Atomistic simulations of structures and mechanical properties of \( \langle 011 \rangle \) tilt grain boundaries and their triple junctions in diamond

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Atomic structures, energies, and stress distributions of symmetrical \( \langle 011 \rangle \) tilt grain boundaries (GB’s) and selected GB triple junctions (TJ’s) in diamond as well as a multiply twinned diamond particle have been calculated using an analytic bond order potential function. In general, energies of \( \langle 011 \rangle \) tilt GB’s are about 1 \( \text{J/m}^2 \) lower than those for \( \langle 001 \rangle \) tilt GB’s calculated with the same analytic potential. Energy ordering for two models of the \( \Sigma = 3(3 \overline{1} 1) \) GB obtained with the present bond-order potential is consistent with results from a tight-binding model. Atomic structures of selected triple junctions of \( \langle 011 \rangle \) grain boundaries are modeled and atomic reconstructions within TJ cores that eliminate dangling bonds are suggested. Despite a perfect geometrical matching of structural units within the triple junction cores, excess energies and stresses exist in the vicinity of these structures. Characteristics of atomic stress distributions in multiply twinned particles agree with predictions of continuum disclination theory.

I. INTRODUCTION

Polycrystalline diamond films obtained by chemical vapor deposition (CVD) have numerous applications due to the unique properties of diamond. These applications include heat spreaders, wear resistant coatings, and optical electronic devices. However, the presence of grain boundaries (GB’s) in the films may adversely affect their mechanical, electrical and optical properties. Tilt GB’s with \( \langle 001 \rangle \) and \( \langle 011 \rangle \) misorientation axes are of practical interest because vapor-deposited diamond films are usually well textured and have primarily \( \langle 011 \rangle \) or \( \langle 001 \rangle \) orientations.\(^1\) High-resolution transmission electron microscopy (HRTEM) studies of CVD diamond films indicate that the most commonly observed defect is the \( \Sigma = 3(111) \) coherent twin.\(^2,3\) Higher order twin boundaries with \( \langle 011 \rangle \) tilt axes \( \Sigma = 9, \Sigma = 27, \Sigma = 81 \) have been identified in CVD diamond as resulting from the intersections between \( \Sigma = 3(111) \) GB’s and one of the higher-order twin boundaries.\(^2\) Intersection points of single GB’s, that are triple and higher order junctions, are important elements of microstructure affecting the bulk polycrystalline materials properties\(^4\) because their physical and mechanical characteristics can be quite different from those of the bulk. A detailed theoretical analysis of the atomic structure of twin intersections observed in CVD diamond films has been carried out by King et al.\(^4\) Another structural element often observed in CVD diamond films are fivefold microcrystals which are formed by intersection of five \( \Sigma = 3(111) \) GB’s during diamond deposition.\(^2,3\) Selected triple junction (TJ) structures as well as a pentatwin particle observed experimentally in CVD diamond films are modeled in the current paper.

A variety of structures of symmetrical tilt \( \langle 011 \rangle \) GB’s in the \( 0^\circ \leq \theta \leq 70.53^\circ \) misorientation range have been experimentally studied in crystalline Si and Ge which also have the diamond cubic lattice.\(^3–11\) Several possible GB structures for a given orientation of the grains have been found for GB’s within the misorientation range \( 38.94^\circ \leq \theta \leq 70.53^\circ \). For example, GB structures composed of two types of structural units (SU’s) and a mix of three types of structural units have been observed.\(^11\) One explanation for this is the contribution of configuration entropy to the free energy at high temperatures due to the multiplicity of the core configurations.\(^12\)

The earliest geometrical modeling of \( \langle 011 \rangle \) tilt GB structures for materials with diamond cubic lattices was carried out by Kohn\(^13\) and Hornstra.\(^14\) All GB structures in the misorientation range \( 0^\circ \leq \theta \leq 70.53^\circ \) contained fourfold coordinated atoms at the interface, while all GB models at \( \theta > 70.53^\circ \) contained dangling bonds. Papon and Petit\(^15\) subsequently developed geometrical models for GB’s without dangling bonds for the misorientation angle \( \theta > 70.53^\circ \). In their models, the introduction of specific atomic patterns to satisfy dangling bonds resulted in double periodicity along the tilt axes. A similar approach has been used in the present work to develop atomic reconstructions along TJ lines that saturate dangling bonds in the TJ cores.

Energetics of the \( \langle 011 \rangle \) symmetrical tilt GB’s in Si have been widely studied with many-body empirical potentials,\(^3,11,16,17\) a bond orbital model,\(^18\) tight-binding models,\(^19\) and combinations of tight-binding and first-principles techniques.\(^20\) Results of the calculations of GB energies versus misorientation angle by different authors are in relative agreement.

Two groups of authors have modeled \( \langle 011 \rangle \) symmetrical tilt GB’s in diamond.\(^3,21\) Energies of \( \Sigma = 9, 19, \) and 33 GB’s were calculated by Narayan and Nandedkar\(^3\) in diamond, Si and Ge using Keating\(^22\) and Tersoff\(^23\) interatomic potentials. It was predicted that GB energies in diamond are about a factor of 6–7 higher than those for Si and Ge. Morris et al.\(^21\) compared GB energies for a variety of \( \langle 011 \rangle \) tilt GB’s calculated with a tight-binding model to values calculated using the Tersoff potential. The GB energies had a similar ranking for both approaches in the misorientation range of \( \theta \approx 70.53^\circ \), and nearly identical structures but different energy ordering for models of high angle \( (2 \overline{1} 1) \) GB and \( (3 \overline{1} 1) \) non-coherent twin boundaries. The GB energies obtained from
the tight-bonding approach were 1.4–1.9 times lower those calculated with the Tersoff potential.

In our previous paper\textsuperscript{24} structures, energies and stress distributions of (001) symmetrical tilt GB’s in diamond were characterized using an empirical bond-order potential.\textsuperscript{23} The same GB characteristics of (011) symmetrical tilt GB’s in the misorientation range $0^\circ \leq \theta \leq 109.47^\circ$ are calculated in the present paper. It was found that the difference between GB energies calculated with our analytic potential and the tight binding model is less than that for the Tersoff potential. Also, the analytic bond-order potential used here reproduces the same energy ranking in the models of the $\Sigma = 3(2\overline{1}1)$ GB as that predicted by the TB calculations.\textsuperscript{21}

\section{II. Calculational Method}

The simulated grain boundary structures were derived from a coincidence site lattice model proposed previously for group-IV materials in which all atoms are fourfold coordinated.\textsuperscript{14} The initial structures were formed by rotating two crystals around a common (011) axes at an angle $\theta$ with a median (0\overline{1}1) plane. After the relative rotation of the two grains, local atomic reconstructions were applied to maintain the smooth coherency of the grains across the interface. The resulting interface structures contain a mix of five-, six- (both chair and boat shape), and seven-member rings.

The computational cell was periodic within a GB plane with free surfaces terminated by hydrogen in the direction perpendicular to the GB plane. The distance between the interface and each free surface was about nine lattice parameters. The computational cell contained up to 1000 atoms for systems containing a single GB, and about 3500 atoms for systems containing triple junctions. Structures and energies of GB’s at 10 misorientation angles were calculated using an analytic many-body bond-order potential.\textsuperscript{25} This function, which is similar in form to Tersoff’s potential,\textsuperscript{23} is based on a second-moment approximation to the local density of states. The binding energy of each atom is modeled by a sum of short-ranged attractive and repulsive pair terms. The former are coupled to a many-body bond-order function. This analytic function reproduces a relatively large database of solid-state and molecular properties of carbon, including the lattice constant, cohesive energy, and bulk elastic properties of diamond. Similar to the Keating\textsuperscript{22} and Tersoff potentials, the potential function used here considers only first and second nearest-neighbor interactions (through an angle bending term) and yields zero energy for twin and stacking fault interfaces (the energy of these structures depend only on the third and higher-order interactions). However, the energy of the twin GB is very low, about 0.11 J/m$^2$ as predicted by density functional calculations.\textsuperscript{26}

Local stress distributions in the vicinity of the GB’s, triple junctions and twinned particles were also calculated from the analytic potential. This entailed combining second derivatives of the potential with local atomic volumes. The latter were calculated via a Monte Carlo method. Details of this procedure are described in a previous paper.\textsuperscript{24}

\section{III. Results and Discussion}

Within the coincident site lattice model, GB structures can conveniently be described in terms of different combinations of a set of characteristic structural units. Furthermore, GB structures within particular ranges of misorientation angle can generally be described using a subset of the structural units associated with a given tilt axis. For the (011) symmetrical tilt GB’s in diamond cubic crystals, the specific ranges are $0^\circ \leq \theta \leq 27.53^\circ$, $27.53^\circ \leq \theta \leq 38.94^\circ$, $38.94^\circ \leq \theta \leq 70.53^\circ$, and $70.53^\circ \leq \theta \leq 180.0^\circ$. In this paper, detailed GB structures are reported for the range of misorientation angle between $0^\circ$ and $70.53^\circ$, and at one angle at $\theta = 109.47^\circ$. GB’s within the former range of angles are most often observed experimentally. The single GB at the higher angle was chosen because previous calculations\textsuperscript{21} showed a discrepancy between predictions of a tight-binding model and analytic potential for two competing structures. Structures and energies of a triple junction and a multiply twinned particle are also discussed at the end of this section.

\subsection{A. (011) tilt GB’s in the $0^\circ \leq \theta \leq 70.53^\circ$ range}

Based on previous calculations on silicon, the lowest energy GB’s in the $0^\circ \leq \theta \leq 70.53^\circ$ range of misorientation angle for the diamond cubic lattice can be constructed from the following characteristic structural units:\textsuperscript{11} C, M (or L), T, P (Fig. 1). A structural unit of the perfect crystal C consists of two six-atom rings in the chair configuration laterally connected along the (111) direction. Two C units are necessary to reproduce the perfect diamond cubic structure in the (011) projection. The L unit is the core of an edge dislocation with a Burgers vector $b = 1/2a_0[01\overline{1}]$ and (100) glide plane. Both the L and M units consist of the pair of five and seven atom rings, but with different connections. The M unit is important for describing GB structures at $\theta \approx 38.94^\circ$ ($\Sigma = 9$) when stable boundary structures are arranged in a zigzag manner (see below). The T unit is six-atom ring in a boat configuration; it is a constitutive unit of the first order twin boundary. The P unit has been suggested as a constitutive unit of a metastable $\Sigma = 3(111)$ boundary.\textsuperscript{11} It is also composed of five- and seven-atom rings but with a connection different than either the L or M units (Fig. 1). It should be noted that for $\theta > 26.53^\circ$, there are also metastable structures containing a T unit inserted between the five- and seven-membered rings constituting the L unit. In this case, the numbers five and seven will be used to denote these rings (for example, 5-T-7 refers to a T unit inserted between these rings). As described below, reconstruction of the group of these units can lower the interface energy and results in structures containing only the units in Fig. 1.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{structure_units.png}
\caption{Structural units of symmetrical (011) tilt GB’s in the misorientation range $0^\circ \leq \theta \leq 70.53^\circ$.}
\end{figure}
Examples of GB's with a uniform arrangement of structural units at the interface, one obtains structures with lower energies than those with the straight arrangement. For example, the energy of the $\Sigma = 19$ GB with a straight arrangement of units (C-L-C-L) is 2.9 J/m$^2$ and that of the boundary with a zigzag arrangement (CCLL) is 4.26 J/m$^2$.

2. Properties of GB’s between $\Sigma = 19(\theta = 26.53^\circ)$ and $\Sigma = 9(\theta = 38.94^\circ)$

The next characteristic range of misorientation is 26.53$^\circ < \theta \leq 38.94^\circ$ (between $\Sigma = 19$ and $\Sigma = 9$ GB's). Simple coincidence site lattice rotation of two grains yields structures with mirror symmetry containing C and L units and a new structural element 7-T-5 consisting of a boat-shaped six-atom ring inserted between seven-and five-atom rings [Fig. 4(a)]. Such structures have high energies and extended stress fields. An appropriate reconstruction is possible$^{14}$ that decreases the energy of these GB’s. The segment (T-5-C) can be converted to a segment (5-7-5) by removing two atoms at the interface [Fig. 4(a), 4(b)]. Because of the symmetry along the GB, this leads to the formation of two equivalent configurations of L units ($L^+$ and $L^-$ in the up and down positions, respectively). Thus, instead of the structure with three structural units at the interface, one obtains structures with two types of units C and L, with adjacent L units in a zigzag arrangement. The structure of the $\Sigma = 27$ GB 7-T-5-C-L-C-L-C [Fig. 4(a)] transforms to the structure 3-L-C-L-C [Fig. 4(b)]. Further reconstruction of the 7-5-C stacking to C-5-7 is possible by a transformation (L'C→CL) that is an analog of dislocation climb and can be realized in modeling by removing two atoms at the interface [Figs. 4(c) and 4(d)]. As a result, from the structure 3-L-C-L-C [Fig. 4(b)] one obtains two additional structures of the $\Sigma = 27$ GB: 2L-L-C-L-C→2L-C-2L-C [Fig. 4(c)]
and 3L-C-L-C→4L-2C [Fig. 4(d)]. Among these, we predict that the structure with the uniform arrangement of units [Fig. 4(c)] is the most stable.

The lowest energy structure of the \( \Sigma = 9 \) GB consists of a zigzag stacking of single type \( L \) or \( M \) structural units [Fig. 5(a)]. This glide-plane model shows a deep cusp in the energy curve (Fig. 3). The \( \Sigma = 9 \) GB with mirror symmetry (a 5-T-7 stacking) has an energy of 4.8 J/m². Similar energy ranking for these two models was obtained by calculations on Si. 18,20 The structure of the \( \Sigma = 9 \) GB, observed in silicon by HRTEM,11 in some cases contains steps equal to \( a/3 \) [Fig. 5(b)]. These originate from the interaction of a grain dislocation (corresponding to the \( M \) unit) with the \( \Sigma = 9 \) GB. This configuration has a more extended stress field and a higher energy than the glide-plane structure of the GB. The motion of GB dislocations, with Burgers vector lying parallel to the GB plane, as in the case of \( \Sigma = 9 \) GB with steps, can lead to an intergranular sliding and lateral migration of the GB. 11

3. Properties of GB’s between \( \Sigma = 9(\theta = 38.94°) \) and \( \Sigma = 3(\theta = 70.53°) \)

Intermediate GB’s between \( \Sigma = 9 \) and \( \Sigma = 3 \) GB’s after the coincidence site lattice rotation of two grains consist of combinations of the structural units of the type 7-nT-5-C [where, for example, \( n = 7 \) for \( \Sigma = 33 \) (455) GB]. The structural units are in a straight arrangement, and groups of units with different \( n \) can coexist along the plane of the same grain boundary (for example \( \Sigma = 153 \)). Such GB structures possess mirror symmetry and have relatively high energies. These grain boundaries can be obtained by inserting \( T \) units between seven- and five-atom rings in the \( \Sigma = 19(\theta = 26.5°) \) boundary [Fig. 2(d)].

It is possible to decrease GB energies significantly and create a wide variety of GB structures by applying a set of three types of structural unit reconstructions that remove two particular atoms from an interface; these are illustrated in Fig. 6. The first reconstruction transfers the segment \( T-5-C \) to segment \( M-5 \) [Fig. 6(a)]. This reconstruction was used to create new structures for the \( \Sigma = 27 \) GB (Fig. 4). The second type of reconstruction converts a \( T-M \) segment to \( M-T \) [Fig. 6(b)]. The third type of reconstruction converts a \( T-M \) segment to \( M-P \) [Fig. 6(c)]. Starting with a 7-nT-5-C structural model, it is possible to obtain numerous models by applying these three reconstructions to all corresponding segments along a GB. For example, these reconstructions can lead to a multiplicity of structures for the \( \Sigma = 11 \) (233) GB as shown in Table I. In addition to eight different models of the
TABLE I. Examples of different GB structures for the $\Sigma=11$(233) GB. Types of reconstruction correspond to those illustrated in Figs. 6(a), 6(b), or 6(c). Numbers in square brackets in the forth column indicate the GB structure from which the given structure was obtained. The segment of the GB structure involved in the reconstruction is underlined in the second column.

<table>
<thead>
<tr>
<th>Structure number</th>
<th>Structure</th>
<th>Energy (J/m²)</th>
<th>Reconstruction type</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1]</td>
<td>TTT5C7</td>
<td>5.1</td>
<td>Fig. 6(a); [1]</td>
</tr>
<tr>
<td>[2a]</td>
<td>$TTM^+M^- TTM^- M^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[3]</td>
<td>$TM^+ TM^-$</td>
<td>3.65</td>
<td>Fig. 6(b); [2]</td>
</tr>
<tr>
<td>[4]</td>
<td>$TM^- P^+M^- (TM^+P^-M^+)$</td>
<td>3.7</td>
<td>Fig. 6(c); [2]</td>
</tr>
<tr>
<td>[5]</td>
<td>$M^- P^+TM^- (M^+P^- TM^+)$</td>
<td>4.75</td>
<td>Fig. 6(c); [3]</td>
</tr>
<tr>
<td>[5a]</td>
<td>$M^- P^-TM^- (M^-P^+ TM^+)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[6a]</td>
<td>$M^+ P^- P^+M^- M^- P^-P^+ M^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[7]</td>
<td>$M^- P^+ M^+ P^-$</td>
<td>5.2</td>
<td>Fig. 6(c); [5]</td>
</tr>
<tr>
<td>[7a]</td>
<td>$M^- P^+M^- P^+ M^-P^- P^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[8]</td>
<td>$M^- TP^- M^- (M^-TP^- M^-)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[8a]</td>
<td>$MTP^-M^- M^+ TP^- M^+$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\Sigma=11$ GB with a single CSL period, selected GB models with a double CSL periodicity are produced by this series of reconstructions. Among the eight metastable structures modeled, the one with the lowest energy is a $TM^+TM^-$ GB (denoted as 3 in Table I). This GB was experimentally obtained in silicon by deforming an initially perfect $\Sigma=9$ GB at low temperature and then studied by HRTEM. The structures and hydrostatic stress fields near two of the lowest-energy GB’s with $\Sigma=11$ are illustrated in Fig. 7. In the GB with the $TM^+TM^-$ structure, the zones of compression and tension correspond to five and seven-membered rings of the $M$ unit and are uniformly distributed along the GB [Fig. 7(a)]. In the GB with the $TMPM$ structure, more extended zones of compression are connected with five-membered rings of $P$ units, and there are different stress distributions in the two grains adjoining the interface [Fig. 7(b)] GB’s containing $P$ units have been experimentally observed in silicon after high temperature deformation of a silicon bicrystal initially containing a $\Sigma=9$ GB. As mentioned above, the $P$ structural unit constitutes a metastable $\Sigma=3_m$ (111) GB, where the subscript $m$ indicates a metastable structure [Fig. 8(a)]. It possesses a relatively high energy of 4.33 J/m². The structure of the $\Sigma=3_m$ (111) GB can be described as formed by two (111) surfaces with mirror symmetry, one of which is an unreconstructed (111) surface, with the second containing Pandey chains. The boundary plane between these surfaces is indicated by the dotted line in the Fig. 8. An example of the interface defect, which can be formed by two (111) surfaces reconstructed to

FIG. 7. Atomic hydrostatic stress distributions for two models of the $\Sigma=11$ GB with corresponding SU’s reconstructions. The stress scale is the same as in the Fig. 2.

FIG. 8. Atomic structures and hydrostatic stress distribution for the high energy model of the first order twin (a) and for the model with doubled defect layer in (111) direction (b).
TABLE II. Energies for the $\Sigma = 3(\bar{2}11)$ grain boundary models calculated with a tight-binding total energy method (Ref. 21) (TB), Tersoff’s bond-order potential (Ref. 23) (TBO), and the potential used in the present paper.

<table>
<thead>
<tr>
<th>Reconstruction</th>
<th>TB (J/m$^2$)</th>
<th>TBO (J/m$^2$)</th>
<th>Present paper (J/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \times 1$</td>
<td>5.9</td>
<td>3.2</td>
<td>5.4</td>
</tr>
<tr>
<td>$1 \times 2$</td>
<td>3.0</td>
<td>5.1</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Pandey chains, is shown in Fig. 8(b). The structure of the $\Sigma = 3_m$ GB is repeated in the $\langle 111 \rangle$ direction in this case. The energy of such an interface defect is 0.2 J/m$^2$ less than twice the energy of the $\Sigma = 3_m$ GB. The hydrostatic stress field is highly localized near the interfaces due to mutual cancellation of long range compressive and tensile elastic fields generated by neighboring five- and seven-atom rings (Fig. 8).

GB energies versus misorientation angle for the entire misorientation range $0^\circ \leq \theta \leq 70.53^\circ$ in diamond and Si (Ref. 18) are plotted in Fig. 3. In general, the calculations predict that energies of $\langle 001 \rangle$ symmetrical tilt GB’s in diamond are 3.6–4.0 times higher than those in Si. The energy values of $\langle 001 \rangle$ tilt GB’s (Ref. 24) in diamond predicted to be approximately 1 J/m$^2$ higher than those for $\langle 001 \rangle$ tilt GB’s. In the work by Morris et al., the $\langle 001 \rangle$ tilt GB energies given by the Tersoff potential are about 1.4–1.9 times higher than those predicted by a tight-binding model. The bond-order potential used here gives GB energies closer to the tight-binding predictions, although they are still 1.2–1.4 times higher than the tight-binding model.

B. Properties of the $\Sigma = 3(\bar{2}11)(\theta = 109.47^\circ)$ GB

In a paper by Morris et al. energies and structures for two models of the $\Sigma = 3(\bar{2}11)$ GB with mirror-plane symmetry were reported using a tight-binding-based total energy approach. The first model possess single periodicity along the $\langle 011 \rangle$ tilt axes and contains dangling bonds ($1 \times 1$ model). In the second model all atoms are four-fold coordinated and the model possesses double periodicity along the tilt axis ($1 \times 2$ model). The tight binding calculations predict that the $1 \times 2$ model is energetically favorable, whereas calculations with the analytic Tersoff potential predict a lower energy for the unreconstructed $1 \times 1$ model of the GB. In contrast, the present analytic potential yields the same ranking of GB energies for these two models as predicted by the TB calculations (Table II).

C. Triple junctions and pentatwin structures

In this section predictions of atomic-scale structures, energies and stress distributions using the analytic bond order potential are reported for two types of triple junctions and a particle containing a pentatwin. The structures studied were motivated by HRTEM images of polycrystalline diamond films.

The triple junctions were constructed in the following way. First, three wedges of material containing relaxed grain boundaries in the center of each wedge were created such that each was terminated by the same type of facet, and the sum of their angles equaled $360^\circ$. The wedges were then rotated and translated to match one another and the system was allowed to relax. Different types of structures are possible at the vertex of the wedges, and therefore different models for particular triple junctions with a different matching of grain boundaries at the core were examined. The pentatwin was similarly constructed using five rather than three wedges.

1. $\Sigma9(221)$:$\Sigma3(111)$:$\Sigma3(1\bar{1}1)$ triple junction

There can be four different kinds of triple junction of type $\Sigma9$:$\Sigma3$:$\Sigma3$, where $\Sigma3$ are coherent twin GB’s. Two of these are obtuse intersections ($109.47^\circ$ between twin GB’s) in which a $\Sigma9$ GB is a coherent second order twin GB $\Sigma = 9\{221\} (\theta = 38.94^\circ)$. Two others are acute intersections ($70.53^\circ$ between twin GB’s), in which a $\Sigma9$ GB has a non-coherent structure [$\Sigma = 9\{411\} (\theta = 141.06^\circ)$]. We will consider the obtuse intersection cases because these are often observed experimentally in diamond films. A typical example of the obtuse intersections is shown in Fig. 9. The triple junctions in Fig. 9 are formed by the coherent second-order twin $\Sigma = 9\{221\}$ GB and two primary twin $\Sigma = 3(111)$ and $\Sigma = 3(1\bar{1}1)$ grain boundaries. Figure 9 also illustrates the stress distribution in the system. Stresses near the triple junctions are more extended than those near the $\Sigma = 9$ GB. Extended zones of compression and tension can be seen near the five- and seven-atom rings, respectively, at the ends of the $\Sigma = 9$ GB near the triple junctions.

Two possible models of a TJ core for the TJ from the left part of Fig. 9 are illustrated in Fig. 10. In the first model two units consisting of two six-member rings in the boat configuration meet at the junction [top frames in Fig. 10(a); two symmetrical energetically equivalent configurations are shown]. In the second model [top frames in Fig. 10(b)], these units are separated by a seven-member ring. Despite geometrically perfect matching of the structural units in the TJ cores, they contain atoms with dangling bonds. These atoms, which have three nearest neighbors, are indicated by similar shading in the top frames of Fig. 10. Two models with reconstructed TJ cores, both of which contain all fourfold coordinated atoms, are illustrated in the center of Fig. 10. The energy of the structure with saturated bonds is 0.15 eV/Å lower than that for the structure with dangling bonds for the first model [Fig. 10(a)]. This difference equals 0.18 eV/Å for the second model [Fig. 10(b)]. The difference in energy of the two structures is calculated as the difference between the total excess atomic energies around the TJ’s per unit length of tilt axes. The reconstruction leading to the full coordination of the atoms requires a double periodicity along the tilt axis. This reconstruction is similar to that suggested by Papon and Petit to eliminate dangling bonds for high-angle GB’s with $\theta > 70.53^\circ$. The reconstructed lateral patterns along the $\langle 011 \rangle$ direction consist of eight-membered rings alternating with five-membered rings [Fig. 10(a), 10(b)]. The energy of the second model [Fig. 10(b)] is 0.67 eV/Å higher than that of the first [Fig. 10(a)] due to the enhanced strain resulting from the reconstruction required to maintain fourfold coordination at the core. The atomic energy distributions for both structures are indicated by the shading in Fig. 10,

FIG. 10. Structures and atomic energy distributions for two models of the Σ9:Σ3:Σ3 triple junction. C patterns along axes of rotation, introduced to satisfy dangling bonds, are illustrated in the bottom of the figure. The top frames illustrate the structures of the TJ cores, including the structures related to these by mirror symmetry. The filled and open circles indicate atoms within the plane of the projection and above it by $a(1\bar{1}0)/4$, respectively.
where the darker the shading, the higher (i.e., less stable) the energy.

2. $\Sigma 27: \Sigma 9: \Sigma 3(21\bar{1})$ triple junction

An atomic configuration for the $\Sigma 27: \Sigma 9: \Sigma 3(21\bar{1})$ triple junction is shown in Fig. 11. The core structure for this triple junction is more complicated than that for the $\Sigma 9: \Sigma 3: \Sigma 3$ triple junction. The initial core structure of this triple junction after rotating and matching the wedges contains three atomic arrays with dangling bonds. These arrays, whose directions are along the tilt axes normal to the illustration in Fig. 11, are indicated by the letters $A$, $B$, and $C$. To eliminate the dangling bonds along the $A$ array of atoms, the same type of reconstruction was applied as was used for the $\Sigma 9: \Sigma 3: \Sigma 3$ triple junction along the axes of rotation. A second reconstruction was applied between atoms of the $B$ and $C$ arrays to form bond-saturated structures. Both types of reconstructions require doubled periodicity along the $\langle 011 \rangle$ axes.

3. Multiply twinned diamond particle

The multiply twinned particles used in the simulations were periodic along the $\langle 011 \rangle$ axes (the analog of a pentagonal needlelike crystal) and had free surface conditions in the two other directions. Particles with radii between 6 and 30 Å were modeled. The largest system required 2900 atoms, and all of the systems were found to be stable. Figure 12 illustrates a multiply twinned diamond particle with radius $R = 20$ Å. The hydrostatic stress distribution in the particle is indicated by the size and shading of the atoms. The stresses are compressive at the inner region of the particle, while near the outer surface the stresses are tensile. The internal stress as a function of distance from the center of the particle is plotted in Fig. 12, right. The stress has a logarithmic dependence, and the point of the transition from compression to tension occurs about one-third of the distance from the center to the edge of the particle. This result is independent of particle size. A multiply twinned particle can be considered a close packing of five tetrahedra separated by twin boundaries. A misfit of $7^\circ 20'8"$ exists in the packing of the tetrahedra that form the pentagonal particle. This degree of mismatch can be described at the mesoscale as a wedge straight-line positive disclination (i.e., a wedge of material removed from the particle interior). Disclination theory predicts that the center of the particle will be under compressive stress, the outer region will be under tensile stress, with a transition between the two occurring at $r/R = 1$, where $R$ is the radius of the particle and $r$ is the distance along this radius from the particle center. Hence our atomic-scale results agree with those predicted by mesoscale disclination theory.

IV. CONCLUSIONS

Atomic structures, energies, and stress distributions of symmetrical $\langle 011 \rangle$ tilt grain boundaries, triple junctions and a

FIG. 11. Atomic structure of the $\Sigma 27: \Sigma 9: \Sigma 3(21\bar{1})$ triple junction. The filled and open circles indicate atoms within the plane of the projection and above it by $a(1\bar{1}0)/4$, respectively.

FIG. 12. Illustration of the structure and the average atomic hydrostatic stress distribution along the radius of the particle.
multiply twinned particle in diamond have been calculated using a bond order empirical potential. Energies of (011) tilt GB’s in diamond are predicted to be a factor of 4 higher than those in Si (as calculated with bond orbital model\textsuperscript{18}). The ranking of GB energies is similar for diamond and Si in the $0^\circ \leq \theta \leq 70.53^\circ$ misorientation range. Energies of (011) GB’s are about 1 J/m$^2$ lower than those for (001) tilt GB’s for diamond. Structures of the $\Sigma 9 : \Sigma 3(111) : \Sigma (111)$ and $\Sigma 27 : \Sigma 9 : \Sigma 3(211)$ triple junctions were also simulated. Several structural models of the triple junction cores with dangling bonds and with all fourfold coordinated atoms were suggested. The reconstructions leading to the bond-saturated structures require a double periodicity along the tilt axis.

Despite geometrically perfect matching of structural units within the triple junction core, excess energies and stresses remain near the triple junction. The character of the atomic stress distributions in the multiply twinned particle calculated with the bond-order potential agrees with those predicted by mesoscale disclination theory.

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