Energetics and structure of <001> tilt grain boundaries in SiC

Marcin Wojdyr[1,2], Sarah Khalil[2], Yun Liu[2] and Izabela Szlufarska[2]
[1] Institute of High Pressure Physics UNIPRESS, ul. Sokolowska 29/37, 01-142 Warsaw, Poland
[2] Department of Materials Science & Engineering, University of Wisconsin, Madison, WI 53706

E-mail: wojdyr@gmail.com, izabela@engr.wisc.edu

Abstract. We have developed a scheme, based on molecular dynamics, that allows finding minimum energy structures of grain boundaries (GBs) with relatively large cell of non-identical displacements. This scheme has been used to study symmetric <001> tilt GBs in cubic SiC. We analyse atomic configurations of dislocation cores found in low-angle GBs and we report structural units found in high-angle GBs. In contrast to what had been previously assumed we find that the lowest energy structures often do not favor perfect coordination of GB atoms and that most of the analysed GBs contain 6- and 7- atom rings. We tested the applicability of existing empirical potentials to studies of high-symmetry GB structures in SiC and we found Tersoff potential to be most appropriate. Knowledge of detailed atomic structures of GBs is essential for future studies of GB-controlled phenomena in SiC, such as diffusion of metallic fission product through this material or GB strengthening.

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1. Introduction

The physical, chemical, mechanical, and thermal properties of polycrystalline materials can be largerly influenced by the type and structure of grain boundaries (GBs) [1-3]. Knowledge of GB energetics and structure is especially important for studies of interface-driven processes, such as sintering or GB diffusion. For instance, diffusion rate along a given GB is controlled by the atomic structure of such interface, e.g., by the presence of dangling bonds [4]. In nanocrystalline materials GBs can even become the dominant feature that determines material's behavior, e.g., plastic deformation, which for small-grain materials is mediated by GB sliding in contrast to dislocation motion that drives plasticity in polycrystalline materials. Since the atomic structure of a GB is not uniquely defined by the misorientation of the grains, methods needs to be developed for identifying atomic-level details of GBs in technologically important materials.

Silicon carbide (SiC) is a promising candidate for a variety of technological applications, including gas turbines, heat exchangers, and coatings in nuclear reactors. This material has many outstanding properties, such as high hardness as well as thermal and chemical stability. The applications of SiC have been shown to be largely affected by the properties of GBs. For example, the failure of TRISO-coated fuel particles in pebble-bed nuclear reactors has been attributed to the GB diffusion of fission products through a SiC coating [5]. One possible way to improve properties of SiC as a diffusion barrier is to engineer GBs of this material. Such approach has been already shown to be effective in reducing oxidation-induced brittleness of SiC [6].

A number of studies have been reported on atomistic modeling of GBs in SiC [2, 7-10]. Specifically, special short-period GBs in SiC have been investigated using *ab initio* [7, 8, 2] and tight binding [9, 2] techniques. Most of the research was focused on the <011> Σ3 and Σ9 GBs, whose atomistic models can be validated against high-resolution transmission electron microscope (HRTEM) observations. Due to the limited number of atoms that can be treated directly in *ab initio* calculations, classical interatomic potentials are used to investigate GB types beyond the short-period ones. For instance, such approach has been used to analyze the energy and structure of symmetric tilt grain boundaries (STGBs) in SiC [11], Si [12], diamond [13] and metals [14-16].

The primary interest in structural analysis of GBs is the atomistic configuration that corresponds to the minimum energy for a given misorientation of grains, i.e., the ground-state structure. The search for this ground-state configuration can be viewed as a global optimization problem, where the energy is the *objective function*

and atomic coordinates are parameters. Although there are many well-known methods to handle this kind of optimization problems, none of them guarantees finding the global minimum in a general case. The most popular methods used to search for ground-state structures of GBs are based on the molecular statics (MS) and molecular dynamics (MD) techniques. MS is fast and allows investigation of a large number of initial configurations [16-18], but is successful only if at least one of the configurations is close to the global minimum. Using MD allows the atoms to overcome local energy barriers in the energy landscape of possible configurations, but this approach is computationally more expensive. Recently, three new heuristic procedures for searching for the lowest energy structures have been proposed [19, 20, 12]. The importance of a robust search procedure is exemplified by the fact that its use allowed the discovery that high-angle short-period twist GBs in silicon are ordered [19, 21] – in contrast to what had been assumed in earlier models. The different search algorithms are reviewed in Section 3.1.

In this paper we introduce a new scheme for searching for ground-state GB structures. We use this scheme to analyze symmetric <001> tilt GBs in cubic SiC. We find that most of the ground state structures of studied GBs contain 6- and 7-atom rings that form tiny channels parallel to the tilt axis. Such structures have lower energies than the structures reported earlier in the literature [11].

2. Methodology

2.1. Bicrystal geometry

The boundary conditions of the modeled system can have a large effect on the atomic structure of the interface and therefore such boundary conditions should be chosen with care. In general, there are three different setups of a bicrystal system used in the literature (e.g. in [20], [15] and [16]) and they are shown in Figs. 1 (a), (b) and (c), respectively. All of these models have orthorhombic cells with periodic boundary conditions (PBC) applied in the directions parallel to the boundary plane. In a setup with free surfaces (Fig. 1(a)) the surfaces are allowed to reconstruct during the boundary structure optimization. In a setup with rigid slabs at the surfaces (Fig. 1(b)) one of the rigid slabs is frozen, to make computations faster, but the other slab is movable to allow a relative displacement of the two grains. The third setup (Fig. 1(c)) contains two GBs, it has no surfaces, and it is periodic also in the direction *z* perpendicular to the boundaries.

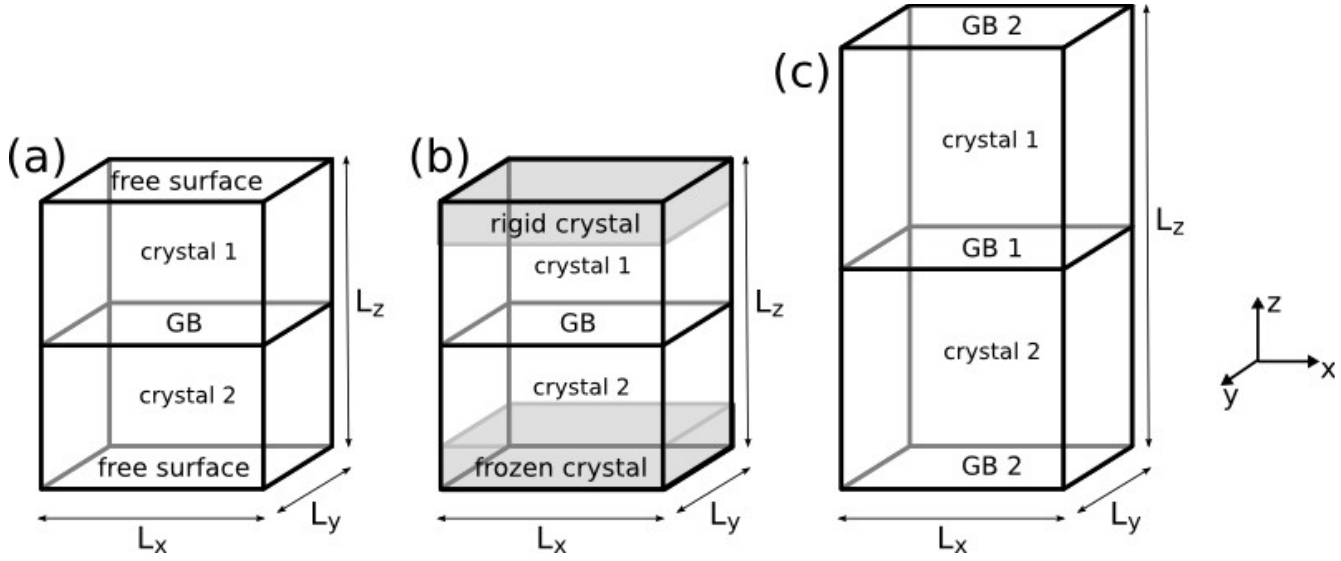

Figure 1. Three geometries commonly used for bicrystal simulations: (a) Free surfaces are allowed to reconstruct. (b) Surfaces are rigid and one of the surfaces is frozen to speed up computations. (c) PBC are applied in all three spatial directions to avoid creation of free surfaces.

Here we performed optimization procedure with all the three setups to determine which one is most efficient. The first two setups (Figs. 1(a) and (b)) give better results than the third one (Fig. 1(c)), because having two GBs reduces relative displacements of grains and makes it less probable for our optimization procedure to find the ground-state structure. In the first two setups the height L_z of the bicrystal in the direction *z* must be large

enough to make interactions of the GB with surfaces negligible. Comparing configurations with the same number of atoms in geometries from Figs. 1 (a) and (b) we found that in the latter the finite size L_z leads to a smaller error in the GB energy than setup in Fig. 1(a). Consequently, the setup from Fig 1 (b) allows for using smaller configurations and is therefore more efficient.

It is also interesting to note that the errors in GB energy that arise when the size L_z is too small are different in setups from Figs. 1(a) and (b). In the geometry with free surfaces the GB energy is underestimated, because only a part of the elastic energy of the boundary is taken into account. In the geometry with rigid surfaces the strain caused by this rigidity leads to an overestimate of the GB energy.

In this study we calculate GB energies using the geometry shown in Fig. 1(b), because this geometry was found to be the most efficient for computations. The dimension L_z is always larger than 3 nm. For each GB we checked if the size is large enough by extending the final system by 2nm in the z direction, relaxing the extended system with the conjugate gradient (CG) method, and calculating the GB energy again. Because we apply PBC in the plane of the GB, the possible system dimensions in the x and y directions depend on the periodicity of the bicrystal within the GB plane. The length L_x in the direction parallel to the tilt axis is the same for all the samples and equal to 0.86 nm, which is twice as large as the period of the GB in this direction. The length L_y is chosen to be either equal to a single period of the boundary in the y direction if the period is larger than 1 nm, or otherwise it is equal to two periods.

2.2. Initial boundaries

The first step in creating GB models is to define macroscopic degrees of freedom, which are associated with the misorientation of the crystals and the inclination of the boundary normal. In the case of a tilt GB, one needs to define a rotation (tilt) axis, a rotation angle, and the boundary plane. The boundary plane can be defined either in the reference system of one of the grains or as a *median plane*, i.e., in the reference system of a *median lattice*. The term *median lattice* refers to the lattice that lies halfway in orientation between the lattices of the two crystals that form a GB.

To construct a symmetric boundary, the median plane must be a mirror plane of the lattice of the crystal. Consequently, in cubic (zinc-blende) SiC all STGBs with the <001> tilt axis must have the (110) median plane (Fig. 2). In this study we investigate structures of such <001> STGBs with rotation angles from 0 to 90°, sampled with increments of about 3°. The angles correspond to misorientations of coincidence site lattices (CSL), which is a necessary condition for a periodic bicrystal [1, 2]. A relaxation of a GB can involve a relative translation of two crystals, which destroys both the symmetry of the structure in the GB plane and the coincidence of the lattices. Despite these changes, such a boundary is still referred to as STGB and a (relaxed) CSL boundary [22], and it is described by the Σ number equal to the inverse density of coinciding sites in the ideal CSL boundary.

GB configurations have been widely studied in fcc and bcc metals. In these two crystallographic structures rotations by angles θ and 90°-θ are equivalent to each other and a plot of GB energy as a function of the angle is approximately symmetric about θ=45° [23]. The minor asymmetry is caused by different crystallographic boundary planes corresponding to angles θ and 90°-θ. Although the zincblende structure of SiC can be viewed as two interpenetrating fcc lattices, it has a lower symmetry than fcc. In particular, in the zincblende structure the <001> axis has a two-fold symmetry (in contrast to the 4-fold symmetry in the fcc structure) and the (100) plane is not a mirror plane. The maximum disorientation (symmetry-reduced misorientation) of two zincblende crystals is equal to 90° and corresponds to the <001> rotation axis [24], which means that all boundaries analyzed in this study have distinct disorientations. Therefore, unlike in the fcc case, one cannot assume that the plot of GB energy vs angle will be approximately symmetric about 45°.

The initial boundaries are created by first constructing two overlapping lattices with a required misorientation (Fig. 2), and then discarding atoms from one lattice on one side of the boundary plane and discarding atoms from the other lattice on the other side. Subsequently, a search procedure, which includes additional removal of atoms, is performed to determine the ground-state structure of the boundary. This search procedure is described in Section 3.

An example of the initial structure is shown in Fig 3(a) for <001> STGB with misorientation 90°, which has the (100) boundary plane. Note that experimental techniques, which are based on the crystallographic orientations of grains determined from Kikuchi patterns, are not able to differentiate between the (100) GB with

disorientation 90° and the ideal zinc-blende lattice, and in general these techniques cannot distinguish between <001> STGBs with rotation angle θ and 90°-θ.

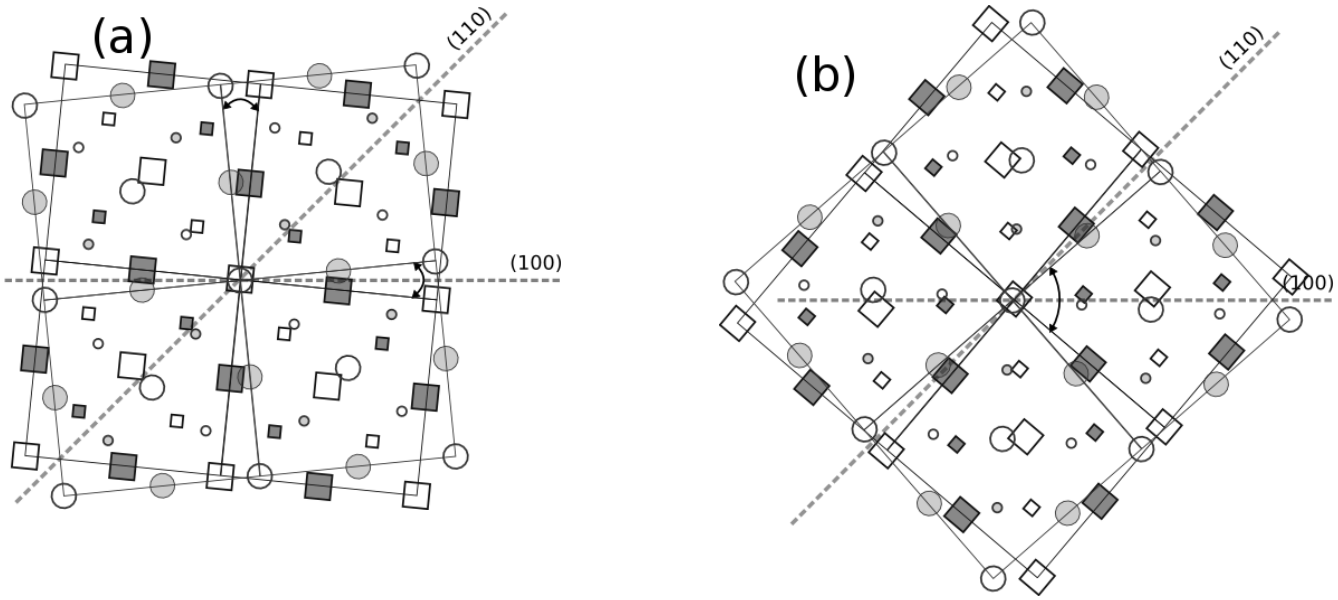

Figure 2. Schematic representation of two overlapping zincblende lattices rotated by (a) 15° and (b) 75° with respect to one another. Rotation axis [001] is orthogonal to the drawing plane. Atoms in one lattice are marked with squares and in the other with circles. Big and small symbols correspond to Si and C respectively. Open and filled symbols are used to distinguish atoms that have different positions in the [001] direction. The (110) plane is the only median plane that allows constructing a symmetric tilt GB.

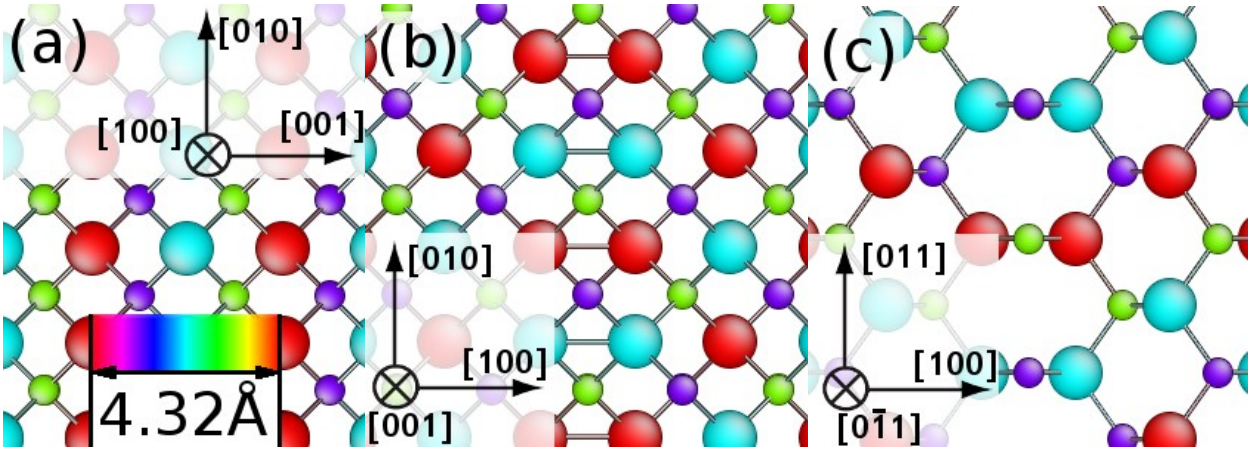

Figure 3. The initial configuration of [100] (001) STGB with angle 90°, created as described in Section 2.2, viewed in (a) the (100), (b) the (001) and (c) the $(0\,\bar{1}\,1)$ projections. Atoms with different colors have different positions along the [001] direction, as shown in (a). The same structure after relaxation is shown in Section 4.2.

2.3. Interaction potentials

Optimization schemes that rely on the MD technique require high-accuracy empirical potentials to describe interactions among atoms. There are two popular families of interatomic potentials for covalent materials: bond-order potentials and the Stillinger-Weber potential and its modifications. Among the Stillinger-Weber potentials, a modification developed by Vashishta *et al.* [25] has been particularly useful for studies of

structural properties of SiC and of amorphous-like GBs [26-28]. This potential reproduces many properties of SiC in excellent agreement with experiment, including elastic constants, melting temperature, stacking fault energies, formation energies of the most stable SiC polytypes, fracture toughness, etc. One limitation of the potential is that it does not reproduce correctly energies of homonuclear bonds (Si-Si and C-C), which is important for the tilt GBs considered here. Therefore in the current study we use a reactive bond order potential that allows for formation of homonuclear bonds.

The most widely used bond-order SiC potential has been proposed by Tersoff in 1989 [29] and over the years a number of small modifications have been introduced to the parameter set. It has been shown that the potential describes properly elastic constants and surface properties only if the potential cut-off has been modified to exclude interactions with the second nearest neighbors [30]. In the original paper by Tersoff [29], the cut-off function is smooth and the Si-Si cut-off is 3.0 Å. Since the distance between the nearest Si atoms in the perfect SiC lattice is 3.05 Å, phenomena such as very high pressure, small lattice distortions, and thermal vibrations can easily reduce the interatomic distance to below 3.0 Å, leading to an increase of the effective coordination number of Si atoms and to an unphysical increase of the energy. A few approaches to correct this issue have been proposed in the literature [30-33, 10]. For instance, for calculations of point defect energies Tersoff *et al.* [31] used a shorter (i.e., 2.5 Å) cut-off with a discontinuity at the cut-off distance. To study bulk properties of SiC Tang *et al.* [30] scaled the cut-off values with the system volume, starting from the value of 2.8 Å for Si-Si bond length at zero hydrostatic pressure. Porter *et al.* [32] adopted the scheme of excluding the Si-Si interactions regardless of their separation in order to calculate finite-temperature properties of SiC [32]. However, as mentioned in previous paragraphs, the ability to form homonuclear bonds in SiC is important to correctly reproduce structures of tilt GBs. Of particular interest to our study is the modification to Tersoff potential that was proposed by Kohler [11] to study tilt GBs in SiC. Specifically, Kohler used a smooth Si-Si cut-off of 2.85 Å and this is the approach that we use in our study. Kohler validated his cut-off value by comparing generated models of a Σ9 GB with published configurations obtained using *ab initio* methods. We have carried out additional validation for Σ5 and confirmed that the structure obtained using the 2.85 Å cut-off is in a better agreement with our *ab initio* calculations than the one generated using the original cut-off from Ref. [29]. We also verified that for other short-period structures, Σ3 and the STGB (100) with tilt angle 90°, configurations obtained with our optimization scheme do not change after an additional relaxation performed using *ab initio* methods based on the density functional theory.

In our study MD simulations were performed using the LAMMPS program [34]. The density functional theory calculations were performed using the Vienna Ab-initio Simulation Package VASP [35]. Details of *ab initio* calculations are given elsewhere [4]. The AtomEye program was used for visualization of structures [36].

3. Optimization scheme

The geometry of the GB is characterised by five macroscopic degrees of freedom (DOF) and four microscopic DOF. Macroscopic DOF are associated with the misorientation of the crystals and the inclination of the boundary normal while the microscopic DOF describe the relative translation of the crystals and the location of the GB plane [1]. In contrast to the macroscopic DOF, the microscopic ones are determined by relaxation processes at the boundary and are assumed to adjust to minimize free energy of the system. The relaxation processes determine also the atomic configuration of the boundary and can lead to insertion or removal of boundary atoms [1].

Searching for the minimum in the energy landscape of a GB is an involved computational task. In mathematical terms, this is a global optimization problem, where the energy is an objective function. This function has both continuous parameters, that correspond to the microscopic DOF and the positions of atoms in the GB, and one or more discrete parameters corresponding to the numbers of GB atoms of each species.

3.1.Previously developed optimization methods

The extensive search for the minimum of energy requires computational power, which has not been available in the times of the early atomistic simulations. In recent years a number of research groups [16-20, 12] have taken advantage of the rapid advances in computer architectures and proposed various optimization methods for discovery of the most stable GB structures. For instance, several authors performed a search for the

lowest energy structures in metals by extensive sampling of the initial configurations and by locally optimizing each sampled point [16-18]. The low cost of local optimization methods, such as the CG, allows for trying of a large number (more than 50,000 in some cases [17]) of initial configurations. The success of this procedure depends on the sampling algorithm. For example, Olmsted *et al*. [17] constructed the initial boundaries by varying the four microscopic degrees of freedom and by discarding overlapping atoms. The cut-off distance that defines the overlap of atoms was varied from 33% to 85% of the nearest-neighbour separation.

A different optimization scheme has been employed by Alfthan *et al.* [19, 21] in their studies of low-period (001) twist GBs in Si. In this method, atoms are systematically discarded up to $2v$-1 of removed atoms, where v is the number of atoms in one atomic layer parallel to the GB plane. All $2v$ initial systems are relaxed during 30 million steps of MD simulations. The MD scheme starts with melting of the region near the GB. The system is then slowly quenched, and when the configuration is stable, the system is heated again. The quenching and heating is repeated a few times, giving a sawtooth temperature profile. During the simulation, the configurations that have not changed the bonding network for more than 20,000 steps are written out, and each such configuration is minimized using the CG method. Yet another search procedure was introduced by Brown and Mishin [20] for studies of asymmetric tilt GBs in copper. In this case the optimization scheme consists of finding the most favourable in-plane (i.e. parallel to the GB plane) grain translation, relaxing positions of GB atoms with fixed relative translation of the grains, and testing if the removal of GB atoms can lower the energy. Unlike in the case of twist Si GBs [19], discarding some of the boundary atoms in Cu did not yield a structure with a lower GB energy. More recently genetic algorithms have been employed by Zhang *et al*. [12] to find minimum energy structures in <001> STGBs in Si. This method is inspired by the 'cut and splice' genetic algorithms used for optimization of atomic clusters [38]. The crossover operation is performed by cutting GBs using an arbitrary plane perpendicular to the GB plane and by combining two parts from different parent structures into a new GB. This scheme did both, reproduced structures consistent with those that had been reported earlier in the literature and it found new GB configurations, but its efficiency has not been compared with that of MD-based schemes.

3.2. Current optimization method

Since SiC is a binary system, SiC boundary has larger number of possible configurations as compared to monoatomic systems (e.g., Si and Cu). The larger number of local minima in the SiC energy landscape requires taking into account an enormous number of initial samples if the search for the global minimum relies only on the conjugate gradient method. On the other hand, the computational scheme proposed by Alfthan [19], in which the entire configurational space is searched using MD simulations that all start from a single point in the landscape, is computationally too expensive for boundaries where the GB period in one direction has several nanometers. Therefore in our study we develop a new optimization method that is based on three elements: varied number of atoms in the boundary (as described in more detail in subsequent paragraphs), sampling different initial displacements of the grains, and finally annealing the system in MD. Similarly to Ref. [17], we use the concept of a cut-off distance to decide which GB atoms are to be discarded from the bicrystal. The cut-off can be different for each pair of atomic species. Two atoms that are separated by a distance smaller than the cut-off are considered to be overlapping. After construction of the initial boundary (Section 2.2) only atoms from different grains can overlap. In an ideal STGB, every atom found at a distance smaller than half of the cut-off from the boundary plane overlaps with its image in the other grain. Since atoms can only overlap with their images, atoms of different species do not overlap and we use only two cut-off distances, r_{Si} and r_C, that correspond to the minimum allowed Si-Si and C-C distances, respectively. The cut-off distances r_{Si} and r_C are allowed to vary from 0 to the nearest neighbour distance in the SiC lattice. The stoichiometric GBs are prepared with $r_{Si} = r_C$. For the majority of the samples analysed in this study, the number of cut-off values that produce distinct structures is smaller than 10.

After removing overlapping atoms from the GB, we sample the relative in-plane displacements of the crystals. The translational symmetry of the bicrystal determines a *cell of non-identical displacements* (CNID). CNID contains all possible in-plane displacements that cannot be mapped onto one another simply by adding a translation vector [1]. We sample the CNID by changing the displacement with increments of 1Å in the x and y directions.

In the final step of the optimization procedure, each bicrystal is relaxed in MD to find a minimum of energy. Relaxation is accomplished in the NVT ensemble and simulations are performed with the time step of

1.5 fs, each having 1.5 ns of the total time. The temperature is first increased to 2,000K and then slowly quenched to 100K. The cycle of heating and cooling is repeated three times, with the peak temperature raised to 2,500K, 3,000K, and 3,500K. Each time quenching takes 200,000 steps. Every 5,000 steps a copy of the atomic configurations is saved in the computer memory and then it is minimized using CG. The system that has the lowest energy among all minimized configurations is considered a relaxed structure.

In the configuration with rigid surfaces (Fig. 1b), the rigid slabs are cooling down the entire system, creating a gradient of the temperature with the maximum near the GB. When the system is heated, it starts melting at the GB. Increasing the peak temperature increases the width of the melted system, which allows searching a larger space in the configuration landscape. However, if the melted area is too wide, it may not recrystalize during quenching. In our study, the peak temperature that allows the most effective search of the ground state structures was found to be 3,000K, i.e., about 50% of the minimum energy structures were found during quenching from this peak temperature. The next most effective peak temperatures were 3,500K and 2,500K.

During the MD relaxation of the GBs, the relative shift of the grains within the GB plane was on the average about 1.1 Å. In most of the GBs several samples relaxed to a configuration very similar to the supposed global minimum, what allows to conclude that the 1Å×1Å grid of initial shifts was dense enough. Figure 4 shows the displacements of grains during relaxation on the example of the Σ5 (210) GB.

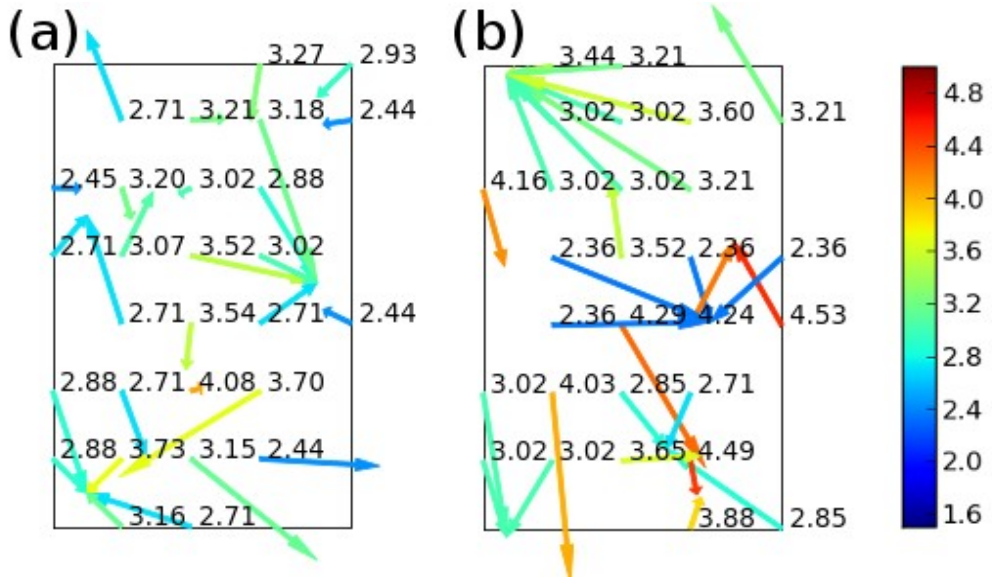

Figure 4. Relative displacements of the Σ5 (210) GB within the GB plane. The cell of non-identical displacements marked by a large black rectangle has the size of 4.32Å × 6.83Å. The initial samples were constructed (a) without removing overlapping atoms and (b) with removing atoms separated by a distance smaller than 1.4Å. Each arrow corresponds to one sample. The start and the end of the arrows show the relative displacement of grains during relaxation. Arrows are coloured according to the final GB energy. The numbers next to each arrow show this value in units J/m^2.

4. Energies and structures of grain boundaries

We employed the newly developed optimization scheme to determine the dependence of GB energy in SiC on tilt angle. To accomplish that we calculated the energies of the ground state structures of 38 stoichiometric <001> STGBs (Fig. 5). In Section 4.1 we report the analysis of low-angle GB in terms of dislocation arrays. The boundaries with larger misorientations are analysed in Section 4.2.

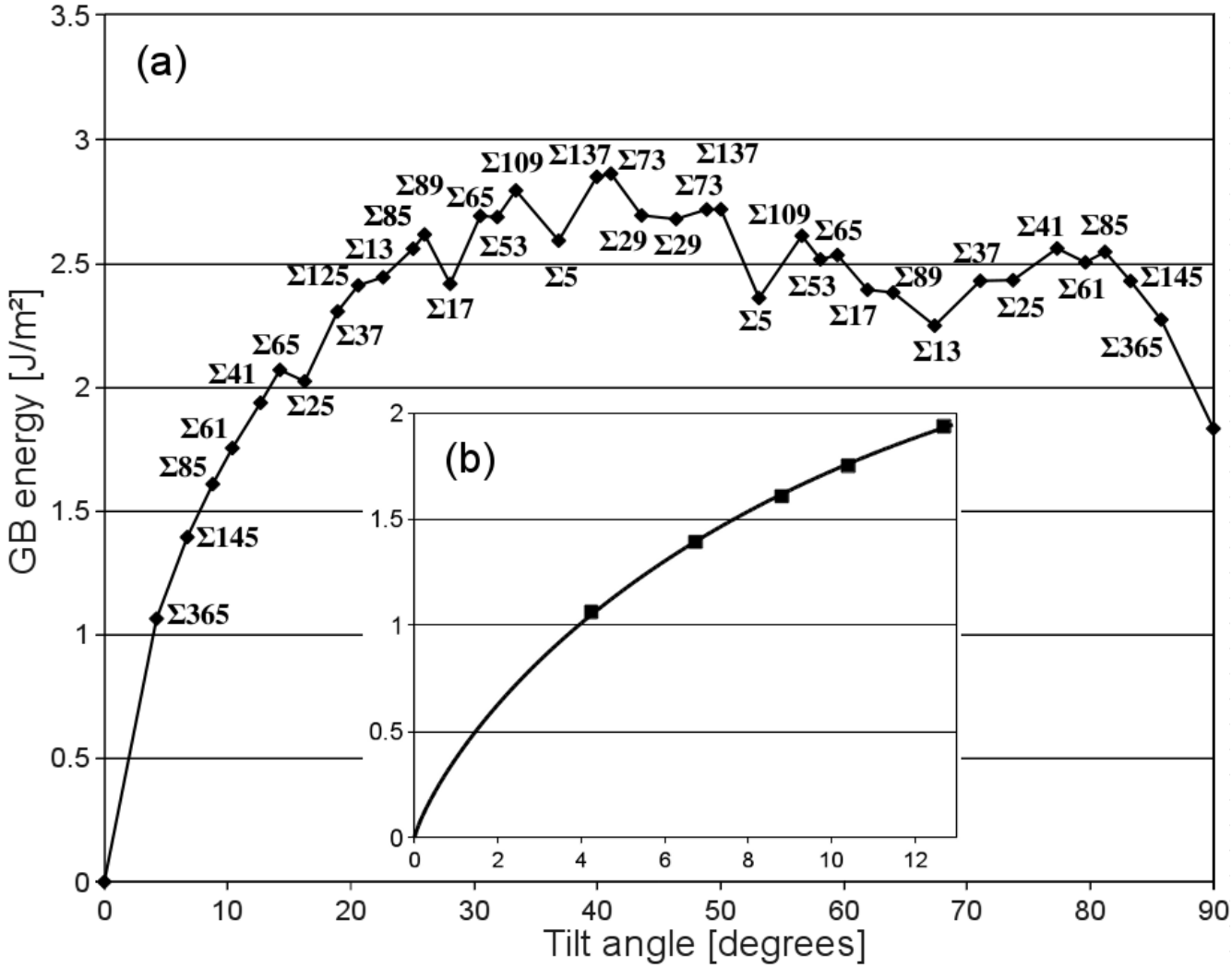

Figure 5. (a) Energy of a stoichiometric <001> STGBs as a function of the tilt angle. (b) Energies of GBs with misorientation angle smaller than 13° (symbols) and a fit to Eq. (3) (solid line).

4.1. Dislocations and small angle GBs

Small angle tilt GBs are comprised of arrays of edge dislocations. The slip system for dislocations in the [001] STGB is (110)[$\bar{1}$ 10]. To find the ground state structure of stoichiometric dislocation, we create a configurations with two edge dislocations of the opposite sign (a dislocation dipole) and we relax it using the same scheme that was used for GBs. The lowest energy structure of the dislocation core is presented in Fig. 6.

We found that when the misorientation of grains is smaller than about 13°, the dislocations formed in stoichiometric STGBs in SiC have the same core structure as that of an isolated dislocation shown in Fig. 6. For larger angles, the dislocation structure is altered and it varies with the misorientation, which can be attributed to the larger interaction of dislocations caused by smaller distance between them.

For the low-angle GBs the energy of the boundary can be approximately described using an analytical function of the misorientation angle θ. The well-established Read-Shockley equation [38] for GB energy is derived from the isotropic dislocation theory based on the assumptions that GB dislocations are equally spaced and that small-angle approximations can be used. In this study we use a more general formula for tilt GB energy, which was derived in a similar fashion as the Read-Shockley equation, but without the small-angle approximations [39, 21]:

$$\gamma = \frac{Gb\alpha\eta_0}{4\pi^2(1-\nu)}[\eta_0 \coth\eta_0 - \ln(2\sinh\eta_0)], \qquad (1)$$

where $\eta_0 = \frac{\pi b}{\alpha D} = \frac{2\pi}{\alpha}\sin\frac{\theta}{2}$, G is the shear modulus, ν is Poisson's ratio, b is the length of the Burgers vector, D is the distance between dislocations in the GB, and α is a factor that accounts for the strain energy at the dislocation cores. The above equation is more accurate than the Read-Shockley equation, however because of the assumption of equally spaced dislocations it shares the same limitation of being valid only for low-angle boundaries. By fitting Eq. (3) to the energies of GBs with misorientations smaller than 15° (Fig. 5b) we obtain $\alpha = 2.9$ and $Gb/(1-\nu) = 63\ \mathrm{J/m^2}$.

Although Eq. (1) is based on the assumption that elastic constants are isotropic, it can be treated as a simplified model for anisotropic crystals. We approximate G in Eq. (1) with the value of the modulus for shearing on the glide plane (110) in the direction of the Burgers vector [$\bar{1}$ 10]. Coincidently, the shear modulus in this direction is equal to $G' = 1/2(S_{11} - S_{12})$, which is also the formula for shear modulus in isotropic materials. S_{11} and S_{12} are two elements of the stiffness matrix. Taking Poisson's ratio $\nu' = -S_{12}/S_{11}$ and substituting the values of elastic constants calculated for the Tersoff potential in Ref. [40], we obtain $G'b/(1-\nu') = 62\ \mathrm{J/m^2}$, which is in a very good agreement with the value 63 J/m^2 that we obtained from a direct fitting of Eq. (3).

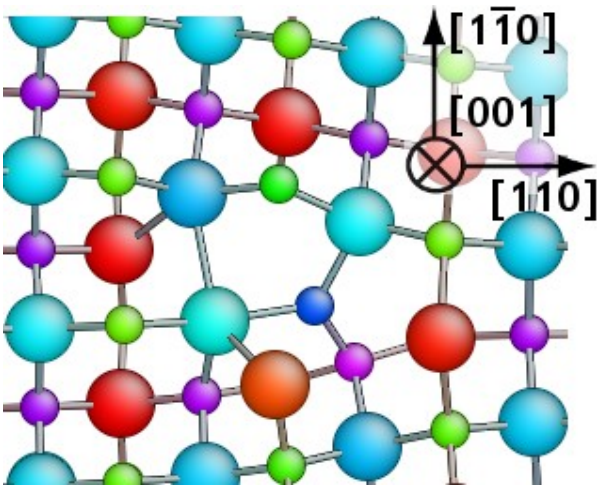

Figure 6. Core structure of stoichiometric edge dislocation with Burgers vector $b = 1/2[\bar{1}\,10]$ and a glide plane (110). Atoms are color-coded in the same way as in Fig. 6.

4.2. High angle GBs

When the misorientation angle is larger than ~13°, the core structure shown in Fig. 6 is no longer stable. The energetically favourable structure of dislocation cores changes with the misorientation of grains up to the angle of about 25°, at which point the separation of the cores vanishes and the structures can be analyzed only in the framework of the structural unit model (SUM).

The boundaries Σ25 θ = 16.3° (Fig. 7(a)) and Σ13 θ = 22.6° (Fig. 7(b)) represent the structures in which dislocations are clearly separated from each other, but the distance between dislocations is small and the interaction between dislocations changes the configuration of the dislocation cores. Both boundaries are comprised of two types of dislocation cores. The cores in θ = 16.3° GB of Si-rich and C-rich, alternately. In the θ = 22.6° GB dislocation cores are stoichiometric, one of them is the same as dislocation shown in Fig. 6.

Figure 8 shows four selected high-angle, short-period GBs. Three of them (Fig. 8(a), (c) and (d)) correspond to minor cusps on the energy vs tilt angle plot. The Σ17 (350) θ = 28.1° GB (Fig. 8(a)) is comprised of the same two dislocation cores as the Σ25 θ = 16.3° GB (Fig. 7(a)), but the period in the y direction is smaller (12.6 Å instead of 21.6 Å) and there is no space for perfect lattice that separates the cores in GBs with lower angles. It is instructive to compare the Σ17 θ = 28.1° GB (Fig. 8(a)) and the Σ29 (370) θ = 43.6° GB (Fig. 8(b)) because these GBs correspond to nearby minima in the energy vs. angle plot (Fig. 5) and they have similar

structures (both GBs contain undercoordinated C atoms and overcoordinated Si atoms). The energy of Σ29 is approximately 10% higher than that of Σ17. One clear difference between these two GBs is that Σ29 contains a 7-atom ring, in addition to the 6-atom rings that are also present in the Σ17 structure. Another comparison can be made between the Σ5 (130) θ = 53.1° GB (Fig. 8(c)) and the Σ13 (150) θ = 67.4° GB (Fig. 8(d)). Both of these GBs are comprised of rings with up to 6 atoms. All atoms in these two GBs have either four or three bonds. The Σ13 GB shows a structural pattern characteristic of all GBs with the misorientation between 60° and 90°, which is the presence of a chain of four-coordinated Si atoms, each having two homonuclear bonds. In Fig. 8(d) this structural feature is marked with a red line. In the structures of <001> STGBs previously reported in the literature [11], the rings in the plane perpendicular to the tilt axis have only up to 5 atoms. This arrangement minimizes the number of under- and over-coordinated atoms. In the current study we find that in most of the boundaries the minimum energy configuration contains larger rings, with 6 or 7 atoms. It is presumably because formation of larger rings allows a reduction in strain energy, which compensates the increase of energy caused by a larger number of atoms with imperfect coordination.

Among the high-angle STGB the lowest energy GB is the one with the maximum misorientation of grains (90°). This boundary has a low-index GB plane (100) and two degenerate configurations corresponding to the minimum of GB energy. In both configurations the CNID is a square with sides represented by vectors $1/2[0\,\bar{1}\,1]$ and $1/2[0\,1\,1]$. Figure 9 shows both structures viewed in the (110), (100) and $(1\,\bar{1}\,0)$ projections. In both structures there are characteristic 3-coordinated C-atoms that make a bridge between Si-terminated surfaces of two grains. As shown in Fig. 5, all but the 90° high-angle boundaries have energy between 2.25 and 2.85 J/m^2. Minor cusps in the energy plot correspond to some of the low-Σ GBs: Σ17(350) θ=28.1°, Σ5(120) θ=36.9°, Σ5(130) θ=53.1°, and Σ13(150) θ=67.4°. Minor cusps at the same angles have been also observed in NiAl alloy [15]. Some authors attribute special properties of GBs to low-index boundary planes rather than to low values of Σ (i.e., a high coincidence of the lattices) [41]. In our study of symmetric boundaries low-Σ values have also low-index GB planes and we cannot separate the effects of the two geometrical features.

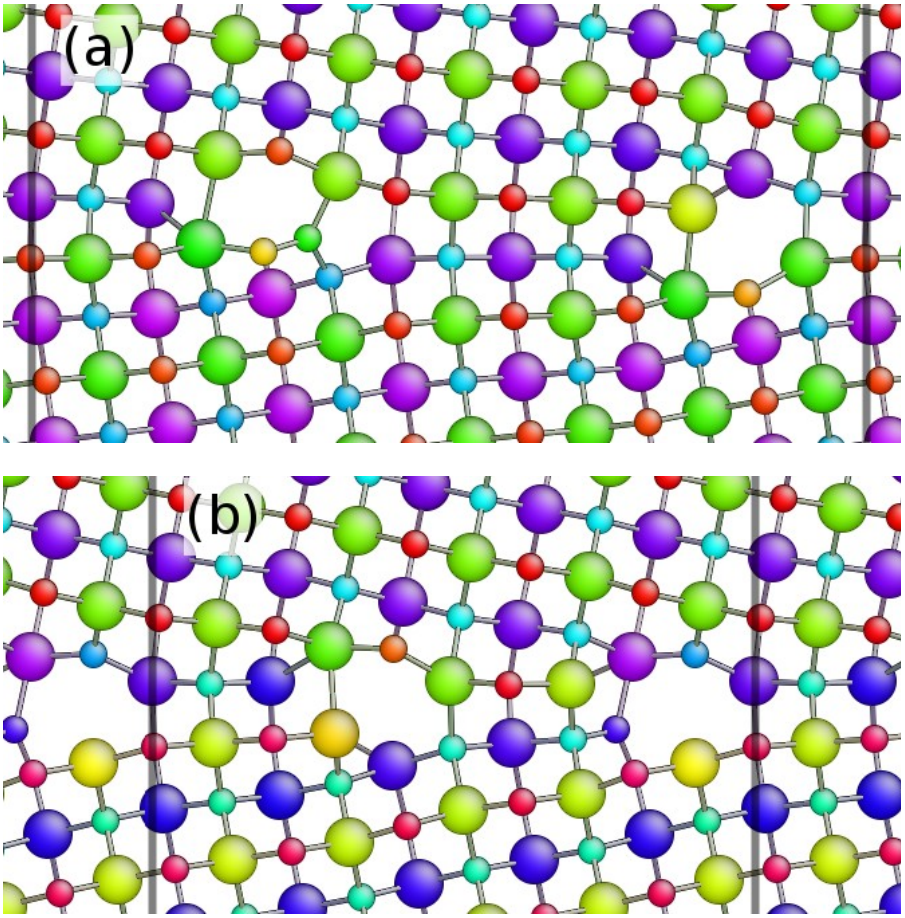

Figure 7. Structures of <001> STGBs (a) Σ25 (340) θ=16.3° and (b) Σ13 (230) θ=22.6°. Atoms are color-coded in the same way as in Fig. 3. The vertical lines show one period of the GBs in the y direction.

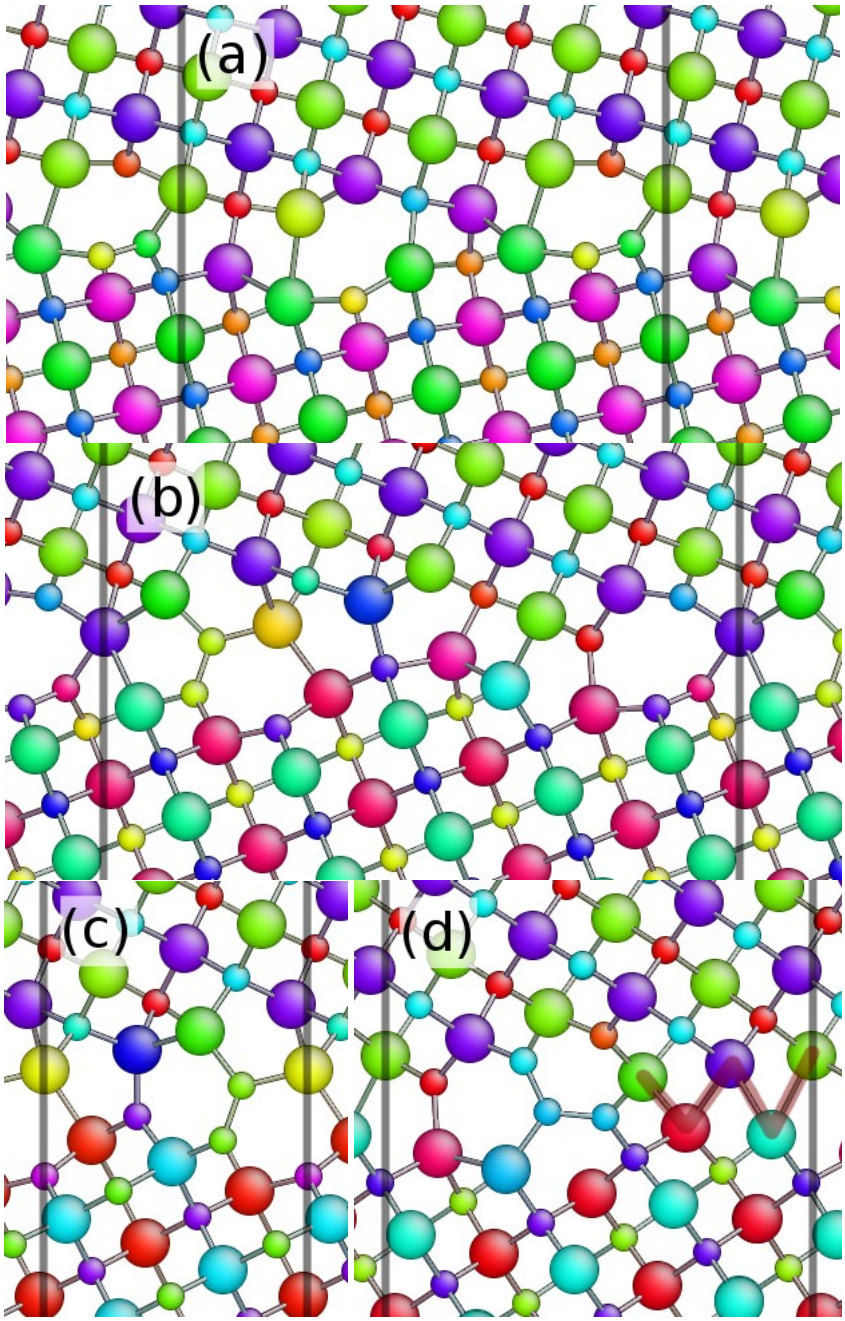

Figure 8. Structures of <001> STGBs (a) Σ17 (350) θ=28.1°, (b) Σ29 (370) θ=43.6° (c) Σ5 (130) θ=53.1° and (d) Σ13 (150) θ=67.4°. The red line in (d) marks a chain of Si-Si bonds, which is characteristic for <001> STGBs with misorienation between 60° and 90°.

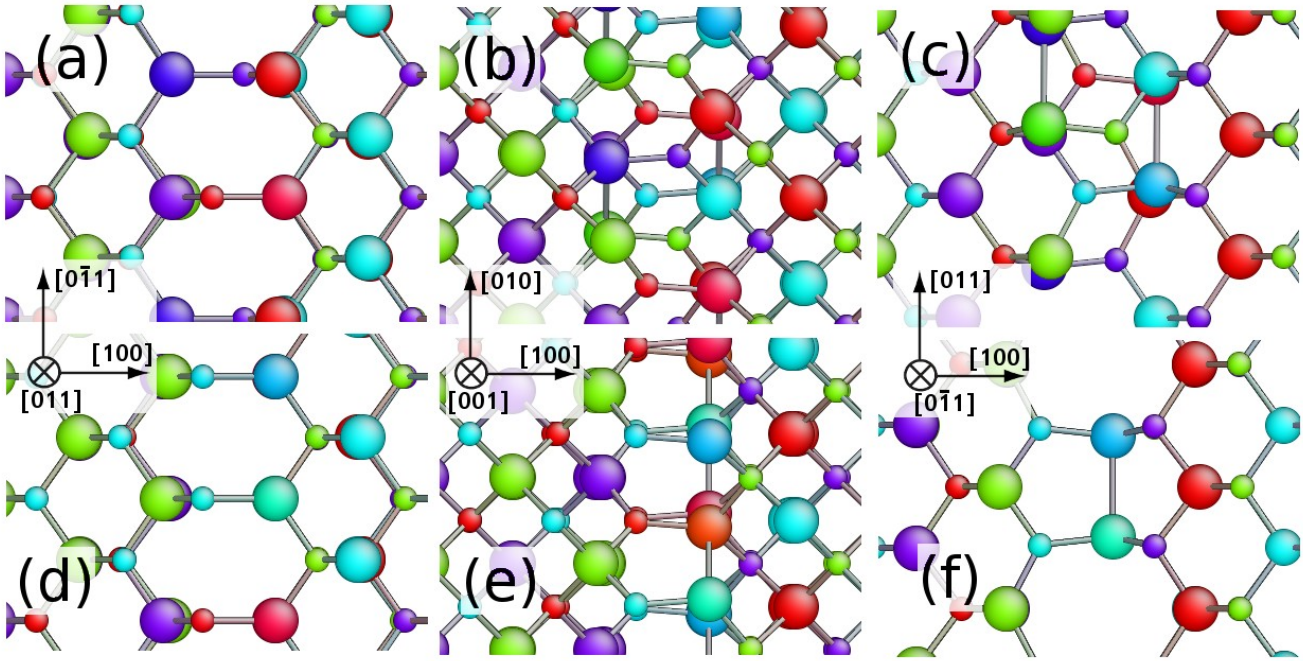

Figure 9. Two stoichiometric structures of <001> STGB with misorientation 90°, which both correspond to the lowest energy. The first structure is shown in (a) the (011), (b) the (001) and (c) the $(0\,\bar{1}\,1)$ projections. The second structure is shown in the same projections in (d), (e) and (f), respectively.

5. Conclusions

We developed an MD-based scheme that allows finding ground state structure of GBs with relatively large cell of non-identical displacements. This scheme was used to study structures of stoichiometric <001> STGBs in SiC. We found that most of the analysed GBs contain 6- and 7- atom rings, what is different from previously proposed structures [11]. These structural features are also different from those found in the same type of GBs in Si, where even 6-atom rings are rare [12]. The realistic GB models that we present in this paper enable future studies of interface-driven processes in SiC, such as diffusion. In particular, it has been shown that the presence of over-coordinated atoms and large rings in the GB will lead to enhanced diffusion of metallic impurities in SiC [4]. Since investigation of diffusion along multiple individual GBs can be computationally prohibitive, knowledge of atomic-level GB structures presented here can accelerate a search for GBs that provide optimal diffusion pathways.

Although several schemes have been reported for finding ground state structures of GBs, many more studies have been dedicated to other structural optimization problems, such as finding minimum energy configuration of atomic clusters. As early as in the 1990's two methods, which are 'cut and splice' genetic algorithm [37] and Monte Carlo-based basin hopping [42], have been found to be more effective than MD annealing in application to atomic clusters. These two methods are now well established. More recently it was demonstrated that for the aforementioned applications it is actually possible to develop MD-based methods that can perform comparably [43] or even better [44] than those based on genetic algorithms and on Monte Carlo. Although genetic algorithms have been recently used for GB structural optimization [12], no systematic study has been carried out to compare the efficiency of these algorithms to those that are based on MD, such as the one developed in our study. We will pursue such comparative analysis in the future.

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