sheds light on the path to explore the ferroelectric vortices. The ring structured multiferroics are also promising for a range of fascinating phenomena such as multiferroic toroidal orders and magnetoelectric couplings.

Nevertheless, unlike the great progress in the fabrication methods of ferroelectric nanodots, such as focused ion beam (FIB) milling, electron beam direct writing (EBDW), anodized alumina (AAO) template-assisted ion beam etching and self-assembly, etc [11,15–19], the fabrication approaches of ferroelectric nanorings are less successful. Compared to the well-studied metallic nanorings [20–23], ferroelectric oxides are very difficult to be patterned into the ring structure by conventional lithography method. Zhu et al. [24] have attempted to fabricate lead zirconium titanate (PZT) nanorings by template assisted wet chemical solution deposition method and Byrne et al. [25] prepared PZT nanorings using a self-assembly technique, while these nanorings are polycrystalline and the ferroelectricity was not reported. Han et al. [26] prepared epitaxial PZT ring-like structure using the laser interference lithography process combined with pulsed laser deposition (PLD), nevertheless the rings exhibits very poor epitaxial quality with some impurities. Therefore, the difficulties in fabrication of high quality epitaxial ferroelectric nanorings have hindered the study of the unique exotic domains and the realization of high-density memory device applications.

In this study, we report an effective two-step nano-patterning method to fabricate well-epitaxial ferroelectric nanorings by patterning high quality ferroelectric films with top-down technique, which is different from the AAO template-assisted pulsed laser deposition and ion beam etching method we proposed very recently [27].. We choose the multiferroic $BiFeO_3$ (BFO) epitaxial thin film grown by pulsed laser deposition (PLD) as the starting material for its strong ferroelectricity [28–30], rich domain structures [31–33], various phase transitions [34–36] and superior magnetoelectric couplings [37–40]. Ordered BFO nanoring array with well-epitaxial structure and good ferroelectric properties is fabricated using this method, which makes it possible for investigation and manipulation of the refined polar domain structures.

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http://dx.doi.org/10.1016/j.ceramint.2017.08.188
Received 26 August 2017; Received in revised form 28 August 2017; Accepted 28 August 2017

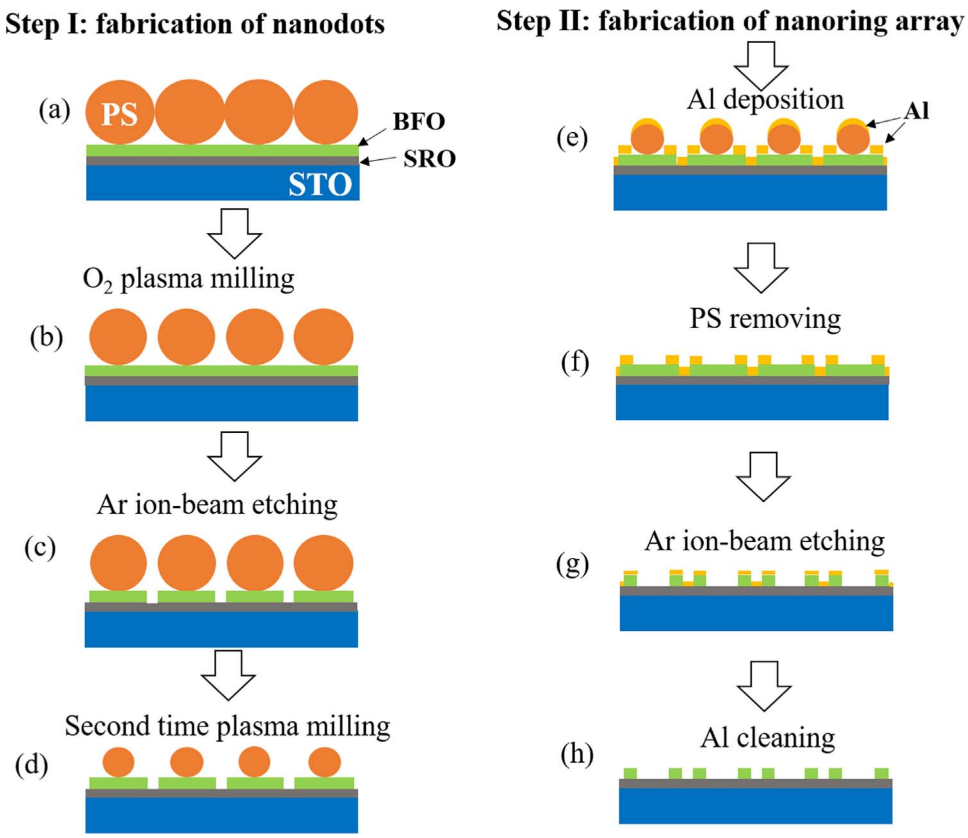

Fig. 1. Schematic diagrams of fabrication process of BFO nanoring structures: Step I, fabrication of nanodots (a–d): (a) monolayer PS transferring, (b) etching PS by O_2 plasma, (c) Ar ion-beam etching of BFO, (d) second time O_2 plasma milling to obtain smaller size PS; Step II, fabrication of BFO nanoring array (e–h): (e) Al deposition, (f) PS removing, (g) using Ar ion-beam etching to form nanoring structures, and (h) Al cleaning.

This method also paves a path for exploring the exotic domains structures (e.g. vortex topological domain) and promotes the realization of nanoscale electronic devices.

2. Experimental details

BFO epitaxial thin films (thickness ~ 40 nm) with 71° stripe domains grown by PLD on single crystal STO (001) substrate with $SrRuO_3$ (SRO, thickness ~ 50 nm) as the bottom electrode are used to fabricate nanorings in this work. The preparation procedures of BFO nanoring structure by a two-step nano-patterning method, including the fabrication of nanodots (step I) and the fabrication of nanoring array (step II), are illustrated in Fig. 1.

To fabricate BFO nanorings, nanodots are firstly produced by polystyrene spheres (PS)-assisted Ar ion-beam etching in Step I, as shown in Fig. 1a–d. First, the monolayer PS (diameter of the nanospheres ~ 500 nm) floating on the mixture of ethanol and water are transferred onto the epitaxial BFO thin film (Fig. 1a). Then, O_2 plasma etching is applied to obtain the isolated monolayer PS array and the size of PS are reduced to around 450 nm, as presented in Fig. 1b. Afterwards, the PS covered BFO thin film is etched by Ar ion-beam to produce the BFO nanodots, as shown in Fig. 1c. Next, O_2 plasma etching is used again to further reduce the size of PS around 250 nm (Fig. 1d) in order to be prepared for the fabrication of BFO nanorings in Step II (Fig. 1e–h).

To synthesize BFO nanoring array, a 12 nm-thick aluminum (Al) thin film is deposited as a mask layer by thermal evaporation, as shown in Fig. 1e. By cleaning the sample with chloroform and acetone, the PS are removed and Al nanoring array are produced (Fig. 1f). Then, Ar ion-beam is applied to etch the sample with appropriate etching time. The Al nanoring array is taken as a scarified mask layer during this process, so that the regions blocked by Al nanorings are protected while the rest areas are etched away. Thereby, the BFO nanoring structure is fabricated as presented in Fig. 1g. Following by cleaning the rest Al mask with NaOH solution, we successfully obtain the ordered BFO nanoring array (Fig. 1h).

3. Results and discussions

After the synthesis of BFO nanoring structure, atomic force microscopy (AFM) and scanning electron microscopy (SEM) are used to measure the topographies. To demonstrate the epitaxy and crystallinity of the nanoring structure, X-ray diffraction (XRD) θ–2θ scan and reciprocal space mapping (RSM) are performed. The ferroelectric properties and polarization reversal behaviors are also characterized by piezoresponse force microscopy (PFM).

To better understand the morphology evolutions in the fabrication process of BFO nanoring array, topography images in some key steps are captured by AFM and SEM, as shown in Fig. 2. The AFM image in Fig. 2a shows the morphology of the sample after O_2 plasma etching (corresponding to Fig. 1b), demonstrating the formation of isolated monolayer PS nanodot array on the BFO thin film. Following the Ar ion-beam etching to synthesize BFO nanodots (Fig. 1c), second time O_2 plasma etching is applied and thus the PS nanodot (diameter ~ 250 nm) covered BFO nanodots (diameter ~ 450 nm) are fabricated, as presented in Fig. 2b which is in accordance with Fig. 1d. After the deposition of the Al thin film, the PS nandots are removed, leading to the production of Al nanorings (Figs. 1f and 2c). Al nanorings are taken as the mask during the following Ar ion-beam etching process (Fig. 1g). Ordered BFO nanoring array (with outer diameter around 400 nm, the width of ring wall around 70 nm, and the height of 15 nm) is obtained after the Al cleaning, as shown in Fig. 2d which is corresponding to Fig. 1h. These AFM images not only demonstrate the morphology evolutions during the synthesis process, but also prove that the two-step nano-patterning approach, proposed in this study, is effective to fabricate BFO nanoring structure. The corresponding SEM images are displayed in Fig. 2e and f, which are consistent with the morphologies in AFM images, further revealing the successful fabrication of ordered