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Formation of stacking faults from misfit dislocations at the $BaTiO_3/SrTiO_3$ interface simulated by molecular dynamics

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Abstract

For advanced electronic devices the deposition of defect free of $BaTiO_3$ thin films on $SrTiO_3$ (0 0 1) substrates is required. The critical thickness, at which the growth mechanism changes from epitaxial growth without defects into pseudomorphic growth by introducing misfit dislocations, has been estimated in a previous study to be about four monolayers. Molecular dynamics simulations were performed in order to clarify the formation mechanism of these misfit dislocations. After the misfit dislocations have formed, they dissociate into a (1 0 1)-stacking fault and one partial dislocation migrates to the interface. The interface energy is lowered in spite of the stacking fault formation. The atomistic structure of the stacking fault on the (1 0 1) plane consists of one oxygen layer in the center and in the next layer Ba- and Ti-atoms facing each other, which is consistent with high-resolution transmission (HRTEM) observations. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Using the recently available experimental techniques, like MBE with pulsed laser deposition, $BaTiO_3$ thin films can be deposited on $SrTiO_3$ (0 0 1) substrates at around 700°C, much lower temperatures than before. At these lower process temperatures the diffusion is slower, so that defects cannot heal out by atom movement. Simulations [1] and TEM-observations [2–6] showed that misfit dislocations, stacking faults and other defects are occurring, which are explained in the following.

During the early stages of deposition the $BaTiO_3$ thin film grows epitaxial on the $SrTiO_3$ substrates. The lattice constants of $BaTiO_3$ ($a = 0.39927$ nm, $c = 0.40356$ nm) and $SrTiO_3$ ($a = 0.3904$ nm) are very similar. Two possible orientation relationships, (1) $(0\,0\,1)_{BaTiO_3} \| (0\,0\,1)_{SrTiO_3}$, $[1\,0\,0]_{BaTiO_3} \| [1\,0\,0]_{SrTiO_3}$, and (2) $(1\,0\,0)_{BaTiO_3} \| (0\,0\,1)_{SrTiO_3}$, $[0\,0\,1]_{BaTiO_3} \| [1\,0\,0]_{SrTiO_3}$ can be considered. The expected distance d between misfit dislocations can be evaluated from the comparison of the lattice constants a- and c-$BaTiO_3$ and a-$SrTiO_3$ at room temperature by searching for the minimum of the function $\min(na_{BaTiO_3} - (n+1)a_{SrTiO_3}) = d$. For the orientation relationship of case (1) d is about 17.56 nm and the number of lattice planes which are matching to each other at the interface is $n = 44a_{BaTiO_3}$ and $n+1 = 45a_{SrTiO_3}$ unit cells. For case (2) the values are $d = 1.71$ nm, and $n = 29a_{BaTiO_3}$ $n+1 = 30a_{SrTiO_3}$. It is expected that the system will choose orientation relationship (1), because the strain, and hence, the energy is lower. This adjustment mechanism of the lattice constants is also called Frank-vander Merwe-type of growth [7]. The critical thickness for epitaxial growth is the upper limit, up to which the lattice of the thin film can be strained.

In a previous study [1] using similar Molecular dynamics (MD) simulations to those reported in this paper, the interface energy as a function of the thickness was calculated for the two different cases, the strained $BaTiO_3$ thin film (hatched line in Fig. 1) and thin film containing with misfit dislocations (solid line in Fig. 1). The data were fitted with the formula $E_{IF} = (AT+B)t^m + Ct$, where the fit parameter A, B, C describe the slope and intercept, and m the exponent of the thickness dependence, respectively. The values were estimated as $A = -0.0792\,mJ/m^{2/3}K$, $B = 123\,mJ/m^{2/3}$, $C = 0$, $m = -0.33$ for the thin film containing the misfit dislocations, and $A = -0.0668\,mJ/m^2$, $B = 105\,mJ/m^2$, $C = 0.85$ l/nm, $m = 0$, for the strained thin film. Hence, the strained layer shows a slight increase of the interface energy of $0.678\,mJ/m^2$ per monolayer. The value for the critical thickness, when the energy of the thin film with misfit dislocations becomes lower than the strained film, has been es-

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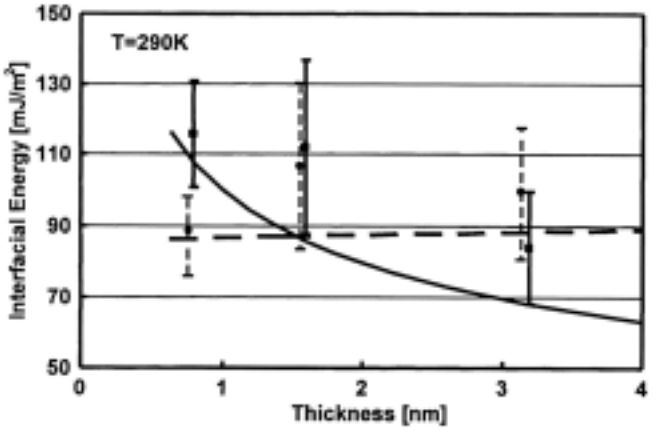

Fig. 1. Interfacial energy as a function of the thickness of the strained (solid line with squared symbols) and the unstrained (hatched line with round symbols) $BaTiO_3$ thin film for room temperature.

timated to four monolayers (ML), which is 1.6 nm at 290 K with a linear increase with temperature.

Experimental observations by cross-sectional transmission electron microscopy (TEM) [2] showed that the misfit dislocations possess in most cases the expected {0 0 1} Burgers vectors. This is in good agreement with the above mentioned simulation results, although it is not quite clear under which conditions dislocations with {0 1 1} Burger vector and stacking faults on (1 0 1) planes appear, up to a distance from the interface of about three unit cells. Furthermore, a non-stoichiometric type of defect appears, the Ruddlesden–Popper planar fault, which is a monolayer of excess BaO with NaCl-structure [3] between perovskite layers. In HRTEM images these defects look quite similar to stacking faults on (1 0 0) planes, but they can be distinguished by image calculations.

The understanding of the formation of stacking faults is very important in order to grow defect free thin films for improving the properties of the thin films. Furthermore, stacking faults on (1 0 0) planes occur, for which an atomistic model of a stacking fault based on experimental results has been presented [2,3]. It has a displacement vector of $1/2a[1\,0\,0]$ on the (0 0 1) plane. Stacking faults on (1 0 1) planes, however, seem to be the more important and more frequently occurring ones [2], because dislocations in perovskite structures usually slip on (1 1 0) planes, where the Peierls force is lower and the Burgers vector shorter than on (1 0 0) planes. Hence, a stacking fault on a (1 1 0) plane can be easily formed by splitting one of these ⟨0 1 1⟩ dislocations into two partials dislocations separated by the stacking fault. Hence, the formation process is easy and also this stacking fault has a lower energy than stacking faults on (1 0 0) planes, because in that case the atomic distances are larger.

Molecular dynamics simulations were performed in order to solve the question about the formation mechanism of these stacking faults and the atomic structure of the (1 0 1) stacking faults. The aim of this paper is to clarify the growth mechanism of the stacking faults and their atomic structure.

2. Experimental method

$BaTiO_3$ thin films were deposited onto $SrTiO_3$ (1 0 0) single crystal substrates by the PLD method using MBE. The substrate was heated to 700°C by infrared substrate heating system. After specimen preparation using a precision ion polishing system (PIPS) from Gatan the specimen were observed in cross sectional view using a Topcon 002B HRTEM, for details see elsewhere [2]. The image simulations were performed with the software "MacTempas".

3. Calculation method

The molecular dynamics program "Moldy" written by Refson [8,9] was used for this study. It allows the use of two-body-central-force-potential including the long-range Coulomb interaction. The Buckingham potential in the following form was applied

$$E_R = \frac{z_i z_j e^2}{r} + f_o(b_i + b_j)\exp\left(\frac{a_i + a_j - r}{b_i + b_j}\right) - \frac{c_i c_j}{r^6}$$

with $f_o = 6.9511 \times 10^{-11}$ N. The adjustable parameters z_i, a_i, b_i and c_i, were taken from previous works [1,10]. The lattice constants and the thermal expansion coefficient are calculated correctly for both materials $BaTiO_3$ and $SrTiO_3$. For the quantitative analysis of the interfacial energy per area in (J/m^2) the following formula was used

$$E_{IF} = \frac{N_{tIF}}{2N_A A}\left(\frac{E_{tIF}}{N_{tIF}} - \frac{E_{tSC}}{N_{tSC}}\right)$$

where E_{tIF} means the total energy of the interface, E_{tSC} that of the single crystal, N_{tIF}, N_{tSC}, are the number of unit cells of the grain boundary and the single crystal calculation, N_A is Avogadros number, A is the area of the interface in (nm^2). The factor of two comes in, because of the doubling of the interface due to the periodic boundary conditions.

The size of the initial supercell contains one period of the misfit dislocation spacing with 44 $BaTiO_3$ unit cells facing 45 unit cells of the $SrTiO_3$ substrate in the x-direction. Perpendicular to the interface in y-direction the supercell consists of a sandwich, namely substrate, thin film, substrate, with sufficiently large dimensions for the substrate (59 unit cells). In z-direction the thickness is one unit cell. In reality misfit dislocations also occur in this direction, but the epitaxy assumed in this model is a reasonable approximation in order to save calculation time. For the thickness of the strained $BaTiO_3$ thin film three monolayers was taken according to the critical thickness [1], followed by unstrained $BaTiO_3$ thin film. In the structural plot Ba atoms are displayed with large, bright, the Sr atoms with large, dark circles, the titanium atoms with middle-sized and the oxygen atoms with very small circles.

4. Results

The initial start configuration had an unlocalized misfit in the upper, unstrained $BaTiO_3$ part at a distance of three layers from the interface, which means that the mismatch is smeared out over the entire region according to the difference in the lattice constants of the substrate and the thin film. Already 0.5 ps later it transforms to a misfit dislocation with a well-defined core, shown in Fig. 2a. After 1 ps, the dislocation migrates and has only a distance of 2 layers from the interface Fig. 2b. After the migration, two barium atoms have a smaller distance to each other than usual. They are the nucleus of a stacking fault, which grows during the next time steps. One of the partial dislocation cores finally migrates to the interface. The stacking fault extends its length, indicated by the line of the plane in Fig. 2c.

The interface energy during this simulation is shown in Fig. 3. The initial configuration with the unlocalized misfit 44:45 lattice plane at the interface changes soon to the dislocation configuration with 70 mJ/m^2. Following this interface energy drop the stacking fault grows and the partial dislocation approaches the interface. The lowest energy of 58 mJ/m^2 is reached, when the partial reaches the interface.

In HRTEM observations this (1 0 1) stacking fault was also found as shown in Fig. 4a by a shift of $a/2$ in the $(\bar{1}\,0\,1)$ lattice planes. It has a length of about 3.2 nm starting from the interface, which is marked by a white line. For detailed quantitative analysis of the HRTEM micrographs, image simulations were performed. Under the usual Scherzer conditions

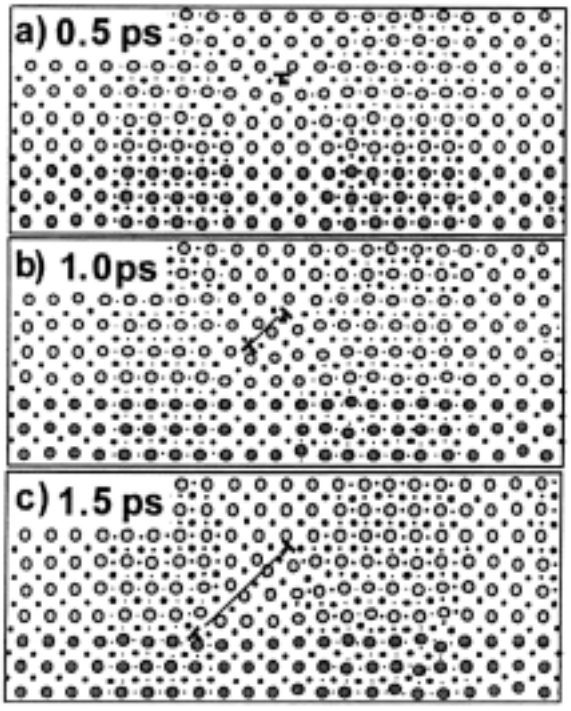

Fig. 2. MD-simulations after (a) 0.5, (b) 1.0, (c) 1.5 ps, which show the formation of a stacking fault. The larger, dark atoms are Sr, the large, grey atoms are Ba, middle-sized atoms Ti and small ones O.

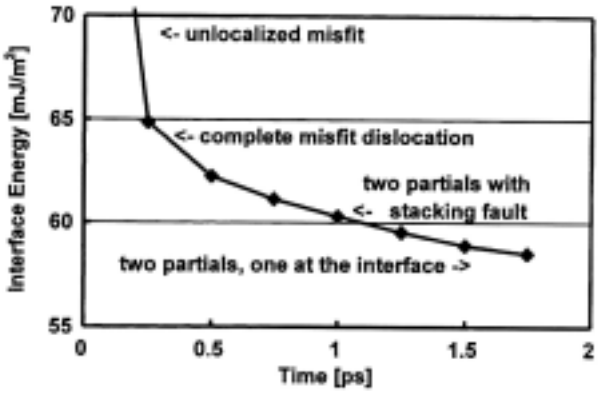

Fig. 3. Interfacial energy as a function of time, with the description of the microstructure according to Fig. 2.

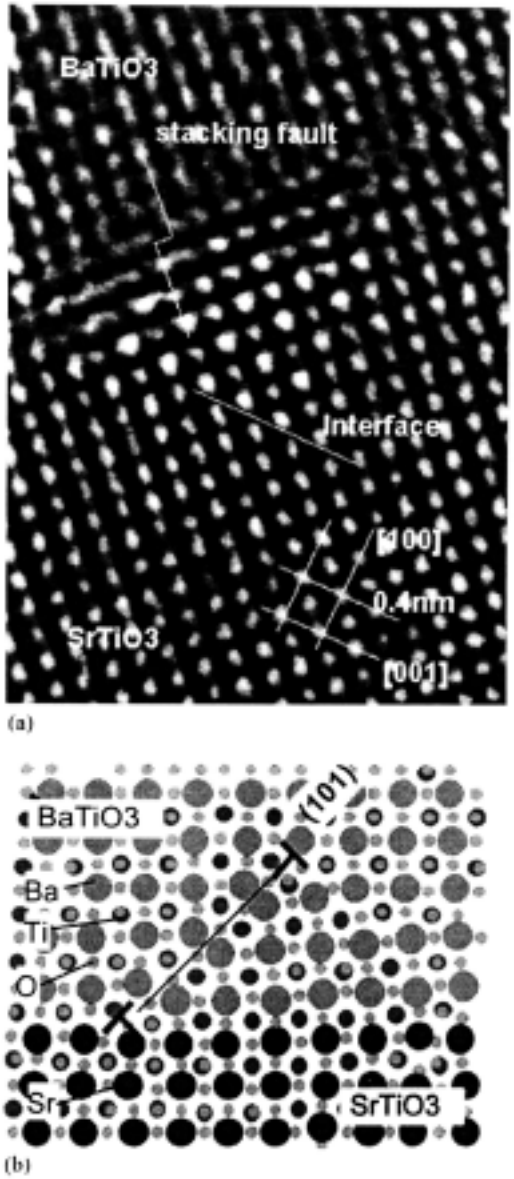

Fig. 4. (a) HRTEM micrograph; (b) MD-calculation result of the atomic structure of the (1 0 1) stacking fault lying at the interface.

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 correspond to the oxygen-atoms [2,6]. 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. The MD-simulations in Fig. 4b shows the center (1 0 1) plane of the stacking fault 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. The original sequence of the $(\bar{1}\,0\,1)$ planes ...acbcacbcacbc... has been changed into ...acbcacacbcac... Hence, the atomic structure obtained from the image simulation of the experimental HRTEM image and the MD-simulations are in excellent agreement.

5. Discussion and conclusion

The growth mechanism of the thin film has been clarified by the MD-calculations. In the beginning perfectly epitaxially-formed $BaTiO_3$ layers are strained to accommodate the misfit. Then, when the thickness has reached the critical value, the misfit dislocations are introduced. Sandwich structured calculations with strained layers thicker than the critical thickness followed by unstrained $BaTiO_3$ layers, showed that the complete misfit dislocation is not able to migrate to the interface position. If the dislocation is three lattice planes away from the interface, it dissociates and one partial migrates to the interface because the combination of two defects, one partial dislocation with the interfaces, has a lower energy (58 mJ/m^2) compared to the creation of the stacking fault. This combination, partial at the interface, has an even lower interface energy than interface with one un-dissociated dislocation (70 mJ/m^2), which is about the same value as in Fig. 1 (at the thickness 1.7 nm = 3 ML). Since these integrated values of the interface energy contains the interface, the partials, and the stacking fault, it is hard to extract the value for the stacking fault energy.

With the calculations of the interfacial energy the critical thickness for epitaxial growth could be estimated. The value of around four monolayers at room temperature decreases at high temperatures. This thickness, up to which a defect free thin film can be grown, corresponds to the value of the annihilation distance in classical metallurgy, which is the spatial distance limit for the annihilation of two passing dislocations with opposite Burgers vector. 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.

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