



Structure Simulation on Twisted Boundaries in SrTiO₃ Bicrystals by Molecular Dynamics Calculation

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Abstract. Bicrystals of SrTiO₃ with twisted boundaries were prepared by a HIP method and were observed with a transmission electron microscope (TEM). The bicrystals exhibited different nonlinear current-voltage characteristics depending on twist angle. A Molecular dynamics calculation was applied in order to understand the detailed interface structure. The periodicity of the $\Sigma 5$ twisted boundary was calculated to be 1.58 times longer than the lattice constant of SrTiO₃ along the (130) axis, and agreed with the periodicity observed by TEM, i.e., 1.57. Coincidence sites formed between Ti ions of the TiO₂ layer and O ions of the SrO layer at the interface and did not shift the positions predicted by a coincidence sites lattice model; such coincidence sites caused the structural periodicity along the interface.

Keywords: SrTiO₃, interface, grain boundary, bicrystals, structure simulation

1. Introduction

Grain boundaries play an important role in physical and electrical properties in many ceramics. For example, SrTiO₃ ceramics exhibit nonlinear current-voltage characteristics which are influenced by structure, impurity-segregation etc. of grain boundaries [1]. Fujimoto et al. [2] formed SrTiO₃ bicrystals joined by a thin film of molten Bi₂O₃ and evaluated their electrical properties and structures. These experiments indicated that bicrystals were useful for the elucidation of the structure and property of the grain boundary.

When a planar interface forms between two misoriented crystals, many atoms are distributed to stabilize the local configuration near the interface. A first approximation for the interface structure is

generally given by a coincidence site lattice (CSL) model. For example, in the CSL model a $\Sigma 5$ boundary has a misorientation angle of 36.9° and its unit cell is $\sqrt{5}a_0$ in length, where a_0 is the lattice constant of the original crystal [3]. However, as the CSL model is purely geometrical, it gives only the initial state of the interface structure before lattice relaxation.

Alternatively, grain boundary structures can be calculated by molecular dynamics. Chen and Kalonji [4] calculated a $\Sigma 5$ tilted boundary of NaCl and obtained a stable structure in which small channels formed along the interface.

In the present paper, SrTiO₃ bicrystals were prepared to form twisted boundaries and the interface structure of the $\Sigma 5$ twisted boundary was investigated with a transmission electron microscope (TEM) and molecular dynamics (MD) calculation.

2. Method

2.1. Experimental Method

Single crystals of SrTiO₃ doped with 0.05 wt % Nb were polished to mirror surfaces and were washed with acetone in an ultrasonic cleaner. To form twist interfaces rotated around the (001) axis, the crystals were fixed at 0° for a Σ1 boundary, at 36.9° for a Σ5 boundary and at 22.6° for a Σ13 boundary using Pt wires. The crystals were fired at 1873 K for 2 h under 50 MPa in Ar by a hot isostatic press (HIP) method. Finally the crystals were annealed at 1573 K for 2 h in air.

The current-voltage (*I-V*) characteristics of the bicrystals obtained were measured by using In-Ga alloy electrodes. Specimens for TEM observation were prepared by ion milling with an Ar⁺ ion beam of 4 keV and a grazing incidence angle of 12°; the specimens were observed at 800 kV by high resolution TEM (Hitachi, H-1500, Japan).

2.2. Molecular Dynamics Calculation Method

MD calculations were carried out for various SrTiO₃ interfaces using the following potential function:

$$u_{ij} = \frac{z_i z_j e^2}{r_{ij}} + f_0 (b_i + b_j) \exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) - \frac{c_i c_j}{r_{ij}^6}.$$

Here, z_i and z_j are the charges of the i -th and j -th ions, respectively, and r_{ij} is their distance. a_{ij} and b_{ij} are the potential parameters corresponding to ionic radius and ionic stiffness, respectively. c_{ij} corresponds to the van der Waals potential related to a non-symmetric electronic distribution. e is an electron charge and f_0 is a constant.

As given by the above equation, the potential function consists of three terms: the first term is an ionic two-body potential, i.e., coulombic interaction, the second term is Born-Mayer type repulsive interaction, and the third term is van der Waals attractive interaction. The parameters used in the present paper are given in Table 1. The program used for the MD calculation was MXDORTO written by Kawamura [5] and running on a DEC AlphaServer 2100 5/250.

The equations of motion were integrated using a predictor method based on the Verlet algorithm with a time step of $\Delta t = 2.5$ fs. All the calculations were performed at a constant temperature and pressure.

In this paper, we consider a bulk SrTiO₃ and a TiO₂/SrO interface. The result for other interfaces (SrO/SrO, TiO₂/TiO₂) will be published elsewhere.

3. Results and Discussion

3.1. Electrical Properties of SrTiO₃ Bicrystals

Figure 1 shows the (*I-V*) current-voltage characteristics of SrTiO₃ twisted bicrystals measured along the c -axis. The *I-V* characteristics are nonlinear, suggesting that an interfacial barrier formed at the bicrystal interface. From Fig. 1, it is found that the nonlinearity of *I-V* characteristics increases in the order Σ1, Σ5 and Σ13, corresponding to the decrease in periodicity along the interface. It is thus considered that a higher electrical barrier forms at a twisted boundary with more disordered atomic configuration which can probably induce interfacial states which are separated from the conduction band in energy.

3.2. Interface Structure of a SrTiO₃ Bicrystal Observed by TEM

Figure 2 shows the TEM image of a Σ5 twisted boundary in a SrTiO₃ bicrystal. This image was observed along the [310] axis and the interface was well joined even at the atomic scale. At the Σ 5 twisted boundary, the lattice constant along the c -axis adjacent to the interface is 1.3 times longer than that of the original SrTiO₃ single crystal, and the periodic length along the interface is 1.57 times longer than that of the SrTiO₃ crystal. The periodicity of $1.57a_0$ corresponds to half of the length of the Σ5 coincident site lattice when the bicrystal is viewed along the [310] axis.

3.3. Determination of Potential Parameters

First, the MD calculation was carried out for a SrTiO₃ bulk crystal to evaluate the parameters in the potential

Table 1. Potential parameters used for the MD calculation. The meanings of z , a , b and c are given in the text

Parameter	z	a	b	c
O	-1.331	1.629	0.1113	20.0
Ti	2.662	1.235	0.0850	0.0
Sr	1.331	1.632	0.0850	15.0

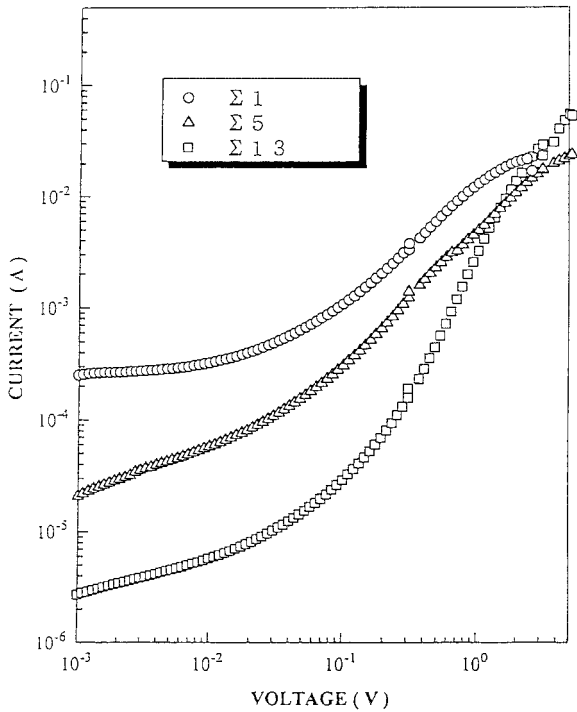


Fig. 1. Current-voltage characteristics of SrTiO₃ bicrystals: ○ plots for $\Sigma 1$, Δ plots for $\Sigma 5$ and \square plots for $\Sigma 13$.

function given in §2.2. The MD basic cell used here consisted of $4 \times 4 \times 4$ unit cells in which 320 ions were placed at positions in an ideal perovskite structure. The MD calculations were iterated for 20000 steps at 300 K and at 1273 K.

The lattice constants determined by the MD calculation were compared with the experimental

values. According to [6], the lattice constant of SrTiO₃ at room temperature is 0.3905 nm and the thermal expansion coefficient is $9.4 \times 10^{-6}/\text{K}$; therefore, the lattice constant at 1273 K is 0.394₁ nm. By changing the parameters in the potential function through trial and error, the final lattice constants were calculated in good accordance with the experimental values as given in Table 2, and the corresponding potential parameters are given in Table 1. Consequently, the parameters in Table 1 were applied also for the MD calculations of twisted interfaces.

3.4. Lattice Relaxation of a SrTiO₃ Twisted Boundary

An initial structure for the $\Sigma 5$ twisted boundary is shown in Fig. 3(a) viewed along the [310] axis. This basic cell (Model 1) has two crystals and two boundaries, and consists of 800 ions. It was assumed that the ionic positions just above and below the boundary did not shift in the xy plane. The coincidence sites of this model are the Ti and O ions as seen in Fig. 3(a). The initial interval between the two crystals was the same as half of the lattice constant of normal SrTiO₃ crystal, i.e., 0.19525 nm. The interval between the two boundaries in the basic cell was assumed to be more than 3 nm for which the boundaries almost did not interact.

The MD calculations were iterated for 20000 steps at 300 K; the resultant structure is given in Fig. 3(b). After the lattice relaxation, the interval at the interface between the two crystals was elongated to about

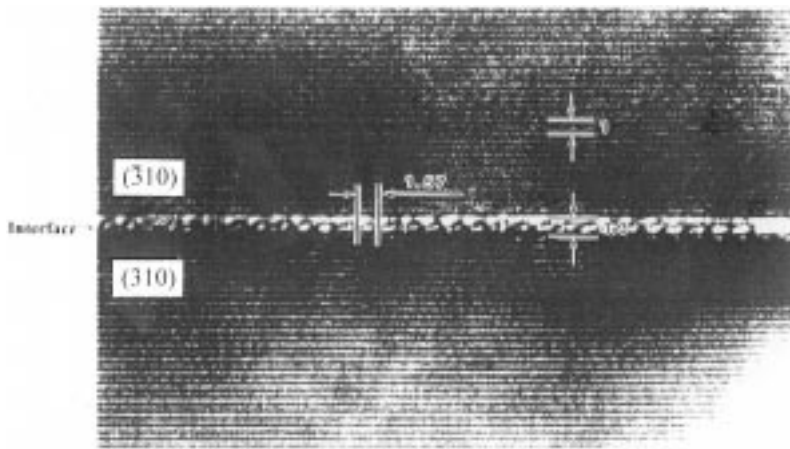


Fig. 2. $\Sigma 5$ twisted boundary of the SrTiO₃ bicrystal observed by TEM along the (310)-axis.

Table 2. Lattice constants of SrTiO₃ bulk system from MD calculation

Lattice constants (nm)	Ref.*	Results calculated		
		<i>x</i> axis	<i>y</i> axis	<i>z</i> axis
300 K 0.3904 ₉	0.3905		0.3904 ₉	0.3904 ₉
1273 K 0.3940 ₉	0.3941		0.3941 ₂	0.3940 ₅

*T. Yonezawa, Crystal Growth Handbook, (1995) 540–543.

0.279 nm. This value is 1.4 times longer than the initial interval. This lattice expansion is in good accordance with the experimental result, 1.3, observed by TEM.

Figure 4 shows the detailed atomic arrangement of the initial (a) and final (b) interfaces. The upper figures are the interface viewed along the [310] axis

and the lower figures that viewed along the *c*-axis. The inside dotted squares in the lower figures indicate the unit cell of the Σ5 coincidence site lattice. The lattice relaxation is very small in the *xy* plane as indicated by small arrows in the right figure, while the atomic position are extensively relaxed along the *c*-axis as shown in the right upper figure. In this relaxation process, it is found that the Ti and O ions originally located at the coincidence sites almost did not shift and kept their initial positions. This relaxation mechanism results in a periodic structure along the interface; the periodicity calculated is 1.58 times longer than the lattice constant of the normal SrTiO₃ crystal along the [130] axis. This result is in very good agreement with the value of Fig. 2 observed by TEM (i.e., 1.57).

On the other hand, MD calculations were also performed for other initial structures for the Σ5

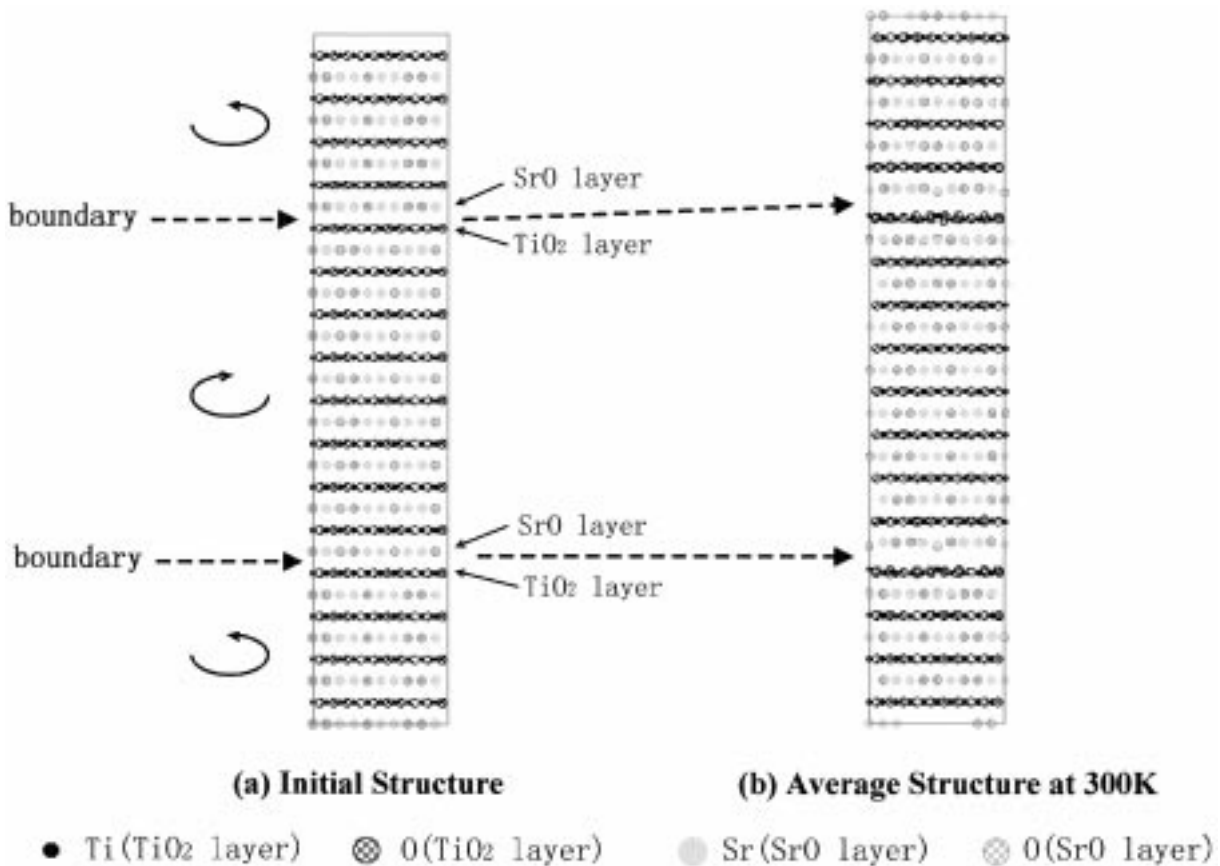


Fig. 3. Σ5 twisted boundary of the SrTiO₃ bicrystal simulated by MD calculation: (a) initial and (b) final average structures at 300 K.

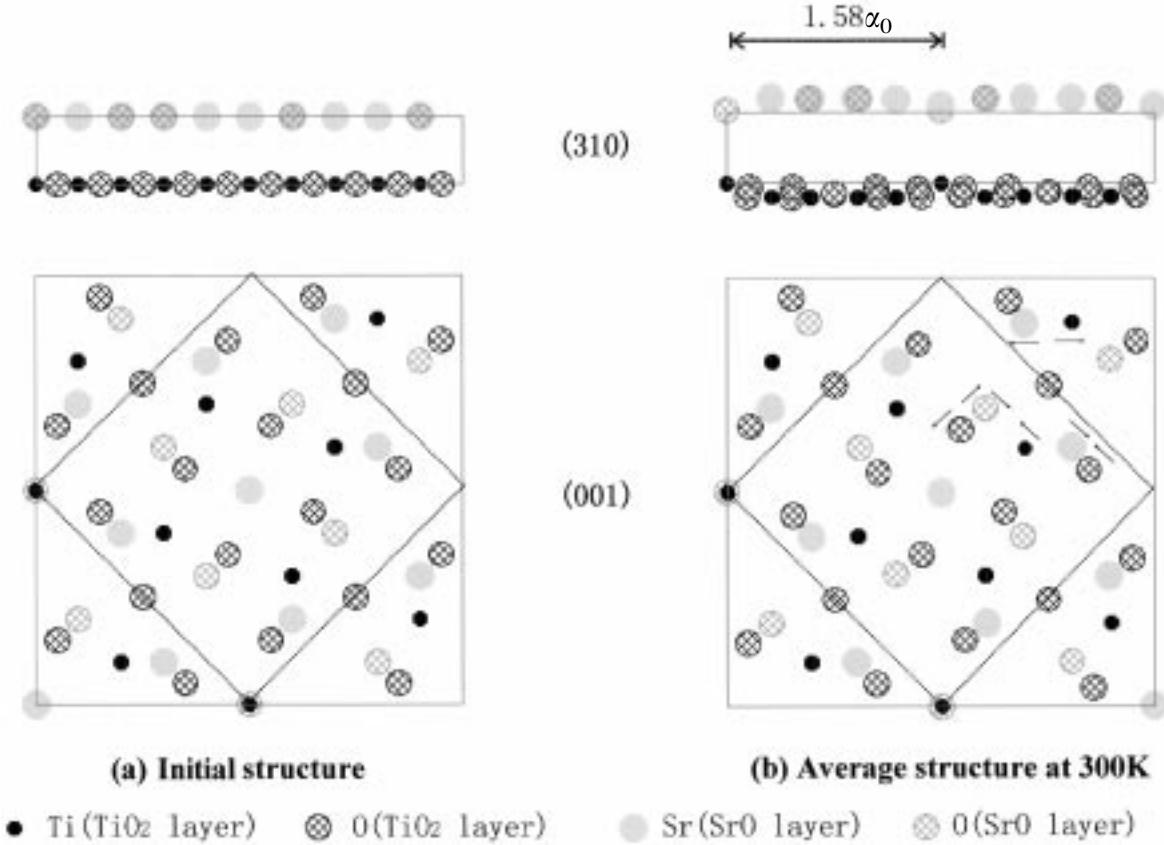


Fig. 4. $\Sigma 5$ twisted boundary of the SrTiO₃ bicrystal simulated by an MD calculation for Model 1: (a) initial and (b) final average structures at 300 K. Upper side: viewed along (310) and lower side: viewed along the c -axis.

twisted boundary. A typical MD basic cell (Model 2) has a boundary structure in which Sr ions above the boundary are coincident with O ions below the boundary as indicated in Fig. 5(a).

Figure 5 shows the detailed atomic arrangements of the initial (a) and final (b) interfaces calculated at 300 K. After lattice relaxation (almost 1100 steps), Sr and O ions originally located at the coincidence sites shifted, and finally the coincidence sites moved from Sr(above)-O(below) to O(above)-Ti(below); thus the interfacial structure obtained was the same as the structure shown in Fig. 4(b).

Table 3 gives the internal energies calculated at 300 K. The internal energy of Model 2 averaged between 1 and 1050 calculation steps (-7094.7 kJ/mol) is larger than the average value calculated between 15000 and 20000 steps (-7095.0 kJ/mol) which is the same as the final value obtained for Model 1 (-7095.0 kJ/mol). This result indicates

that the coincidence site lattice for Ti and O ions is more stable than the coincidence site lattice for Sr and O ions. It is thus considered that the Ti ion with a large electric charge forms a stronger bond with the O ion compared to the Sr ion at the $\Sigma 5$ twisted boundary.

3.5. Stable Local Atomic Configuration of Ti

Figure 6 indicates local atomic configurations around

Table 3. Average internal energy for two boundary models estimated by MD calculation at 300 K. See the text for model 1 and 2

Calculation Steps	Bulk system	(kJ/mol)	
		Model 1	Model 2
1 ~ 1050	-7115.3	-7094.8	-7094.7
15000 ~ 20000	-7114.6	-7095.0	-7095.0

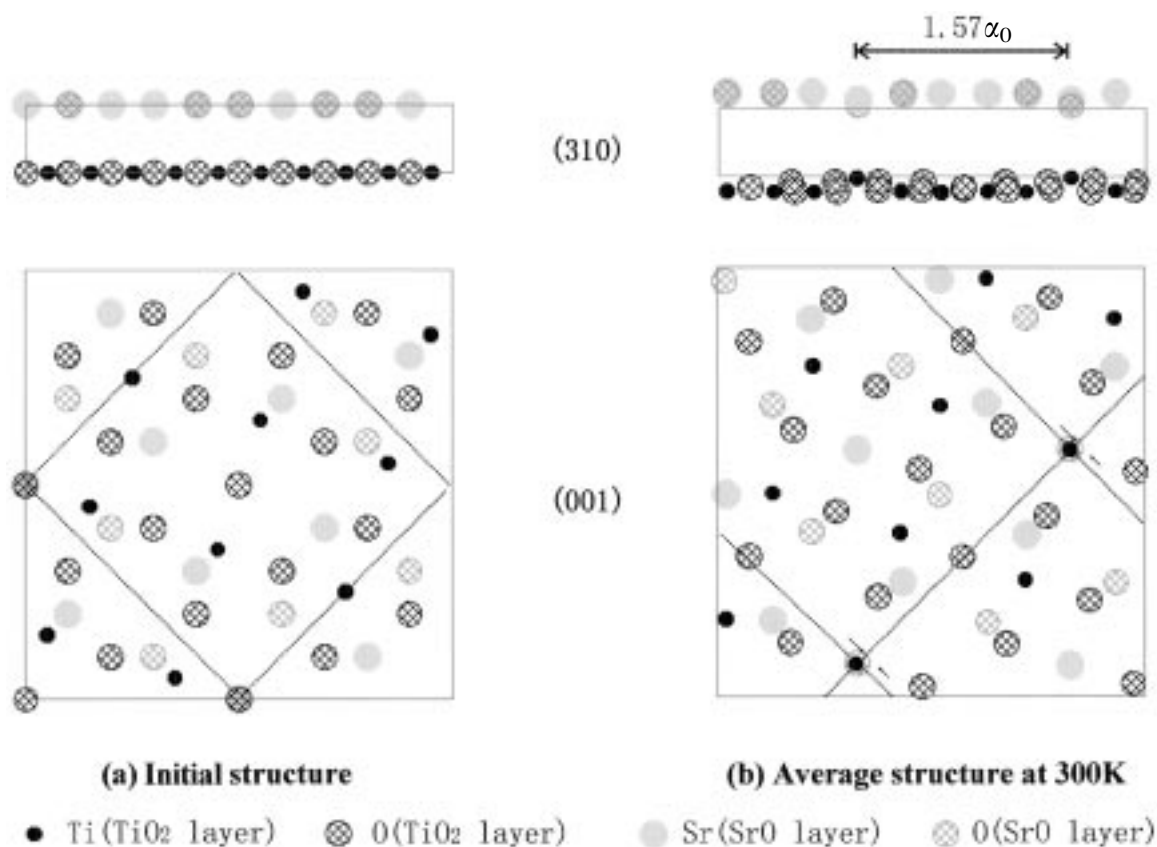


Fig. 5. $\Sigma 5$ twisted boundary of the SrTiO_3 bicrystal simulated by an MD calculation for Model 2: (a) initial and (b) final average structures at 300 K. Upper side: viewed along (310) and lower side: viewed along the c -axis.

Ti ions in the bulk (a), at a coincidence site of the $\Sigma 5$ twisted boundary (b) and at a noncoincidence site of the $\Sigma 5$ twisted boundary (c) after the lattice relaxation. At the coincidence site, the local configuration around the Ti ion (b) had an octahedron of six O ions, similar to the bulk (a), though the Ti ion in the octahedron (b) moved upwards slightly. At the noncoincidence site, the O ion above the Ti ion moved further away from the Ti ion than the other five O ions and a Sr ion approached the upper O ion and central Ti ion. This gives a 5 coordinated configuration (pyramid) of O ions around Ti ion; this local configuration might be unstable. However, it is thought that the interface was stabilized by the total configuration involving the coincidence sites.

At the SrO/TiO_2 interface, a very distorted local configuration did not appear in the $\text{TiO}_2/\text{TiO}_2$ twisted boundary as shown in Fig. 7. Fig. 7(a) shows a distorted octahedron of six O ions around Ti and Fig. 7(b) shows a 9 coordinated configuration of O ions

around Ti ion. These distorted local configurations are considered to be related to the origin of an interfacial state causing the nonlinear I - V characteristics. Molecular orbital calculations for Figs. 6(c), 7(a), 7(b), etc. are under investigation.

3.6. Temperature Dependence of Interface Structure

Figure 8 shows the high temperature variation calculated for the $\Sigma 5$ twisted boundary. From the trajectory plots of instantaneous ionic positions, it is seen that when the temperature is increased, atomic disordering, i.e., melting, takes place from the interface, indicating that chemical bonding at the interface is weak and unstable. It is worth noting that diffusion along the interface occurs in the order O, Sr and Ti with the increase of temperature.

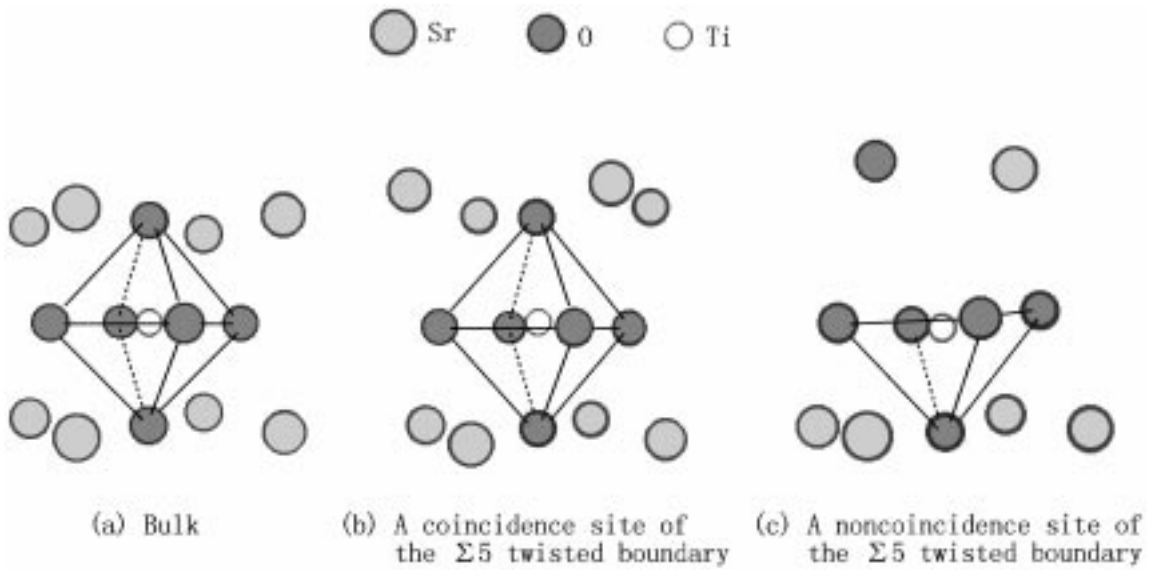


Fig. 6. Local atomic configurations around Ti ions: (a) bulk part, (b) at a coincidence site of a $\Sigma 5$ twisted boundary and (c) at a noncoincidence part of a $\Sigma 5$ twisted boundary.

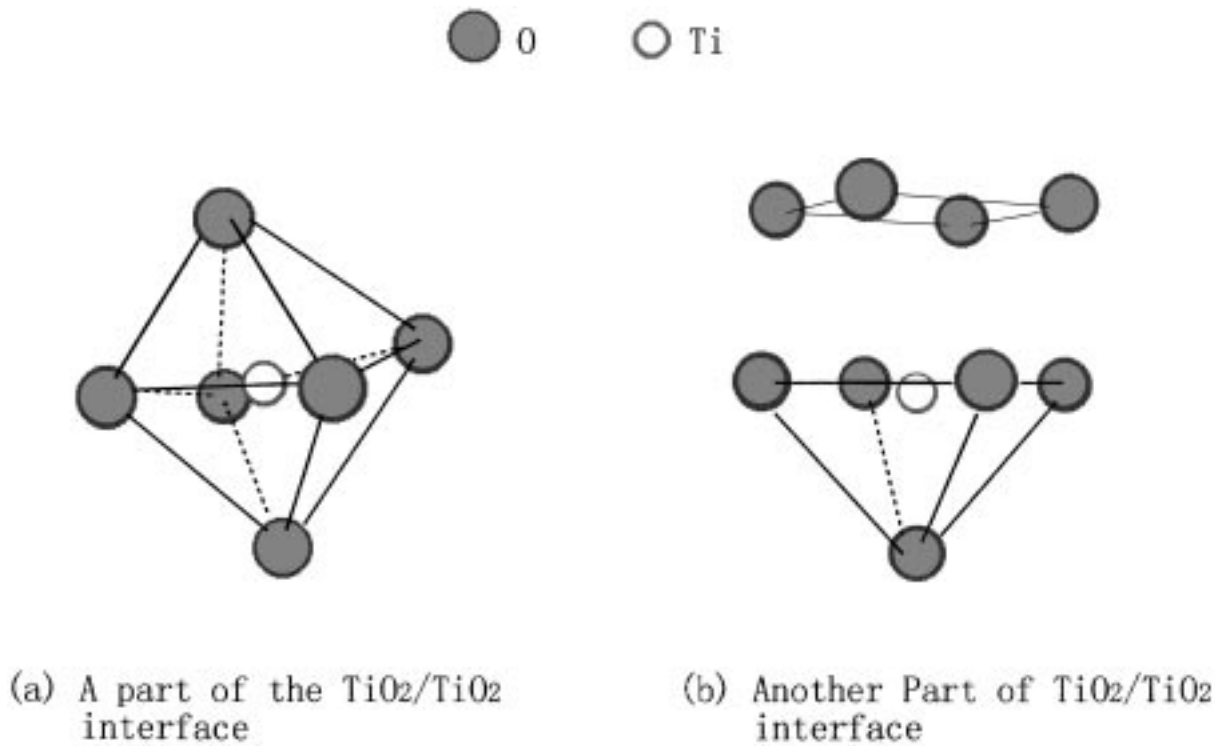


Fig. 7. Distorted atomic configurations calculated for a TiO₂/TiO₂ interface.

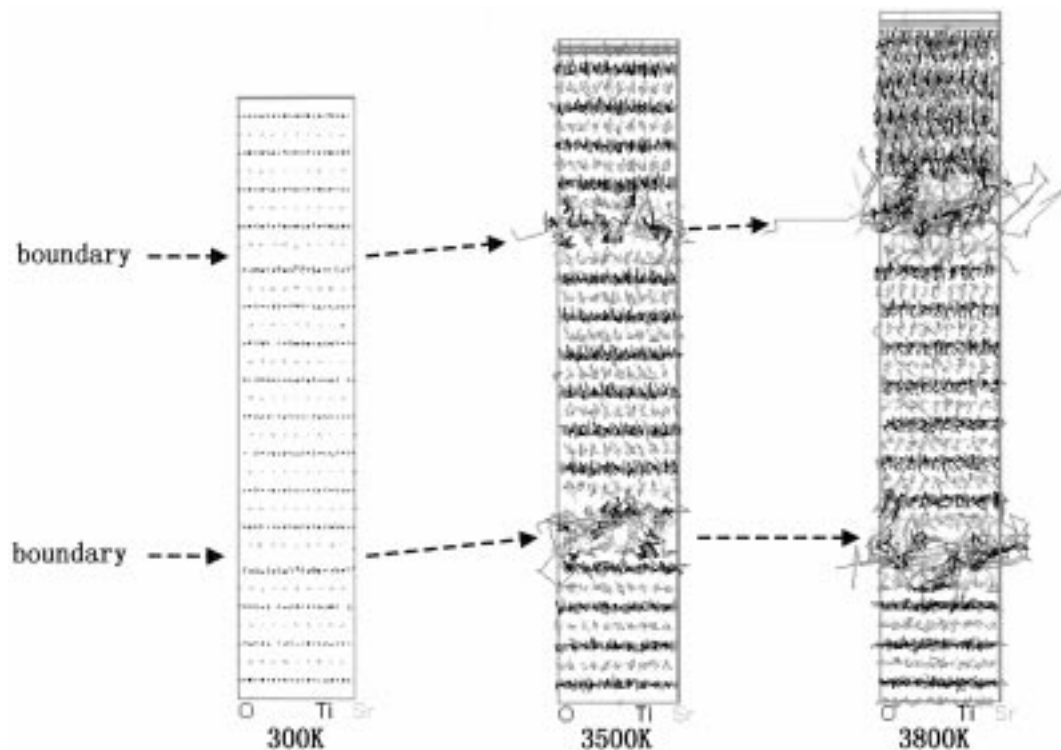


Fig. 8. Trajectory plots of instantaneous ionic positions in a SrTiO₃ $\Sigma 5$ twisted boundary at three different temperatures.

4. Conclusions

SrTiO₃ bicrystals with a $\Sigma 5$ twisted boundary were prepared by a HIP method. The bicrystals exhibited nonlinear current-voltage characteristics. From TEM observations, the interval of the $\Sigma 5$ twisted boundary was 1.3 times longer than the lattice constant of a normal SrTiO₃ crystal, and the periodicity along the interface was 1.57 times longer than the SrTiO₃ lattice constant along the (130) axis. Molecular dynamics calculation indicated that the lattice relaxation at the twisted interface took place for the coincident sites, Ti(below the interface)-O(above), to keep their original positions and for other ions to shift along the *c*-axis at 300K. At the coincidence sites, the Ti ion was surrounded by an octahedron of six O ions, similar to the bulk configuration. At the noncoincidence sites, the configuration around the Ti ion consisted of a distorted octahedron of six O ions and a Sr ion. It is shown that the interface structure relaxed in order to stabilize the local configuration around Ti.

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