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Citation: [Applied Physics Letters](#) **91**, 252906 (2007); doi: 10.1063/1.2819684

View online: <http://dx.doi.org/10.1063/1.2819684>

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Interface structure and strain relaxation in BaTiO₃ thin films grown on GdScO₃ and DyScO₃ substrates with buried coherent SrRuO₃ layer

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(Received 24 May 2007; accepted 9 November 2007; published online 20 December 2007)

To obtain the electrical properties of strained ferroelectric thin films, bottom electrodes with lattice constants and thermal coefficients matched to both films and substrates are needed. The interface structure, strain configuration, and strain relaxation in such bilayer systems are different from those in single layer systems. Here, we report transmission electron microscopy studies of epitaxial BaTiO₃ films grown on GdScO₃ and DyScO₃ substrates with buried SrRuO₃ layers. We found that the different strain relaxation behaviors observed in the bilayer are mainly dependent on lattice mismatch of each layer to the substrate and the thicknesses of each layer. © 2007 American Institute of Physics. [DOI: 10.1063/1.2819684]

Barium titanate (BaTiO₃) thin films are widely used in modern electronic and optical devices, such as optical switches and modulators. It is well known that the properties of BaTiO₃ thin films and the performance of related devices are strongly dependent on thin film microstructures, strains, and defects.¹⁻³ On the other hand, the strain resulting from the mismatch in lattice constants and thermal expansion coefficients between the substrates and BaTiO₃ films can be used to manipulate the properties of the BaTiO₃. Strain in epitaxial thin films can be controlled by carefully choosing the structure and orientation of substrates and/or epitaxial buffer layers with suitable lattice constants and thermal expansion coefficients. Recently, a series of rare earth scandates (including DyScO₃ and GdScO₃) have been used as substrates for the growth of strained BaTiO₃ thin films because their lattice constants (considered as pseudocubic structure) and thermal expansion coefficients closely match those of BaTiO₃.^{4,5} Choi *et al.* reported the enhancement of Curie temperature of BaTiO₃ thin films from 400 °C when grown on GdScO₃ to 540 °C by using DyScO₃ as substrates (the Curie temperature of bulk BaTiO₃ is 130 °C). They also showed an increase in the remnant polarization in these strained BaTiO₃ thin films over that in bulk BaTiO₃.⁶ The key to the improvement of the physical properties in these BaTiO₃ thin films is the existence of a uniform strain induced by the coherently epitaxial growth on the rare earth scandate substrates. In contrast to the rich understanding of strain relaxation in semiconductor thin films,⁷ strain relaxation studies in perovskite oxide thin films have mainly focused on single layer films grown on substrates.⁸ To determine the electrical properties of epitaxial ferroelectric thin films, a bottom electrode such as epitaxial SrRuO₃ is required. The strain configuration and its relaxation mechanism in such bilayer and multilayer systems may be different from those in single epitaxial films. As yet, there are few reports on strain relaxation and defects in bilayer perovskite oxide

systems.⁹ Therefore, it is important to understand the strain relaxation phenomena of bilayer such as BaTiO₃/SrRuO₃ grown on substrates. In this paper, transmission electron microscopy (TEM) was carried out to study the microstructures, the interface structures, and defect configurations of epitaxial BaTiO₃ thin films grown on (110) GdScO₃ and (110) DyScO₃ substrates with buried coherent SrRuO₃ buffer layers. The strain relaxation in these BaTiO₃ films was addressed by thermodynamic equilibrium theory accounting for the thickness and lattice mismatch of each layer with respect to substrates.

Three epitaxial BaTiO₃/SrRuO₃ bilayer films with different thicknesses were prepared by pulsed-laser deposition: BaTiO₃ (200 nm)/SrRuO₃ (50 nm)/(110) GdScO₃, BaTiO₃ (50 nm)/SrRuO₃ (200 nm)/(110) DyScO₃, and BaTiO₃ (100 nm)/SrRuO₃ (100 nm)/(110) DyScO₃. Details of the growth condition and TEM observations have been described elsewhere.^{6,10}

Figure 1(a) shows a typical low-magnification cross-sectional bright-field image of a BaTiO₃ (200 nm)/SrRuO₃ (50 nm) bilayer grown on (110) GdScO₃. It shows that both BaTiO₃/SrRuO₃ and SrRuO₃/GdScO₃ interfaces are free of dislocations. The dark band at the BaTiO₃/SrRuO₃ interface is due to diffraction contrast at the interface. The atomic structures at the BaTiO₃/SrRuO₃ and SrRuO₃/GdScO₃ interfaces, with electron beam aligned along the [100] zone axis of BaTiO₃, are shown in Figs. 1(b) and 1(c), respectively. It can be seen that the both interfaces are fully coherent and atomically sharp.

Similar results were obtained from BaTiO₃ (50 nm)/SrRuO₃ (200 nm) bilayer grown on (110) DyScO₃. Figure 2(a) shows a cross-sectional TEM image in which both BaTiO₃/SrRuO₃ and SrRuO₃/GdScO₃ interfaces are free of dislocations. High-resolution transmission electron microscopy (HRTEM) images (not shown here) show the coherent, atomically sharp interfaces similar to Figs. 1(b) and 1(c). As the thickness of the BaTiO₃ layer increases, the interface between BaTiO₃ and SrRuO₃ becomes partially relaxed and misfit dislocations form at the interface. Figure

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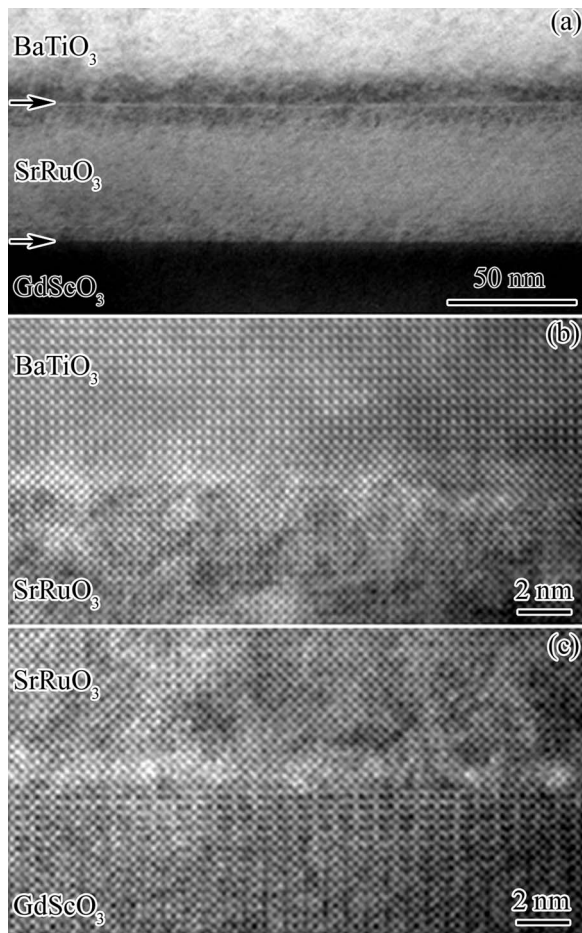


FIG. 1. (a) Cross-sectional TEM image of the BaTiO₃ (200 nm)/SrRuO₃ (50 nm) bilayer grown on (110) GdScO₃ showing the sharp interfaces between BaTiO₃ and SrRuO₃ as well as between SrRuO₃ and GdScO₃. The interfaces are indicated by arrows. (b) HRTEM image of the BaTiO₃/SrRuO₃ interface. (c) HRTEM image of the SrRuO₃/GdScO₃ interface.

2(b) is a cross-sectional image of a BaTiO₃ (100 nm)/SrRuO₃ (100 nm) bilayer grown on (110) DyScO₃. Dislocation cores at the BaTiO₃/SrRuO₃ interface are observed, while the SrRuO₃/DyScO₃ interface is free of dislocations. Both diffraction contrast images and HRTEM images (not shown here) prove that the Burgers vector of the misfit dislocations is $a\langle 100 \rangle_{\text{BaTiO}_3}$. The distribution of dislocations along the BaTiO₃/SrRuO₃ interface is inhomogeneous. The average dislocation spacing of about 58 nm is much larger than the theoretical equilibrium dislocation spacing of 25 nm,¹⁰ which indicates that BaTiO₃ thin film is partially relaxed. Figure 2(c) is a planar-view TEM image of the same film. The orthogonal dislocation network consists of two perpendicular edge dislocation lines with Burgers vectors $a[100]_{\text{BaTiO}_3}$ and $a[010]_{\text{BaTiO}_3}$, respectively. X-ray energy dispersion spectroscopy analysis confirmed that the area imaged includes BaTiO₃, SrRuO₃, and DyScO₃.

The above TEM results show that the 200 nm BaTiO₃ thin film grown on a GdScO₃ substrate with a 50 nm coherent SrRuO₃ layer is still strained with fully coherent interfaces, while critical thickness of BaTiO₃ thin films grown on DyScO₃ substrate with coherent SrRuO₃ layer is between 50 and 100 nm. These results can be understood via thermodynamic equilibrium theory. In general, to ensure coherent growth in bilayer systems, the important structural param-

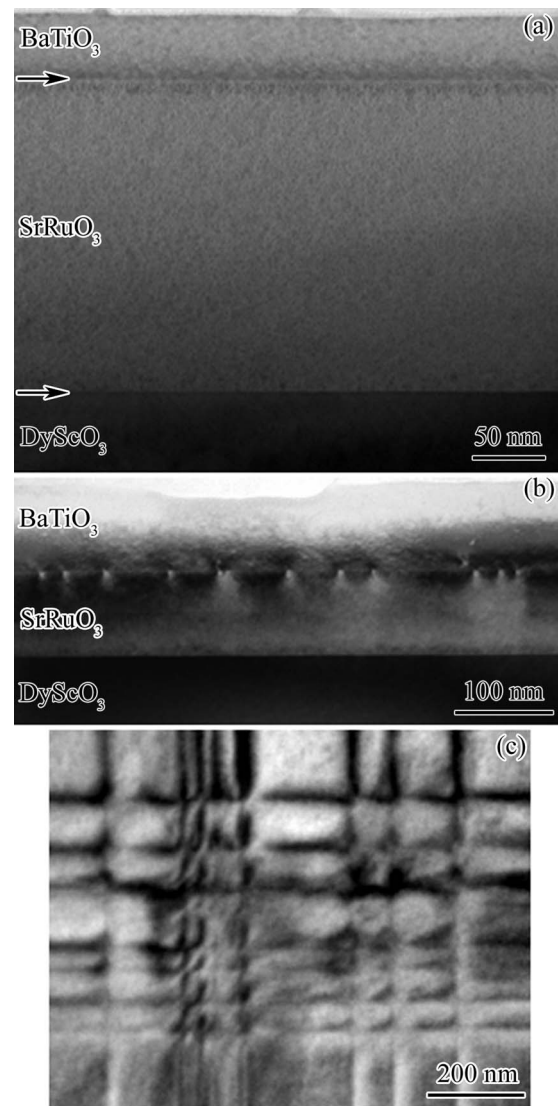


FIG. 2. (a) Cross-sectional TEM image of the BaTiO₃ (50 nm)/SrRuO₃ (200 nm) bilayer grown on (110) DyScO₃ showing coherent sharp interfaces between BaTiO₃ and SrRuO₃ as well as between SrRuO₃ and DyScO₃. The interfaces are indicated by arrowheads. (b) Cross-sectional image of the BaTiO₃ (100 nm)/SrRuO₃ (100 nm) grown on (110) DyScO₃ showing the dislocation cores at interface between BaTiO₃ and SrRuO₃. (c) Planar-view TEM image of the same sample showing a two-dimensional dislocation network.

eters are the thicknesses of each layer and the lattice mismatch between each layer and substrate.¹¹ As a rule of thumb, if the buffer layer in a bilayer system is coherent and very thin relative to the substrate, then layers that are subsequently grown on top of the buffer layer will be strained to match the substrate, as though there were no buffer layer present. When the misfit strain between the two layers is of an opposite sign, as in the case for BaTiO₃ and SrRuO₃ layers on either GdScO₃ or DyScO₃ (Table I), then it will be energetically unfavorable to lose coherency at the substrate/buffer-layer interface before losing it at the second interface. In other words, the critical thickness for a second layer on a coherent buffer layer is expected to be identical to the critical thickness in a single layer configuration, provided the strains in the two layers are of opposite signs. If the strains in the two layers are of the same sign, it could be energetically favorable to relax the strains in both layers by losing coherency at the substrate/buffer-layer interface, before reaching

TABLE I. The average lattice mismatch between BaTiO₃ (SrRuO₃) and GdScO₃ (DyScO₃) (Refs. 4 and 5), where the lattice mismatch is defined as $f = (a_{\text{sub}} - a_{\text{film}}) / a_{\text{film}}$, a_{sub} and a_{film} are the average in-plane spacings of the substrate and thin films, respectively.

Film/substrate	Average mismatch (%)
SrRuO ₃ /DyScO ₃	0.41
BaTiO ₃ /DyScO ₃	-1.20
SrRuO ₃ /GdScO ₃	1.10
BaTiO ₃ /GdScO ₃	-0.56

the critical thickness at which coherency is lost at the second interface.

Within the framework of a thermodynamic equilibrium theory, there are two widely accepted criteria for the critical thickness: the Matthews-Blakeslee (mechanical equilibrium) model¹¹ and the People-Bean (energy equilibrium) model.¹² The former model requires the total energy being at its minimum under critical thickness, while the latter assumes that the elastic energy is equal to the dislocation energy at critical thickness. Generally, the Matthews-Blakeslee model, which has its physical basis stemming from force balance, is frequently used to describe strain relaxation in thin film systems, while the People-Bean model is more accurate in certain thin film systems which have extremely low initial dislocation densities, low dislocation mobility at growth temperature and small lattice mismatches (<1.0%) between the thin films and the substrate.^{12,13} The critical thicknesses calculated by the Matthews-Blakeslee model and the People-Bean model for different lattice mismatch values are shown in Fig. 3. In the present experiments the critical thickness of the BaTiO₃ film at which coherency is lost at the BaTiO₃ / SrRuO₃ interface is significantly greater than that expected from the classical Matthews-Blakeslee model, and might appear to be more consistent with the People-Bean model (Fig. 3). However, it should be recognized that the Matthews-Blakeslee model provides a lower thermodynamic bound,

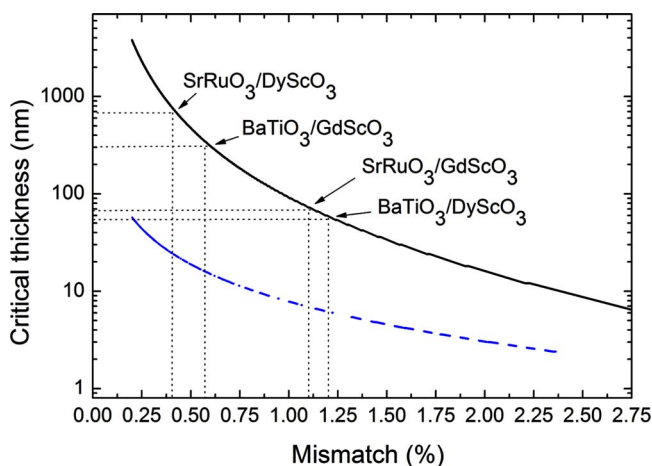


FIG. 3. (Color online) The theoretical critical thickness for strain relaxation in single layer systems as a function of lattice mismatch between film and substrate, calculated via energy balance model (black curve) and mechanical equilibrium model (blue curve).

based on equilibrium considerations, to the thickness at which coherency is lost. In practice, misfit dislocations might not be observed in the TEM until thicknesses considerably in excess of those predicted by Matthews-Blakeslee because of either kinetic limitations or nucleation limitations. Therefore, the experimental critical thickness for strain relaxation may depend on experimental conditions such as growth temperature, stoichiometry, postgrowth annealing, etc.^{10,14,15} More studies must be conducted to fully understand strain relaxation behaviors in these systems.

In conclusion, we have studied strain relaxation of BaTiO₃ thin films grown on (110) GdScO₃ and DyScO₃ substrates with buried coherent SrRuO₃ layer by transmission electron microscopy. The different strain relaxation behaviors in BaTiO₃ films are mainly dependent on lattice mismatch of each layer with respect to the substrate and the thicknesses of each layer. Therefore, strain engineering of multifunctional oxide multilayer is feasible by choosing suitable substrate and controlling thickness of each component layer.

This work was supported by the Department of Energy (DE-FG02-07ER46416) and the National Science Foundation (DMR-0313764, DMR-9871177, and ECS-0210449), and the Chinese Natural Science Foundation (50428202). The authors (X.Q.P. and Y.B.C.) would like to thank Professor Michael Thouless for discussions on strain relaxation mechanism in thin films.

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