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# Structural evolution of dislocation half-loops in epitaxial $BaTiO_3$ thin films during high-temperature annealing

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$BaTiO_3$ thin films were grown on (001) $SrTiO_3$ by reactive molecular beam epitaxy. Transmission electron microscopy studies showed that there is a high density of dislocation half-loops inside 8- and 12-nm-thick films. By thermal annealing at 1000 °C, the isolated small dislocation half-loops grow and combine to form a self-assembled regular dislocation network at the film/substrate interface. Threading dislocations in the films are removed and the lattice mismatch strain in the film is nearly completely relaxed by annealing at high temperature. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1789233]

Epitaxial oxide thin film heterostructures have a wide range of applications in modern electronic and optical devices. The performance of the devices is strongly controlled by the strain and defect configurations in the epitaxial layers. Depending on the film thickness and growth conditions the lattice misfit strain can be relaxed by the formation of dislocations. Thus, knowledge about the nucleation, propagation, and interaction of misfit dislocations in strained epitaxial systems is crucial to the control of strain and defect configurations in the fabrication of devices.

Considerable work has been devoted to understanding the mechanism of strain relaxation by dislocations in epitaxial films.[1–4] Usually, a very thin epitaxial layer on a lattice-mismatched substrate is strained to maintain a coherent interface. At a critical thickness, the commensurate film breaks down and misfit dislocations begin to nucleate near the film surface and grow with further growth of the film. These dislocation half-loops may react with each other to form arrays at the film/substrate interface which will release the misfit strain. The driving force for the nucleation and growth of dislocation half-loops is the reduction of the total energy in the strained heterostructures. When the film is very thin, strain energy may be insufficient to drive the nucleation and growth of a high density of half-loops, especially for systems in which dislocation loops may be pinned by defects. This is particularly true for the growth of oxide thin films under high vacuum conditions where a high density of point defects such as oxygen vacancies exists during film growth. As a result, a high density of dislocation half-loops and inclined threading dislocations may exist in such thin films. A typical example is the dislocation configurations in thin $BaTiO_3$ films grown on (001) $SrTiO_3$.[5,6]

In this letter we investigate the effect of high temperature annealing on the structural characteristics of dislocation half-loops in thin $BaTiO_3$ films. We find that during annealing at high temperature, isolated half-loops grow and react with each other to form a self-assembled regular dislocation array at the film/substrate interface, as directly revealed by transmission electron microscopy (TEM) observations.

Epitaxial $BaTiO_3$ thin films with thicknesses of 8 and 12 nm were grown on (001) $SrTiO_3$ substrates by reactive molecular beam epitaxy. Details of the growth conditions as well as crystal structure data of the two materials can be found elsewhere.[6] Each as-grown film was cut into two pieces. One was directly used for TEM observations to examine the dislocation configurations in the as-deposited condition, while the other was annealed in air at 1000 °C for 2 h before investigation by TEM. Cross-sectional and planar-view TEM samples were prepared by mechanical polishing followed by argon ion milling (PIPS, Gatan, Inc.). The planar-view samples were ion-milled from the $SrTiO_3$ substrate side. Both a high-resolution electron microscope (JEOL4000EX) and an analytical electron microscope (JEOL2010F) were used for these studies. The surface morphology of both the as-grown and annealed films was measured by atomic force microscopy (AFM, Digital Instruments NanoScope IIIa) in contact mode.

A high density of dislocation half-loops were found in the 8- and 12-nm-thick $BaTiO_3$ films in their as-grown state, as shown in Figs. 1(a) and 2(a), respectively. These TEM images are bight-field diffraction contrast images obtained using a 110 reflection under two beam conditions.[7] The short dark-line segments were determined to be dislocation half-loops. The half-loop density in the 12-nm-thick film is higher than that in the 8-nm-thick film. The majority of the half-loops align along either of the two perpendicular [100] and [010] directions. The nucleation and growth of half-loops near the film surface continues to occur once the critical thickness has been exceeded. Generally speaking, the half-loops with different sizes are uniformly distributed in a random way throughout the film.

After annealing, regular dislocation arrays were observed in both the 8- and 12-nm-thick films, as shown in Figs. 1(b) and 2(b), respectively. The dislocation lines are along either the [100] or [010] direction of $BaTiO_3$. It appears that the dislocation array in the 12-nm-thick film is more regularly organized than that in the 8-nm-thick film.

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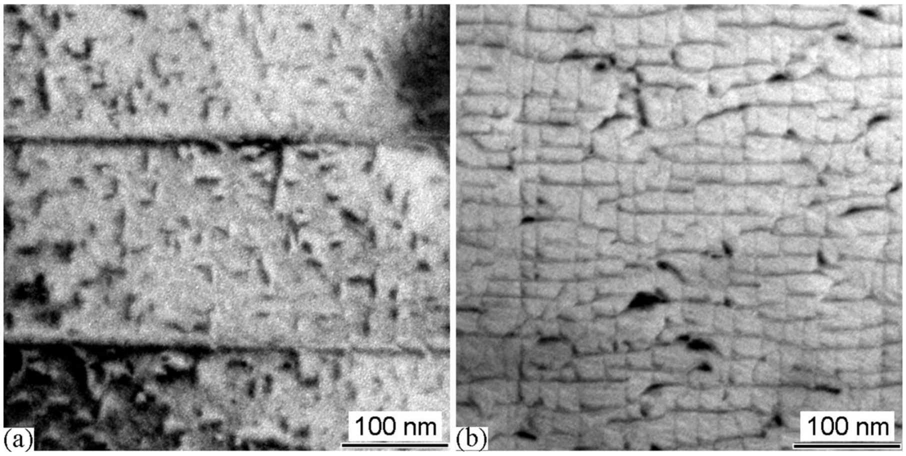

FIG. 1. Planar-view TEM images of the dislocation array in the 8-nm-thick $BaTiO_3$ film (a) before annealing and (b) after annealing.

Furthermore, the interfacial segments of the dislocations (misfit dislocations) are longer in the 12-nm-thick film than in the 8-nm-thick film. In the 8-nm-thick film many of the interfacial segments of the dislocations are short, implying the existence of threading dislocations that run from near the termination points in the array to the film surface. The average spacing between the dislocation lines in the array is about 20 nm for the 8 nm film and 18 nm for the 12 nm film. Both values are quite close to 17.7 nm predicted for a fully relaxed $BaTiO_3$ film grown on $SrTiO_3$, which has a lattice misfit at room temperature of 2.2%.[6] This indicates that during annealing at high temperature the misfit stain in a very thin $BaTiO_3$ film is nearly fully relaxed by the formation of a dislocation array through the growth and reaction of preexisting dislocation half loops.

Cross-sectional TEM images obtained from the same films corroborated the formation of the dislocation arrays seen in the planar-view specimens in Figs. 1(b) and 2(b). Figure 3 shows that the misfit dislocation array is located at the $BaTiO_3/SrTiO_3$ interface. The pitch of the array is in agreement with that measured from the planar-view samples. The inset in the upper right-hand corner of Fig. 3 is a high-resolution TEM image of a dislocation core. By drawing a Burgers circuit around the dislocation core, the dislocation was determined to be a [100]-type edge dislocation.

The above-noted observations can be described as the annealing-induced self-assembly of a regular array of misfit dislocations at the film/substrate interface from preexisting dislocation half-loops. Each dislocation half-loop is comprised of two threading dislocations and a segment of an edge dislocation (see Fig. 4). The threading dislocation segments are inclined or perpendicular to the interface, while the edge part is parallel to the interface. A half-loop is formed when certain atoms are removed from the (100) or (010) plane of the $BaTiO_3$ film (the hatched area in Fig. 4). Two or more half-loops may meet and react to form a long straight edge dislocation segment at the interface. The growth and combination of half-loops helps to relax the misfit strain. The threading dislocation portion of the half-loops does not contribute much to stain relaxation. Through such dislocation reactions during the annealing at high temperature, the

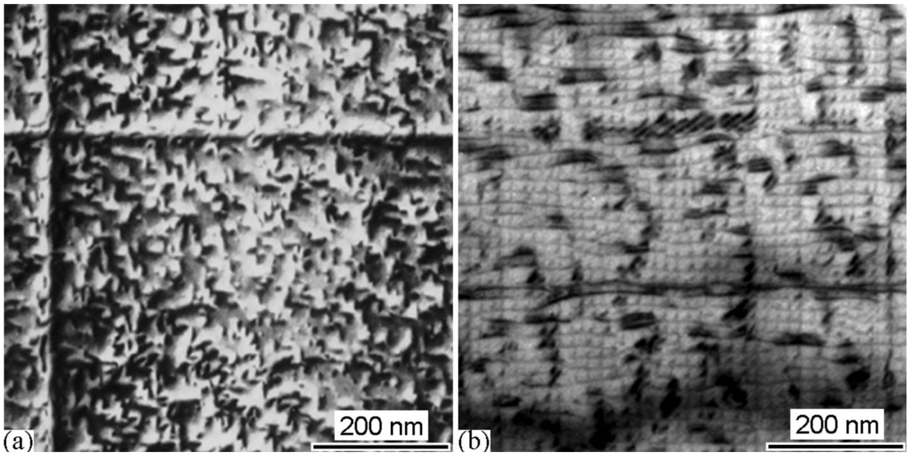

FIG. 2. Planar-view TEM images of the dislocation arrays in the 12-nm-thick $BaTiO_3$ film (a) before annealing and (b) after annealing.

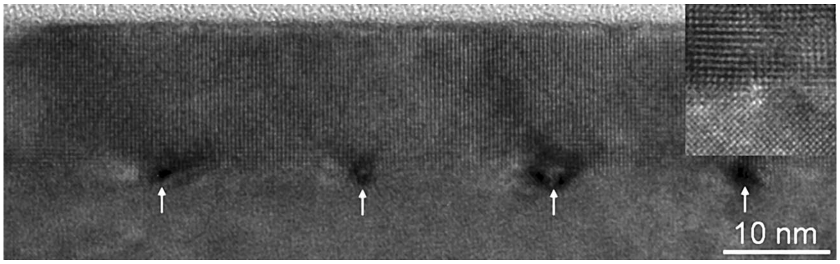

FIG. 3. Cross-sectional TEM view of the dislocation cores at the interface in the annealed 12-nm-thick $BaTiO_3$ film. The inset in the upper-right corner is an HRTEM image of a dislocation core showing a [100]-type edge dislocation.

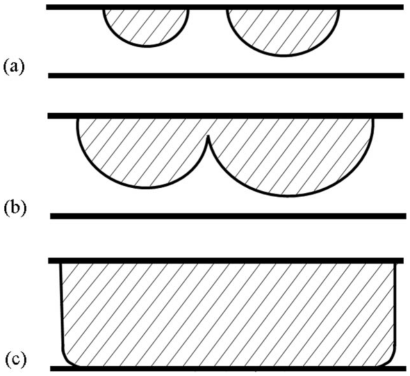

FIG. 4. Schematic depicting (a) nucleation, (b) growth, and (c) combination of dislocation half-loops in epitaxial $BaTiO_3$ thin films. The inclined portion of the half-loop is called a threading dislocation.

threading dislocations are annihilated from the film, improving the film quality.

Since the dislocation half loops are $\langle 100\rangle$-type edge dislocations, the growth and evolution of these dislocations to form a misfit dislocation array at the film/substrate interface proceeds through climb, which involves mass transportation about the dislocation cores. Since each half loop has two termination points at the film surface, the growth of the dislocations during annealing may change the surface roughness, particularly at the termination points of dislocation lines. This is confirmed by AFM studies conducted on the annealed $BaTiO_3$ films. Figures 5(a) and 5(b) are AFM images taken from the 12 nm $BaTiO_3$ film before and after annealing at 1000 °C. Before annealing, the rms roughness is 0.123 nm. After annealing it becomes 0.5 nm. These results show that, after annealing, the film surface becomes rougher than before. This is caused by the diffusion of material in the film to the film surface. As dislocation half-loops extend toward the film/substrate interface and react with other half-loops, atoms are removed from the core regions of the dislocations and diffuse toward the film surface. The diffusion of point defects may occur preferentially along the dislocation lines.

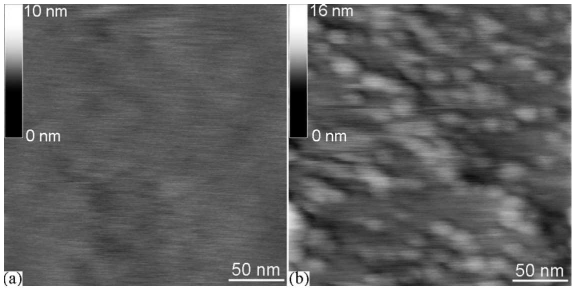

FIG. 5. AFM image of the surface of a 12-nm-thick $BaTiO_3$ thin film (a) before and (b) after annealing.

For a very thin film, the total strain energy is small and the growth temperature (700 °C) may not be high enough to overcome the activation barrier for dislocation motion and reaction. During annealing at higher temperature (1000 °C), however, the driving force for the atomic diffusion is significantly enhanced by the increase in thermal energy. Thus, the dislocation half-loops are able to grow and react with each other to form a self-assembled misfit dislocation array during annealing. A similar phenomenon was reported for Ge films grown on Si,[8] in which an ordered dislocation array forms only when the growth temperature is above 550 °C. The present work shows that postdeposition annealing at high temperature provides a way to remove half-loops and threading dislocations to improve the crystalline quality of the film. Such a treatment has been used to create $(Ba,Sr)TiO_3$ buffer layers of high crystalline quality with a desired lattice constant in the 0.39–0.4 nm range.[9]

In conclusion, a high density of preexisting dislocation half-loops in as-grown $BaTiO_3$ thin films grown at relatively low temperatures can be eliminated and transformed into a misfit dislocation array by annealing at high temperature. As a result, the lattice misfit strain in the epitaxial film is nearly fully relaxed by the formation of a self-assembled misfit dislocation array at the film/substrate interface. Furthermore, the threading dislocation density of the film is significantly reduced by annealing, improving its crystalline quality.

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