Acta Materialia 118 (2016) 286–295

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

Atomistic simulations of symmetrical low-angle [100] (01l) tilt boundaries in $SrTiO_3$

Amr H.H. Ramadan*, Roger A. De Souza

Institute of Physical Chemistry and JARA-FIT, RWTH Aachen University, Landoltweg 2, 52056 Aachen, Germany

ARTICLE INFO

Article history:
Received 20 April 2016
Received in revised form
8 July 2016
Accepted 19 July 2016

Keywords:
Atomistic simulations
Dislocation structure
Grain-boundary structure
Perovskites
Strontium titanate

ABSTRACT

The structural properties of symmetrical low-angle [100] (01l) tilt grain boundaries in the perovskite oxide $SrTiO_3$ were investigated by empirical pair potentials and energy minimisation techniques. Thirteen interfaces with misorientation angles varying between $\theta = 3°$ and $\theta = 22.6°$ were studied in both stoichiometric and oxygen deficient forms. Examination of the relaxed simulation cells indicated that *all* the studied grain boundaries consisted of some combination of two different types of dislocation core. The structures of the two types of dislocation core remain unchanged at low misorientation angles but become increasingly distorted at the highest angles examined. Simple rules were derived to predict the type, arrangement and alignment of the dislocations at a given interface.

1. Introduction

The perovskite oxide strontium titanate ($SrTiO_3$) has long been considered a model material for studying experimentally the structures of grain boundaries in the huge family of perovskite-type oxides. This is because $SrTiO_3$ combines high mechanical and chemical stability with a simple, high-symmetry cubic structure [1–3]. In addition, $SrTiO_3$ provides an ideal oxide material in which the interactions of grain boundaries with point defects may be examined quantitatively [4–6], as the behaviour of point defects in bulk $SrTiO_3$ has been elucidated to a degree unrivalled by any other complex oxide [3,7–11]. Such knowledge allows strong conclusions to be drawn for interfacial behaviour.

Low-angle grain boundaries in $SrTiO_3$, in particular, have received much attention, because—consisting of a periodic array of dislocations—they allow structure-property relationships to be elucidated [6,12–16] and they allow the properties of dislocations to be studied. Thus, not only the atomistic structures of selected [100] low-angle boundaries have been investigated [17–24], but also their resistance to charge transport [12–16,22], their interaction with oxygen vacancies [6,22], and their influence on oxygen diffusion [22]. It has been suggested [25] that dislocations constitute the active filaments in resistive switching devices of $SrTiO_3$, but recent evidence militates against this view [22,26,27].

Despite the concerted effort, there is much debate, still, regarding the structure of low-angle [100] tilt grain boundaries in $SrTiO_3$. These interfaces are reported variously to consist of one type [23], of two types [17,20,22,24], or even of three types [21] of dislocation cores. The dislocations, furthermore, may be aligned [17,21–23], or non-aligned in a zigzag pattern [20,24]. In addition there are reports of considerable cation disorder at the dislocation cores [21,23], and also reports in which no such disorder was observed [17,20,24]. All studies do agree, though, that dislocations are oxygen deficient and dissociated; and that the average dislocation separation at a given [100] tilt boundary is given by Frank's Formula [28],

$$d_{\mathrm{Frank}} = \frac{|\mathbf{b}|}{2\sin(\theta/2)}, \tag{1}$$

with Burgers' vector **b**. (For these tilt boundaries, $|\mathbf{b}| = a[100]$, where a is the lattice constant of $SrTiO_3$) [12,13,17,21–23].

In a previous study [22] we used atomistic simulation techniques to examine the structure, the energetics and the point-defect processes at a 6.0°[100](0119) tilt grain boundary in $SrTiO_3$. We confirmed the structural model proposed by Zhang et al. [17], that the tilt boundary consists of two types of dislocation cores (termed SrO-type and TiO_2-type), and that both dislocation types

* Corresponding author.
E-mail address: amr.ramadan@rwth-aachen.de (A.H.H. Ramadan).

http://dx.doi.org/10.1016/j.actamat.2016.07.035
1359-6454/

are non-dissociated when stoichiometric and only dissociate when oxygen vacancies are introduced at the dislocation cores. Here, we extend our investigations to a wide variety of other misorientation angles of symmetrical tilt grain boundaries. Our general aims are to investigate the effect of the tilt angle (θ) on the grain-boundary structure, excess energy and excess volume for both stoichiometric and oxygen deficient dislocation cores. To this end, we employ well established static atomistic simulation techniques [29–31] with high quality empirical pair potentials [32]. Based on our results, we are able to resolve several apparent discrepancies in the literature regarding the atomistic structure of low-angle grain boundaries. Specifically, we find that various dislocation configurations are possible at [100](01l) symmetric tilt boundaries in $SrTiO_3$: the dislocations may be equally spaced or not; they may display one or two types of dislocation cores; and they may be aligned or not. Furthermore, we demonstrate that it is possible to predict the specific dislocation configuration (spacing, type and alignment) based solely on knowledge of the grain-boundary plane.

2. Computational methods

The tilt-boundary angle is given by the angle between the planes of the two grains that form the boundary, which for cubic systems is given by

$$\cos\theta = \frac{h_1h_2 + k_1k_2 + l_1l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2}\sqrt{h_2^2 + k_2^2 + l_2^2}}, \quad (2)$$

where h_i, k_i and l_i are the Miller indices of the planes and θ is the corresponding tilt angle. For all simulated interfaces the rotation axis is the [100] direction and the grain-boundary normal prior to rotation is the [001] direction. Thus, for all the investigated boundaries, $h_1 = h_2 = 0$. In this study we set $k_1 = k_2 = 1$, so that the only variable is l. As we only investigate symmetrical tilt boundaries, then $|l_1| = |l_2|$ in all cases. These conditions lead to discrete tilt angles, which can be determined using Equation (2).

With the GBStudio package [33], we constructed initial geometric configurations of the grain-boundary simulation cells that yield the investigated interfaces listed in Table 1 with their various parameters. The cells are a single $SrTiO_3$ unit-cell thick and consist of two (anti-parallel) grain boundaries, such that the simulation cells are periodic in all three dimensions. We employ this anti-parallel configuration of the tilt boundaries, so that the resulting simulation cells are macroscopically unstrained.

The initial atomic configurations at the grain boundaries contained overlapping ions and large voids. We performed careful rearrangements of these configurations and/or removal of ions in order to have reasonable preliminary structures for the energy minimisation. All structural adjustments maintained the stoichiometry of $SrTiO_3$, that is, the removal or addition of ions occurred in units of $SrTiO_3$, such that the simulation cell remained stoichiometric.

In these classical simulations, the interactions between the ions were described with empirical pair potentials of the form

$$V_{ij} = \frac{z_iz_je^2}{4\pi\varepsilon_0 r} + D_{ij}\left\{\left[1 - e^{-a_{ij}(r-r_0)}\right]^2 - 1\right\} + \frac{C_{ij}}{r^{12}}, \quad (3)$$

where the first term describes the long-range Coulomb interactions; the second term is a Morse function to describe short-range repulsive interactions; and the third term is an additional repulsive term, which only becomes important when performing molecular dynamics simulations, as it prevents inter-ion distances from becoming unphysically small. The values of the potential parameters were taken directly from Pedone et al. [32] (see Table 2), without any further optimisation, as they reproduce both experimental bulk and defective lattice properties very well [22,34,35].

All degrees of freedom within each prepared simulation cell were relaxed until a minimum energy configuration was obtained. Subsequent defect calculations were limited to anion deficiency. Dislocations with cation non-stoichiometry are left for future investigation, as the complexity of the topic renders it outside the scope of this study.

The calculations of fully oxygen-deficient dislocation cores (*i.e.* removal of entire oxygen-ion columns) were performed at constant volume with the supercell method. The net charge that arises from the investigated defects was compensated by a neutralising background charge. Isolated point defects in the bulk and at a dislocation (*i.e.* oxygen vacancies at infinite dilution), were investigated with the Mott–Littleton approach [36]. Although this method is not designed specifically for the study of point defects at grain boundaries, it is considered sufficient for requirements of this study (in accordance with previous findings [22,37]). All atomistic simulations presented here were implemented in the Gulp code [38].

3. Results

3.1. Structural characteristics

Initial examination of the thirteen (energy-minimised) stoichiometric boundaries shown in Fig. 1 reveal several common characteristics. First, all boundaries consist of an array of edge dislocations. Second, the average separation of dislocations is consistent with the theoretical values calculated with Frank's formula (see Table 1). Third, all simulated interfaces consist of non-dissociated dislocations. The thirteen corresponding oxygen-deficient boundaries are shown in Fig. 2. (Removal of an oxygen ion from a dislocation core corresponds in supercell simulations to the removal of an entire column of oxygen ions, as the simulation cell is only one unit cell thick.) Here, the interfaces consist of dissociated dislocation cores, but otherwise these oxygen-deficient

Table 1
Summary of the simulation cell parameters for the various tilt angles θ as well as the corresponding grain-boundary planes. d_{Frank} is the distance between dislocations as determined by Frank's formula and corresponds to the determined average dislocation separation for all investigated grain boundaries.

θ /°	h	k	l	a /Å	b /Å	c /Å	d_{Frank} /nm	d_{Frank} /a
3.0	0	1	38	3.92	149.15	153.76	7.45	19.0
3.3	0	1	35	3.92	137.38	153.96	6.86	17.5
4.2	0	1	27	3.92	106.01	154.18	5.30	13.5
5.5	0	1	21	3.92	82.49	154.45	4.12	10.5
6.0	0	1	19	3.92	74.65	155.39	3.73	9.5
7.2	0	1	16	3.92	62.90	155.02	3.14	8.0
7.6	0	1	15	3.92	58.98	154.85	2.95	7.5
8.2	0	1	14	3.92	55.07	154.10	2.75	7.0
8.8	0	1	13	3.92	51.16	153.82	2.56	6.5
10.4	0	1	11	3.92	43.34	155.24	2.17	5.5
12.7	0	1	9	3.92	35.53	153.74	1.77	4.5
16.3	0	1	7	3.92	27.75	153.45	1.39	3.5
22.6	0	1	5	3.92	20.01	152.44	1.00	2.5

Table 2
Parameters of the empirical pair potentials as derived by Pedone et al. [32].

	D_{ij} /eV	a_{ij} /Å^{-1}	r_0 /Å	C_{ij} /eV Å^{12}
$Sr^{1.2+}\cdots O^{1.2-}$	0.019623	1.886000	3.328330	3.0
$Ti^{2.4+}\cdots O^{1.2-}$	0.024235	2.254703	2.708943	1.0
$O^{1.2-}\cdots O^{1.2-}$	0.042395	1.379316	3.618701	22.0