

Molecular dynamics calculations about misfit dislocations at the BaTiO₃/SrTiO₃-interface

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Abstract

When BaTiO₃ thin films are deposited on SrTiO₃ (001) substrates at low temperatures at approximately 700°C, at first epitaxial growth without defects occurs, but at a critical thickness it changes into pseudomorphic growth by introducing misfit dislocations. Cross-sectional high-resolution transmission-electron microscopy shows that these dislocations lie at the interface and stacking faults on (101) planes are also observed. Molecular dynamics simulations were performed in order to understand the formation of these dislocations. The critical thickness for occurrence of misfit dislocations is found to be approximately four monolayers with a slight increase with temperature. The misfit dislocations dissociate into partial dislocations and migrate to the interface by forming stacking faults on (101) planes. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

BaTiO₃ perovskites deposited on SrTiO₃ substrates are promising candidates for future applications in new electronic devices, like microwave resonators, advanced optical devices, multilayer ceramic capacitors or even for the next generation of dynamic or ferroelectric random access memories (DRAM, FRAM) for computers. The knowledge about the critical thickness for pseudomorphic growth of BaTiO₃-layers is important for improving the properties of the thin films. At early stages thin films of BaTiO₃ grow epitaxially in the van-der-Merwe-type [1,5–7] on SrTiO₃ substrates. The BaTiO₃ thin film is strained because the lattice constants of BaTiO₃ ($a = 0.39927$, $c = 0.40356$ nm) and SrTiO₃ ($a = 0.3904$ nm) are very similar for both possi-

ble orientation relationships: (I) $(001)_{\text{BaTiO}_3} \parallel (001)_{\text{SrTiO}_3}$, $[100]_{\text{BaTiO}_3} \parallel [100]_{\text{SrTiO}_3}$, and (II) $(100)_{\text{BaTiO}_3} \parallel (001)_{\text{SrTiO}_3}$, $[001]_{\text{BaTiO}_3} \parallel [100]_{\text{SrTiO}_3}$. The lattice constants of the thin film adjust to the substrate and differ from the single crystal values. In this paper this case is called the strained or metastable state. When the film thickness exceeds a critical thickness, the growth changes from epitaxial to pseudomorphic growth by the introduction of misfit dislocations and the lattice constants of the additional layers will be similar to those of the stable BaTiO₃ lattice. The formation of misfit dislocations consumes a lot of energy, since the stress field of a dislocation, especially in perovskite ceramics, drops off after a long distance. However, the epitaxial growth of BaTiO₃ upon SrTiO₃ also consumes energy to strain the BaTiO₃ unit cells in order to provide the perfect matching. The system has to find a balance between lattice straining and dislocation formation. The critical thickness for epitaxial growth is the upper limit, up to which the lattice of the thin film

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can be strained. Above this limit, the formation of dislocations is energetically more favorable.

The expected distance d of misfit dislocations can be evaluated from the comparison of the lattice constants a - and c -BaTiO₃ and a -SrTiO₃ at room temperature by searching for the minimum of the function

$$\min(na_{\text{BaTiO}_3} - (n+1)a_{\text{SrTiO}_3}) = \min(d) \quad (1)$$

For the orientation relationship of case (I) d is approximately 17.56 nm and the number of lattice planes which are matching to each other at the interface is $n = 44$ BaTiO₃ unit cells and $n + 1 = 45$ SrTiO₃ unit cells. For case (II) the values are $d = 11.71$ nm, $n = 29$ a_{BaTiO_3} , $n + 1 = 30$ a_{SrTiO_3} . It is expected that the system will choose the orientation relationship (I), because the strain and, hence, the energy is lower. Experimental high-resolution transmission-electron microscopy (HRTEM) studies [1] (Wunderlich et al., unpublished) [2,3] support this assumption: the average spacing of the misfit dislocations is approximately 15 nm, mostly with Burgers vectors of the type $b = [001]$. The dislocations usually migrate to the interface because the combination of the two defects, the interface and the dislocation, has a lower energy.

Furthermore, stacking faults on (101) and (100) planes occur. For the latter one, an atomistic model of a stacking fault based on experimental results has been presented [1,4]. It has a displacement vector of $1/2a[100]$ on the (001) plane. Stacking faults on (101) planes, however, are more frequently occurring [1], when dislocations slip on (110) planes, where the Peierls force in this perovskite structure is lower and the Burgers vector shorter than on (100) planes. Hence, splitting one of these $\langle 011 \rangle$ dislocations into two partial dislocations can easily form a stacking fault on a (110) plane, which has a lower energy than stacking faults on (100) planes.

Molecular dynamics (MD) calculations of BaTiO₃ and SrTiO₃ have already been performed, either to search for suitable potentials or for calculating properties [9]. Using potential parameters for MD calculations is a simplified parameter description of the complex interaction between two atoms. Although for a variety of ceramic materials three-body potentials are available, which are usually more accurate and stable,

the quality of two-body potentials is improving. Two-body potentials are preferred for practical use, because the calculations are much faster, which is especially necessary for large systems. For BaTiO₃ and SrTiO₃ several two-body potentials have been published [8–10]. All three sets of parameters were checked carefully, but the Kawamura-potential [9,10], as shown in Table 1, was found to have the smallest deviation from the experimental values and the highest stability. The aim of this paper is to calculate the critical thickness of pseudomorphic growth of BaTiO₃ thin films on SrTiO₃ substrates.

2. Calculation method

2.1. Potential parameters

The molecular dynamic program Moldy written by K. Refson [11,12] was used with the Buckingham two-body central-force potential parameters in the following form:

$$E_{\text{R}} = \frac{z_i z_j e^2}{r} + f_0 (b_i + b_j) \exp\left(\frac{a_i + a_j - r}{b_i + b_j}\right) - \frac{c_i + c_j}{r^6} \quad (2)$$

where $f_0 = 6.9511 \times 10^{-11}$ N. The adjustable parameters z_i , a_i , b_i , c_i , with the indices i and j for the two kind of atoms in this pair potential, are shown in Table 1 and were taken from previous works [9]. This set of parameters shows the best performance compared to other sets for calculating the properties of both materials BaTiO₃ and SrTiO₃ and the calculated lattice constants and the thermal expansion coefficient have smaller deviations to experimental values and converge faster during long term simulation runs.

2.2. Interface energy

The total energies of SrTiO₃ and BaTiO₃, necessary for the quantitative calculations of the interface energy, were calculated as a linear function of the temperature. These calculations were performed for 5000 time-steps of 10^{-3} ps for temperatures of 290, 490 and 1320 K. The interface was modeled as described in the

Table 1
The MD-parameters for BaTiO₃ and SrTiO₃ after Kawamura [9]

	Z_i (e)	Mass (amu)	a_i ($A = 0.1$ nm)	b_i ($A = 0.1$ nm)	c_i ($A^3 / (\text{kJ} \times \text{mol})^{1/2}$)
Sr	1.331	87.62	1.6320	0.0850	15.0
Ti	2.662	47.867	1.2350	0.0850	0.0
Ba	1.331	137.327	1.8200	0.0800	20.0
O	-1.331	15.9994	1.6290	0.1113	20.0

following chapters. For the interaction of the atoms at the interface the same interaction parameters were used as in the single crystal, no additional assumptions had to be made. Although the input temperature has been set to lower values, it increased during the run. For the quantitative analysis of the interfacial energy per area, E_{IF} in mJ/m^2 , the following formula was used:

$$E_{\text{IF}} = \frac{N_{\text{t IF}}}{2N_{\text{A}}A} \left(\frac{E_{\text{t IF}}}{N_{\text{t IF}}} - \frac{E_{\text{t SC}}}{N_{\text{t SC}}} \right) \quad (3)$$

where $E_{\text{t IF}}$ means the total energy of the interface, $E_{\text{t SC}}$ that of the single crystal, $N_{\text{t IF}}$, $N_{\text{t SC}}$, are the number of unit cells of the grain boundary and the single crystal, respectively, N_{A} is Avogadro's number, and A is the area of the interface. Since the supercells that were used for the quantitative energy calculations had periodical boundary conditions, two interfaces between BaTiO_3 and SrTiO_3 appear, which consist of the same input structure. Therefore, the energy of the system was divided by a factor of two in order to get the interfacial energy for one particular interface.

The interfacial energy E_{IF} was calculated for three different temperatures and four different thicknesses of the thin film. A statistical analysis was performed in order to model the dependence on the interface energy on both, the thickness t and the temperature T . The resulting equation is:

$$E_{\text{IF}} = (AT + B)t^m + F' \quad (4)$$

where the fit parameters A and B describe the slope and intercept of the temperature dependence, and m the exponent of the thickness dependence, respectively.

2.3. Interface model

The size of the initial supercell should contain at least one period of this dislocation spacing, as schematically displayed in Fig. 1. Herein, the dimension d of the supercell is equal to the distance of the misfit dislocations. In the perpendicular direction, the width w was set to one unit cell of the SrTiO_3 -substrate (0.3904 nm). As the model assumes epitaxy, it is a reasonable approximation despite the fact that in reality misfit dislocations also occur in the perpendicular direction. The thicknesses of the strained BaTiO_3 -layer t_{BS} (Fig. 1), the unstrained BaTiO_3 -layer t_{BU} , and the SrTiO_3 -substrate t_{S} are chosen as parameters.

The atomic structures of the supercells were displayed by commercial programs for crystallography. Fig. 2 shows the atomic configuration after 0.5, 1, 1.5 ps with the mismatch at the interface. At the start of the MD-simulation an atomic structure with a 'smeared-out' misfit between both lattices was assumed. After a

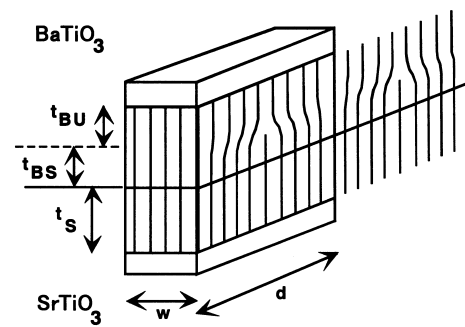


Fig. 1. The initial supercell for MD-calculations contains one spacing of the misfit dislocations. d and w are the dimensions, t_{BS} is the thickness of the strained layer of the BaTiO_3 thin film, t_{BU} is the thickness of the unstrained layer of the BaTiO_3 thin film, t_{S} the thickness of the SrTiO_3 substrate.

short calculation time this structure changes into configurations with misfit dislocations. The terminating layer at the $\text{BaTiO}_3/\text{SrTiO}_3$ interface and at the surface is chosen as an oxygen-titanium-layer, because there are some experimental evidences that the oxygen layer is the usual terminating layer at least under the usual ambient conditions with high oxygen partial pressure. Since the calculated lattice spacings for the single crystals are slightly larger than the experimental ones, the distance of the misfit dislocations also changes slightly: The ratio becomes $32 c_{\text{SrTiO}_3}:33 c_{\text{BaTiO}_3}$ (instead of 44:45) lattice spacings for the orientation relationship I, and $25 a_{\text{SrTiO}_3}:26 a_{\text{BaTiO}_3}$ (instead of 29:30) for II, which lead to a dislocation spacing of 12.95 and 10.20 nm, respectively. Orientation relationship II is considered in this paper.

The interface was modeled as a composite-model in which the same sequence of substrate and thin film is put upside down on top of the thin film. Although the use of this design doubles the size of the initial supercell, it has the advantage that surfaces are avoided. The most effective strategy for the calculations was to compare the interface energy for two cases: one with strained, and the other one with the unstrained BaTiO_3 lattice. The thicknesses of the layers were $t_{\text{BS}} = 2, 4, 8, 16$, $t_{\text{BU}} = 0$ ML (monolayers), and for the second case $t_{\text{BS}} = 0$, $t_{\text{BU}} = 2, 4, 8, 16$. t_{S} was adjusted in both cases, so that the final thickness of all layers together was 75 ML. The size of the final supercell was $19.525 \times 17.5725 \times 0.3904 \text{ nm}^3$ containing 1125 Sr-, 1345 Ti-, 220 Ba- and 4035 O-atoms. Reliable calculations of the critical thickness for epitaxial growth could be reached by using these models.

3. Results

3.1. Stacking fault formation

At first a composite model with combination of three layers of unstrained BaTiO_3 , strained BaTiO_3 , and the

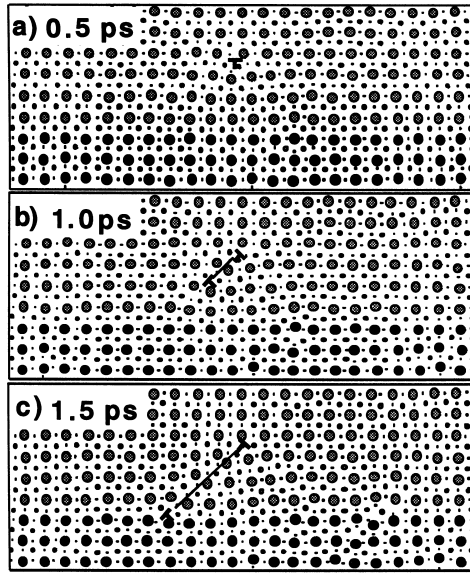


Fig. 2. MD-simulations after (a) 0.5, (b) 1.0, (c) 1.5 ps, which show the formation of a stacking fault. The larger, dark atoms are Sr, the large, gray atoms are Ba, middle-sized atoms Ti and small ones O.

SrTiO₃ substrate with thicknesses of $t_{\text{BU}} = 8$, $t_{\text{BS}} = 3$, $t_{\text{S}} = 25$ ML was used. The results are displayed in Fig. 2 for the inner part of the supercell only. After 0.5 ps, a misfit dislocation with a well-defined core already formed (Fig. 2a). After 0.1 ps the dislocation migrates and has only a distance of two layers from the interface (Fig. 2b). After the migration of the dislocation, two barium atoms have a smaller distance to each other than in the single crystal structure. They are the nucleus of a stacking fault, which grows during the next time-steps (Fig. 2c). The dislocation dissociates and one partial finally migrates to the interface. The stacking fault extends in its length, indicated by the line in Fig. 2c. The same type of stacking fault was also initiated in another run from the surface. The stacking fault lie on a (101) plane with a core of an oxygen layer, and on both sides barium- and titanium-atoms are sitting in alternating sequence and are facing each other (Fig. 2c). The original sequence of the ($\bar{1}01$) planes ...acbcacbcacbc... has been changed into...acbcacacbcac... Fig. 2a–c shows that the occurrence of misfit dislocations and the formation of stacking faults are closely related to each other.

In HRTEM observations this (101) stacking fault was also found and recognized by a shift of $a/2$ in the ($\bar{1}01$) lattice planes [1,4]. It has a length of approximately 3.2 nm starting from the interface. Image simulations were performed to obtain detailed quantitative analysis of the HRTEM micrographs. They show that under the usual Scherzer conditions for optimal image quality, the strong bright spots correspond to the position of barium- or strontium-atoms, the weaker, bright spots to that of titanium-atoms, while the dark areas corre-

spond to the oxygen-atoms [1]. Since a dark layer is found in the center of the stacking fault, it can be deduced, that indeed the experimentally observed stacking fault also consists of an oxygen layer in the center plane, in good agreement with the MD-simulations.

In the HRTEM-images misfit dislocations with [100] Burgers vector are found along the interface. Sometimes they are split into two dislocations, each with a Burgers vector of $1/2\{101\}$ type. The distance between the [100] dislocations is approximately 12 nm in average. Most of the dislocations are lying at the interface plane but sometimes the distance of the misfit dislocations from the interface is three monolayers (3 ML), which is consistent with the simulations.

3.2. Critical thickness

In order to calculate the value of the critical thickness, two other series of supercells were built. One consists of a misfit dislocation containing, unstrained BaTiO₃ with a length d of 26 unit cells, and thicknesses $t_{\text{BU}} = 2, 4, 8, 16$ and $t_{\text{BS}} = 0$ ML. The second consists of metastable, strained BaTiO₃ with $d = 25$ unit cells with $t_{\text{BU}} = 0$ and $t_{\text{BS}} = 2, 4, 8, 16$ ML. Fig. 3a

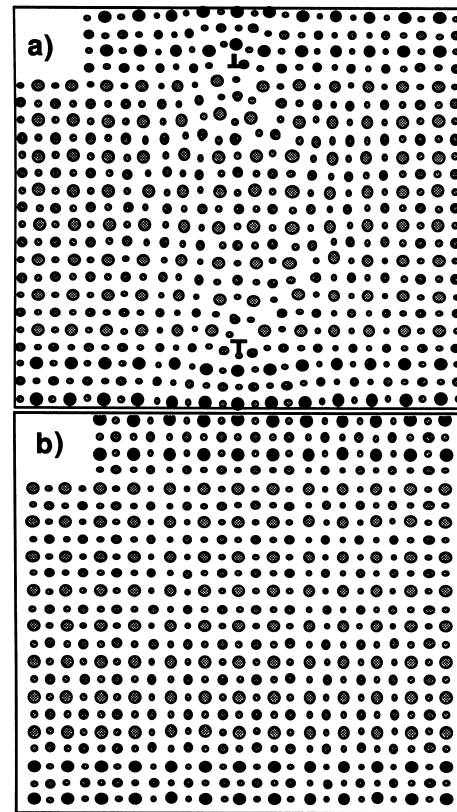


Fig. 3. Calculation using the composite model with thicknesses: (a) $t_{\text{BS}} = 4$, $t_{\text{BU}} = 0$ ML, and (b) $t_{\text{BS}} = 0$, $t_{\text{BU}} = 4$ ML of the strained and the unstrained BaTiO₃.

represents the first case and Fig. 3b for the strained BaTiO_3 thin film after 1.5 ps. Since there is not much microstructural difference between the input structure and that after the calculation, the critical thickness can only be estimated by calculating the interfacial energy.

The results are shown in Fig. 4, where the energy is plotted as a function of the BaTiO_3 layer thickness t_B for three different temperatures. The quantitative analysis describes the thickness and temperature dependence correctly for the whole range in spite of deviations for particular values with one formula. In the case of the strained BaTiO_3 thin film, the interfacial energy is constant as a function of the layer thickness. In the case of the misfit dislocation containing thin films, the interface energy decreases with the thickness with a $t^{-1/3}$ dependence ($m = -0.333$). The fit parameters were estimated as $A = -0.0792 \text{ J/m}^{2/3} \text{ K}$, $B = 123 \text{ J/m}^{2/3}$ for the misfit dislocation case and $A = -0.0668 \text{ mJ/m}^2$, $B = 105 \text{ mJ/m}^2$, and $m = 0$ for the strained case. In spite of the quite large scattering of each data point the fit has reasonably low deviation.

The system is expected to take the microstructure with the lowest energy. For a small thickness of the thin film the strained BaTiO_3 lattice has a lower energy. At the crossover point of the interfacial energy the stable BaTiO_3 lattice containing the misfit dislocation becomes energetically favorable compared with the strained lattice. Hence, the thickness at the crossover is the critical thickness. These values are plotted as a function of the temperature in Fig. 5. The thick line represents the fitted data. The critical thickness t_C has a slight, linear decrease with the temperature with a function

$$t_C = CT + D \quad (5)$$

where the slope C and the interception D were estimated as $C = -0.00028 \text{ nm/K}$ and $D = 1.69 \text{ nm}$, respectively. The value of the critical thickness is 1.6 nm (= 4 ML) at room temperature, 1.32 nm (3.5 ML) at the process temperature of 1000 K.

4. Discussion

Using the calculations of the interfacial energy the critical thickness for epitaxial growth could be estimated. The values of three monolayers at high temperatures and four at room temperature correspond very well to the values obtained by structural analysis. These results showed that the dislocation is not able to migrate to the interface, when the distance from the interface is more than four lattice planes, but it can if it is less. The energy difference between both cases is rather small, so in the case of four layers the driving force on the dislocation is very small, even though the energy of the system after migration would be lower.

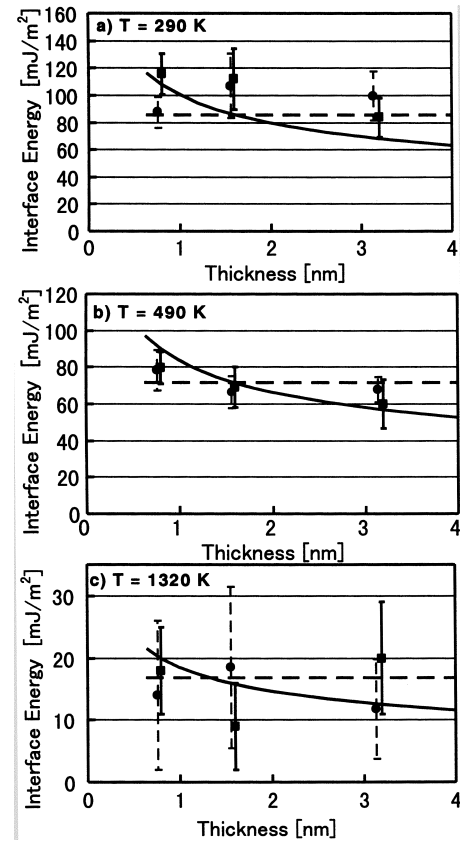


Fig. 4. Interfacial energy as a function of the thickness of the strained (solid line with squared symbols) and the unstrained (hatched line with round symbols) BaTiO_3 thin film for temperatures: (a) $T = 290 \text{ K}$, (b) $T = 490 \text{ K}$, (c) $T = 1320 \text{ K}$.

Assuming this result is typical, it can be concluded that a thickness of four monolayers is the limit up to which defects can be healed out, at least up to temperatures of 1300 K. In classical metallurgy an annihilation distance is defined as the limit for annihilation of two passing dislocations. The critical thickness for epitaxial growth seems to be related or even the same. In reality, the critical thickness may be enlarged in the case of kinetic barriers or lowered in the case of disturbances due to defects or other uncertainties.

The simulations confirmed the following growth mechanism: from the beginning, the growth is perfectly

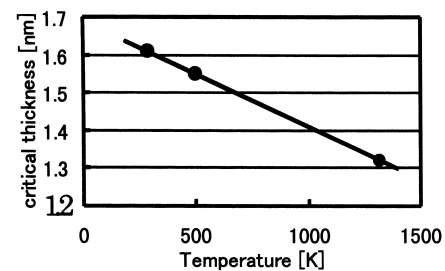


Fig. 5. Critical thickness as a function of the temperature. The straight line is derived from Eq. (5).

epitaxial and these early-formed layers of BaTiO₃ are strained in order to accommodate the misfit. Above the critical thickness the misfit dislocations dissociate and the partial migrates towards the interface, because combining two defects, the dislocation and the interface, reduces the energy. This migration creates a stacking fault on a (101) plane and is so fast that additional atoms (1 Ba, 1 Ti, and 3 O atoms per unit length) cannot diffuse fast enough to the surface.

The potential parameters for the BaTiO₃ and SrTiO₃ lattice could describe the lattice parameters and the thermal expansion very well. However, they still can be improved, in order to show better stability during long-term calculations, especially when surfaces are involved. This vacuum instability is hard to compare with experimental data and a sufficient criterion has to be defined. The interaction parameters should be revised by validation on other physical properties of the material like fracture toughness, heat capacity, etc. The phase transformations should also be included.

5. Conclusions

1. The critical thickness for the occurrence of misfit dislocations at the pseudomorphic growth of BaTiO₃ layers on SrTiO₃ (001) substrates was deduced from the interface energy calculated by the Molecular Dynamics method. This critical thickness is about 4 ML (= 1.6 nm) at 300 K and about 3.5 ML (= 1.32 nm) at 1300 K, and its temperature dependence is weak with linear slope expressed by a fitted equation.
2. The misfit dislocations in the MD simulations and in the experimental HRTEM images have a Burgers vector of the {100} type. In some cases dissociated misfit dislocations with Burgers vector $1/2\{101\}$ were found experimentally and in MD calculations.
3. A model for the formation mechanism of stacking faults on the (101) plane was deduced from structural plots of the MD simulations. After misfit dislocations are formed, they migrate towards the interface, which is the state of lowest energy. This means the formation of misfit dislocations and stacking faults are closely related to each other.
4. The atomistic structure of the stacking fault on the (101) plane consists of one oxygen layer in the center and in the next layer Ba- and Ti-atoms facing each other. The atomic structure of the stacking fault obtained by MD-simulations is the same as observed by HRTEM observations.

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