Structural engineering of Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ epitaxial films

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1. Introduction

Ferroelectric thin films including BaTiO$_3$ (BTO), SrTiO$_3$ (STO) and (Ba, Sr) TiO$_3$ (BSTO) have received great attention because of their potential applications for various functional devices [1,2]. In BSTO films, the observed temperature ($T_c$) for the phase transition from paraelectric cubic to ferroelectric tetragonal and the stability of different phases depends on the microstructure and strain of the films. More significantly the peak in the temperature dependence of the dielectric permittivity is broader than that observed in bulk BSTO [3,4]. A broad peak in the dielectric response is desirable as the performance of the devices becomes less sensitive to temperature variations. Thus it is imperative to engineer a temperature-stable film to improve high-resolution transmission electron microscopy with temperature.

BSTO single-layered and BSTO/STO multilayered films exhibited broader phase transition and improved thermo-stability. The microstructure of these epitaxial films was investigated using high-resolution transmission electron microscopy in details. Misfit and threading dislocations were observed in the single-layered film, while threading dislocations were dramatically decreased and no misfit dislocations were found in the multilayered film. It is suspected that the difference in dislocation densities is responsible for the different behaviors of the permittivity with temperature.

2. Experimental details

1-μm-thick single-layered and multilayered films were epitaxially grown on a (001) LaAlO$_3$ substrate using PLD technique. As shown in Fig. 1, a single-layered epitaxial film was prepared using a single target of Ba$_{0.5}$Sr$_{0.5}$TiO$_3$, while the multilayered film with a periodic superlattice structure of BTO and STO layers with same thickness (~2 nm) was obtained using two stoichiometric targets of BaTiO$_3$ and SrTiO$_3$. The Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ target for the PLD system was made using a mixed oxide route [5], while ultra-pure (Alfa Aesar) powders were used for the preparation of the BTO and STO targets.

The thin films were grown by laser ablation (Neocera PLD system with a Lambda Physik KrF laser, λ = 248 nm) on a 5×5 mm$^2$ LaAlO$_3$ substrates. The substrates were secured by silver paste onto the stainless-steel resistive heater. The thin films were deposited from 20-mm-diameter stoichiometric targets of BaTiO$_3$, SrTiO$_3$ and Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ in an oxygen pressure of 40 Pa. The distance between the target and the substrate was 50 mm. The substrate temperature was kept at 750 K, and controlled using a thermocouple embedded in the heater during the deposition. The energy density of the laser spot (2×10 mm$^2$) was 2.5 J/cm$^2$. The film thickness was controlled by the number of pulses shot on the targets. From the sample thickness measured using a Dektak 11A, the film growth rate was 1 μm/min.
estimated to be 0.05 nm/pulse. The total number of pulses was 5000 with a repetition rate of 8 Hz. Once the ablation was over, the samples were annealed for 1 h in an oxygen rich environment (1.01325×10\(^5\) Pa) in order to reduce the oxygen vacancies, and then slowly cooled down to room temperature at a rate of 10°C/min.

The specimens for TEM examination were prepared in a cross-sectional orientation ([010] zone-axis for the LaAlO\(_3\) substrate) using conventional techniques of mechanical polishing and ion thinning. The ion milling was performed using a Gatan Model 691 Precision Ion Polishing System. The bright-field (BF) imaging, selected-area electron diffraction (SAED) and HRTEM examinations were carried out using a JEOL JEM 2100F transmission electron microscope operating at 200 kV.

The electrical measurements of both single layered and multilayered films in a temperature range between 100 K and 400 K were performed on a Janis research cryogenic probe station. Agilent 4287A RF LCR meter operating at 200 kV.

3. Results and discussion

The single-layered film had capacitance vs. temperature dependence typical for a BSTO film with a Ba/Sr stoichiometry of 50/50, while the multilayered film had an almost linear dependence with an increment of ~0.1 pF/°C. Detailed electrical properties of the single-layered and multilayered films have been reported in Ref. [3]. It has been found that the multilayered film with the same stoichiometry exhibits broader phase transition and improved thermo-stability [3,4]. The temperature dependence is consistent with the previous study [6] of the BTO/STO superlattice grown on Nb-doped STO substrate. The multilayered films have reduced temperature dependence of capacitance, which indicates that it is much more promising for device applications. In order to give a comprehensive understanding of the differences in the electrical properties, we carried out a detailed investigation of the microstructure using conventional TEM and HRTEM.

Fig. 2(a) is a cross-sectional BF TEM image of the single-layered sample, while Fig. 2(b) is a cross-sectional BF TEM image of the multilayered sample. These diffraction contrast images were taken under a two-beam condition with \(g = 200\). Inset in Fig. 2(a) shows a typical [010] zone-axis SAED pattern taken from the single-layered film. The upper inset in Fig. 2(b) shows a typical [010] zone-axis SAED pattern taken from the multilayered superlattice. The lower inset is an enlarged TEM image of the BTO/STO superlattice. This is consistent with the report of BSTO multilayered superlattices grown on Si substrates [7].

In order to clarify the nature of the defects, HRTEM was performed on both single-layered and multilayered films. Extensive HRTEM examinations showed that there are two kinds of dislocations in the single-layered sample while only one kind of dislocation exists in the multilayered film.

Fig. 3 shows an example of misfit and threading dislocations in the single layered sample. The misfit dislocation is shown in Fig. 3(a). Careful examination of Fig. 3(a) demonstrates that there is one extra half plane along the [101] direction and another extra half plane along the [101] direction near the interface regions, indicating that they belong to pure-edge type dislocations. The extra half planes are indicated by arrows for D1 and D2 in Fig. 3(a).

To determine the Burgers vectors for the dislocations, Burgers circuits are drawn to enclose the dislocations. It can be clearly seen from Fig. 3(a) that there is a gap between the starting and ending point in each Burgers circuit, which is indicated by an arrow. The Burgers vector for dislocations D1 is determined to be \(\frac{1}{2}[101]\). The Burgers vector for dislocations D2 is determined to be \(\frac{1}{2}[010]\). Fig. 3(b) shows an
example of a threading dislocation. The Burgers vector for this threading dislocation is determined to be $1/2 \langle 101 \rangle$, which belongs to a partial dislocation. Similar dislocations have also been reported in the single-layered Ba$_{0.75}$Sr$_{0.25}$TiO$_3$ epitaxial films [8]. Antiphase boundaries were also observed in the Ba$_{0.75}$Sr$_{0.25}$TiO$_3$ epitaxial film [9]. However, they have not been observed in the Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ epitaxial film.

Fig. 4 shows an HRTEM image of a perfect region in the multilayered film. It can be clearly seen from Fig. 4 that there is no misfit dislocation in the multilayered film. The darker regions are BTO layers, while the brighter ones are STO layers. The thickness of each layer is about 2 nm, which corresponds to a stacking of 5-layered BTO and 5-layered STO. The lattice parameters of the BTO and STO layers were measured by a quantitative analysis of the HRTEM images using Gatan DIGITALMICROGRAPH software. In the HRTEM images, the positions of the intensity maxima at each barium and strontium atom column (bright spots in Fig. 4) were taken to measure the lattice constants. The measured lattice parameters for BTO/STO superlattices and theoretical lattice parameters for bulk BTO and STO are shown in Table 1. By comparing the lattice parameters for the bulk and superlattices in Table 1, it can be deduced that STO develops a tetragonal distortion. It has been reported that STO in the BTO/STO superlattices could have an orthorhombic distortion [10–12].

From the above analyses, it can be seen that the defect states are clearly different in the single-layered and multilayered films. This is associated with the critical thickness for the formation of misfit dislocations. In order to determine the critical thicknesses for the formation of misfit dislocations in the single layered Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ and BTO/STO superlattices, Matthews–Blakeslee and other critical thickness models [13–15] have been used. The critical thickness for the single-layered film is calculated to be 2.62 nm, while for the BTO/STO superlattices, the critical thickness is calculated to be 4.62 nm. The single layered Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ film (1 μm) is much thicker than the critical thickness, while the superlattice layer (2 nm each layer) is thinner than the critical thickness. Therefore, the lattice mismatch between LaAlO$_3$ substrate and Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ single-layered film could only be released through the formation of misfit dislocations, while the lattice mismatch between BTO and STO superlattices can be accommodated by the lattice elastic distortion. That is why a lot of misfit dislocations are included in the single layered film, and no misfit dislocations are observed in the multilayered film. This might be one cause of the different behaviors of the permittivity with temperature in the single-layered and multilayered films.

In addition, it should be noted that STO layer in the multilayered film undergoes a tetragonal distortion. It was found that the dielectric properties of films were sensitive to the lattice distortion ratio $D = \text{in-plane lattice constant}/\text{out-of-plane lattice constant}$, and a

### Table 1

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<th>Materials</th>
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<td>$a$</td>
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<td>BTO superlattice</td>
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<td>BTO bulk</td>
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<td>STO superlattice</td>
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film under small tensile stress showed the largest dielectric permittivity and tenability [16]. Therefore, the tetragonal distortion of STO layer could be another cause of the improved thermo-stability for the multilayered film.

4. Conclusions

In conclusion, Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ single-layered and (BTO)$_5$(STO)$_5$ multilayered epitaxial films have been grown on a (001) LaAlO$_3$ substrate using single target and dual target PLD, respectively. Misfit and threading dislocations have been observed in the single-layered Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ film while only threading dislocations are found in the multilayered BTO/STO film. It is suspected that the difference in dislocation densities is responsible for the different behaviors of the permittivity with temperature.

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References