Theoretical Calculations of the Structure and Energy of the $\Sigma=5$ Tilt Grain Boundary in Silicon*

By Masanori KOHYAMA,** Ryoichi YAMAMOTO,*** Yoshihiro EBATA** and Makoto KINOSHITA**

Synopsis

The structure and energy of the $\Sigma=5$ ($1\bar{3}0$) symmetrical tilt grain boundary in Si were calculated theoretically. The valence force fields, the bond orbital model, and the semiempirical tight-binding method with the use of the supercell technique were used and the computed results were compared with each other. All the computations have shown that the structural model by Bacmann *et al.* is more energetically favored than that by Hornstra and that the optimum rigid-body translation of the former model is characterized by a translation of about $\frac{1}{3}a_0$ along the $\langle 001 \rangle$ direction. These results are in good agreement with the experimental observation of a germanium bicrystal. However, there are differences in the absolute values of calculated boundary energies. The energy values obtained by the valence force potentials with the parameters fitted to the elastic constants and by the bond orbital model are overestimated, although the energy values by the valence force potential with the parameters fitted to the finite wave vector modes of lattice distortions are comparable with those by the semiempirical tight-binding method.

Key words: grain boundary; theoretical calculation; silicon; semiconductor; valence force field; bond orbital model; semiempirical tight-binding method; supercell method.

1. Introduction

Recently, great interest has been shown in the study of grain boundaries in covalent materials for the following two reasons. Firstly, polycrystalline semiconductors are expected to be used for solar cells and various electronic devices. Complex and disordered structure of grain boundaries affects the electronic properties of bulk polycrystals. Thus it is essential to investigate the structures and properties of grain boundaries in semiconductors. Secondly, various properties of the covalent bonding ceramics such as SiC and Si₃N₄ are dominated by grain boundaries. It is of much importance to study the energies, atomic structures and fundamental properties of grain boundaries in these ceramics in order to improve the sintering and mechanical properties.

For the grain boundaries in covalent semiconductors, Si and Ge, the experimental observations using advanced electron microscopy techniques have enabled us to construct the structural models at an atomic level.¹⁾ On the other hand, theoretical approaches such as calculations of atomic configurations, grain boundary energies and electronic structures²⁻¹¹⁾ are playing an important role in the study of grain boundaries as well as other lattice defects in semiconductors.

At present, the principal problem about the atomic and electronic structure of grain boundaries in semi-

conductors is whether the deep states in the fundamental gap observed frequently in polycrystalline semiconductors should be attributed to an intrinsic structural effect such as dangling or distorted bonds or should be attributed to an extrinsic effect such as additional defects or segregated impurities.¹²⁾ Therefore, in theoretical approaches, it is necessary to determine firstly the most stable atomic configuration by calculating the total energy within appropriate approximations. In other words, it is essential to determine what degrees of the structural disorders such as dangling bonds, bond-length and bond-angle deviations, odd-membered rings, *etc.* exist in the boundary core regions. This aspect is common to the theoretical approaches to the dislocations in semiconductors.¹³⁾ The core structures of grain boundaries are considered to be constructed by the structural units similar to those in the dislocation cores.^{14,15)}

In the present paper, we calculate theoretically the stable atomic configuration and the boundary energy of the $\Sigma=5$ ($1\bar{3}0$) symmetrical tilt grain boundary in Si. This boundary is one of the coincidence $\langle 001 \rangle$ symmetrical tilt grain boundaries in the diamond structure.¹⁵⁾ Experimental and theoretical studies have been concentrated on the $\langle 011 \rangle$ tilt grain boundaries and the studies of the $\langle 001 \rangle$ tilt grain boundaries are few except several experiments^{16,17)} and calculations.¹¹⁾ The $\Sigma=5$ ($1\bar{3}0$) tilt grain boundary is formed by rotating two crystals around the common $\langle 001 \rangle$ axis by 53.13° with median plane ($1\bar{1}0$).¹⁵⁾ Two reconstructed models have been proposed so far. The first model was proposed by Hornstra¹⁵⁾ and the second model was proposed by Bacmann *et al.*¹⁷⁾ These two models consist of straight and zigzag arrangement of the 5-3 units at the interface, respectively, and are denoted by models A and B in this paper. The 5-3 unit corresponds to the reconstructed core structure of the edge dislocation with $\vec{b}=\frac{1}{2}a_0[1\bar{1}0]$ and consists of a pentagon and a triangle in the $[001]$ projection. In this paper, we determine theoretically the most stable atomic geometry of the two models of the $\Sigma=5$ ($1\bar{3}0$) tilt grain boundary in Si.

We used several methods, the valence force field model, the bond orbital model and the supercell method based on the semiempirical tight-binding method. These theoretical schemes have been widely used for calculations of the total energy and the stable geometry of various types of lattice defects in semiconductors. The present two reconstructed models of the $\Sigma=5$

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** Glass and Ceramic Material Department, Government Industrial Research Institute, Osaka, Midorigaoka, Ikeda, Osaka Pref. 563.

*** Department of Metallurgy and Materials Science, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113.

(130) tilt grain boundary have no dangling bonds and thus these methods can be used as they are free from consideration of the complicated problem of the dangling bond energy. Thus this is a good example to discuss the utility of the present various theoretical schemes.

II. Methods of Calculations

1. Valence Force Fields

The simplest method to calculate the total energy and the stable atomic geometry of largely extended defects such as grain boundaries is to use valence force fields.^{2,3,6,9)} In the valence force field model, the basic assumption is that the change in the total energy induced by lattice distortion can be expressed as a function of changes in the valence coordinates such as bond-lengths, bond-angles, *etc.* This method is useful in the systems such as covalent materials and molecules where structural properties are explained by localized bonds between atoms.

The simplest form of valence force potentials in tetrahedral semiconductors is that proposed by Keating.¹⁸⁾ This potential takes into account contribution only from the changes in the bond-lengths and the bond-angles in the harmonic approximation and is expressed as

$$E_i = \frac{3\alpha}{16r_0^2} \sum_{j=1}^4 (r_{ij}^2 - r_0^2)^2 + \frac{3\beta}{16r_0^2} \sum_{j \neq k}^4 \left(\frac{\vec{r}_{ij} \cdot \vec{r}_{ik}}{r_0^2} + \frac{r_0^2}{3} \right)^2, \quad \dots\dots\dots(1)$$

where, E_i : the elastic energy of an atom i
 r_0 : the nearest-neighbor distance in the perfect crystal
 j, k : the nearest-neighbor atoms of an atom i .
The parameters α and β are the bond-stretching and bond-bending force constants, respectively. In the systems with larger strains, it is necessary to include the lattice anharmonicity. The following potential was proposed¹⁹⁾ by modifying the anharmonic Keating potential²⁰⁾ as

$$E_i = \frac{3\alpha}{16r_0^2} \sum_{j=1}^4 (r_{ij}^2 - r_0^2)^2 \exp \left[\frac{4\sqrt{3}\gamma'}{3\alpha r_0} (r_{ij}^2 - r_0^2) \right] + \frac{3\beta}{16r_0^2} \sum_{j \neq k}^4 \left(\frac{\vec{r}_{ij} \cdot \vec{r}_{ik}}{r_0^2} + \frac{r_0^2}{3} \right)^2 \exp \left[\frac{4\sqrt{3}\epsilon'}{3\beta r_0} (r_{ij}^2 - r_0^2) \right] + \frac{\sqrt{3}\delta'}{4r_0^3} \sum_{j \neq k}^4 \left(\frac{\vec{r}_{ij} \cdot \vec{r}_{ik}}{r_0^2} + \frac{r_0^2}{3} \right)^3. \quad \dots\dots\dots(2)$$

All the parameters $\alpha, \beta, \gamma', \epsilon'$ and δ' were fitted so as to reproduce the second-order and third-order elastic constants of bulk Si,^{18,20)} and listed in Table 1.

On the other hand, for the description of the localized distortions around lattice defects, it is more appropriate to use the potentials determined so as to reproduce the finite wave vector modes of distortion rather than the distortion modes of long wave lengths, *i.e.*, the elastic constants. Baraff *et al.*²¹⁾ modified the bond-stretching and bond-bending parameters, α and β in Eq. (1) so as to reproduce the vibration modes throughout large portions of the Brillouin zone, and

Table 1. Parameters of valence force potentials in Si.

	Values by Keating (1966) ^{18,20)}	Values by Baraff <i>et al.</i> (1980) ²¹⁾
α (J/m ²)	48.5	51.51
β (J/m ²)	13.8	4.70
γ (J/m ³)	-3.51×10^7	—
δ (J/m ³)	0.47×10^7	—
ϵ (J/m ³)	-0.47×10^7	—

$$\gamma' = \frac{1}{2}\gamma, \quad \delta' = \frac{1}{2}\delta, \quad \epsilon' = \frac{3}{2}\epsilon.$$

The values of α and β by Keating are common in both Eqs. (1) and (2).

the parameters are listed in Table 1. It is noticeable that the bond-bending parameter β is reduced by a factor of 3 in this modification.

In the valence force field model, the total energy and the force acting on each atom are given by analytic functions and lattice relaxation of a system with a large number of atoms can be carried out with short computing time and good numerical accuracy.

2. Bond Orbital Model

The bond orbital model, the tight-binding type electronic theory,^{22,23)} has been successful for various problems in semiconductors.^{7,8,11,24-27)} In this model, the change in the total energy induced by lattice distortion is calculated quantum-mechanically as the deformation of sp^3 covalent bonding states.

An sp^3 hybrid orbital set is taken and only the Hamiltonian matrix element between two sp^3 hybrid orbitals belonging to the same bond is taken. The matrix element t can be expressed as

$$t = \frac{1}{4} \left[t_{ss} + \sqrt{3}(P_i - P_j)t_{ss} - 3P_i P_j t_{ss} + 3(P_{ij} - P_i P_j)t_{\pi\pi} \right], \quad \dots\dots\dots(3)$$

$$\text{where, } P_i = l_i l_i + m_i m_i + n_i n_i, \\ P_j = l_j l_j + m_j m_j + n_j n_j, \\ P_{ij} = l_i l_j + m_i m_j + n_i n_j.$$

(l_i, m_i, n_i), (l_j, m_j, n_j) and (l, m, n) are the directions of lobes of two hybrid orbitals and the direction cosines between two atoms, respectively. The terms t_{ss} , t_{ss} , t_{ss} and $t_{\pi\pi}$ are the two-center hopping integrals between atomic orbitals. The bonding energy level E_B is given by $E_B = E_h - |t|$, where E_h is the hybrid energy level and given by $E_h = \frac{1}{4}(E_s + 3E_p)$. The band structure energy is given as a sum of $2E_B$ for all the bonds. The other contribution in the total energy is a short-range repulsive energy arising from ion core interactions and overlap interactions. We used the Born-Mayer potential,

$$f(r_{ij}) = f(r_0) \exp [-P(r_{ij} - r_0)]. \quad \dots\dots\dots(4)$$

The two-center hopping integrals are assumed to have the same exponential dependence on the interatomic distance as

$$t_{ij} = t_{ij}^0 \exp [-q(r_{ij} - r_0)]. \quad \dots\dots\dots(5)$$

We evaluated t_{ij}^0 from Harrison's universal tight-

binding parameters.²³⁾ The remaining parameters p , q and $f(r_0)$ were determined so as to reproduce the cohesive energy, the bulk modulus and the bulk equilibrium condition. These parameters are listed in Table 2.

The total energy is given as a function of the atomic positions and the directions of lobes of sp^3 hybrid orbitals of each atom. The stable geometry is given by lattice relaxation where each atom is moved and sp^3 hybrid orbitals of each atom are rotated according to the energy gradients about the position and the directions of sp^3 hybrid orbitals of each atom.

In the bond orbital model, the Hamiltonian matrix represented by an sp^3 hybrid orbital set is transformed unitarily to that represented by a basis set of bonding orbitals $|B\rangle$ and antibonding orbitals $|A\rangle$, both of which are composed of two sp^3 hybrid orbitals for respective bonds. The main assumption in the bond orbital model is the neglect of all the elements of the submatrixes of the Hamiltonian, H_{AB} and H_{BA} , between bonding orbitals and antibonding orbitals.²³⁾ Thus the band structure energy E_{bs} is given without diagonalization of the Hamiltonian matrix by the trace of the submatrix H_{BB} as

$$E_{bs} = 2 \sum_B \langle B | \mathbf{H} | B \rangle = 2 \sum_B E_B. \dots\dots\dots(6)$$

The optimization of the directions of sp^3 hybrid orbitals of each atom in the lattice relaxation procedure corresponds to setting the sp^3 hybrid orbital basis set so as to minimize the effect of the neglect of the non-zero matrix elements between neighboring bonding and antibonding orbitals.

3. Semiempirical Tight-binding Method

In the valence force field model and the bond orbital model, the change in the total energy induced by lattice distortions is calculated as a perturbation or deformation of sp^3 bonding states. Thus the utility of these methods is doubtful or at least qualitative in the system with large lattice deformations where the effects of dehybridization or rehybridization must be taken into account. In such a case, more fundamental approaches involving a solution of the Schrödinger equation are necessary. We used the semiempirical tight-binding method^{28,29)} with use of a supercell technique for calculations of the two reconstructed models of the $\Sigma=5$ (130) tilt grain boundary in Si. This method has been used successfully for describing surfaces,^{28,29)} clusters^{30,31)} and boundaries.^{4,5)} This method is very useful for treating a system with hundreds of atoms in one unit cell, whereas in the first-principles density functional theory the tractable size of one unit cell is limited to be small.⁵⁾

The total energy is given as a sum of two terms,

$$E_{tot} = E_{bs} + U. \dots\dots\dots(7)$$

Table 2. Parameters of the bond orbital model in Si.

r_0 (nm)	E_s (eV)	E_p (eV)	p (nm ⁻¹)	q (nm ⁻¹)	$f(r_0)$ (eV)
0.235	-13.55	-6.52	18.25	9.432	6.234

The band structure energy E_{bs} is a sum of occupied one-electron energies of the first-neighbor tight-binding Hamiltonian and expressed as

$$E_{bs} = \sum_{n,\vec{k}}^{occ.} E_{n,\vec{k}}. \dots\dots\dots(8)$$

$E_{n,\vec{k}}$ is the eigen-energy with wave vector $\vec{k}$ and band index n . The other term U is the ion-ion interactions minus the double-counting electron-electron interactions in E_{bs} and is modeled as a short-range repulsive pairwise energy. We used Chadi's form^{28,29)} as

$$U = \sum_{i>j} (U_1 \epsilon_{ij} + U_2 \epsilon_{ij}^2), \dots\dots\dots(9)$$

where, ϵ_{ij} : the fractional change in the bond-length between atoms denoted by i and j .

We used the tight-binding parameters given by Chadi.²⁹⁾ These parameters were assumed to have an r^{-2} dependence on the nearest-neighbor distance r . The parameters U_1 and U_2 were determined so as to reproduce the bulk modulus and the bulk equilibrium condition. All the parameters used are listed in Table 3.

Periodicity normal to the boundary plane is imposed in the supercell method. Each unit cell contains two boundary planes with inversion symmetry to each other and symmetrical boundary planes are alternately repeated with the same distance normal to the boundary plane. The electronic structure of the supercell structure with a large unit cell is calculated.

In the lattice relaxation procedure, each atom is moved according to the Hellmann-Feynman force acting on it. The Hellmann-Feynman force can be calculated very easily in the tight-binding scheme by Hellmann-Feynman theorem as

$$\begin{aligned} \vec{F}_i &= - \sum_{n,\vec{k}}^{occ.} \left\langle n, \vec{k} \left| \frac{\partial \mathbf{H}}{\partial \vec{t}_i} \right| n, \vec{k} \right\rangle \\ &= - \sum_{n,\vec{k}}^{occ.} \sum_{i\alpha} \sum_{j\beta} C_{i\alpha}^{n,\vec{k}*} C_{j\beta}^{n,\vec{k}} \left\langle i\alpha, \vec{k} \left| \frac{\partial \mathbf{H}}{\partial \vec{t}_i} \right| j\beta, \vec{k} \right\rangle, \end{aligned} \dots\dots\dots(10)$$

where $|n,\vec{k}\rangle$ is the eigen vector with wave vector $\vec{k}$ and band index n and expressed as $|n,\vec{k}\rangle = \sum_{i\alpha} C_{i\alpha}^{n,\vec{k}} \times |i\alpha, \vec{k}\rangle$, where $|i\alpha, \vec{k}\rangle$ is a Bloch basis function composed of α -th orbital of i -th atom located at $\vec{t}_i + \vec{R}$ with reference to the lattice vector $\vec{R}$. The matrix elements of the gradient of the Hamiltonian in Eq. (10) can be expressed analytically as already pointed out.^{29,32)} This simple expression of the Hellmann-Feynman forces in the supercell method is essentially equal to those using

Table 3. Parameters of the semiempirical tight-binding method in Si.

E_s	E_p	$V_{ss\sigma}$	$V_{sp\sigma}$	$V_{pp\sigma}$	$V_{pp\pi}$	U_1	U_2
-5.25	1.20	-1.938	1.745	3.050	-1.075	-16.28	55.38

All the parameters are expressed in eV. The choice of E_s and E_p sets the zero of energy at the bulk valence-band maximum.

the bond order³²⁾ or the density matrix.

III. Results and Discussion

In the practical calculations using the valence force fields and the bond orbital model, atoms within about 25 Å in both sides of the interface between the two fixed crystals were relaxed. The periodic boundary conditions parallel to the boundary plane were used. The optimum rigid-body translations of the two crystals were found by repeating lattice relaxations.

In the calculations using the supercell method based on the semiempirical tight-binding method, each unit cell contains 120 atoms and the distance between the two boundary planes is about 26 Å in both models A and B. The supercell structure of model A is orthorhombic and that of model B is monoclinic. In calculations of the band structure energy and the Hellmann–Feynman forces shown in Eqs. (8) and (10), integrations over the occupied states in the Brillouin zone were carried out using the special point method³³⁾ because the electronic structure of the present boundary structures is not metallic and there are no deep states in the fundamental gap in accordance with the absence of dangling bonds. Practically, iterative diagonalization of the 480×480 Hamiltonian must be carried out in the lattice relaxation procedure. This type of computation is much accelerated by the use of the supercomputer. The optimum rigid-body translations were also found by iterating lattice relaxations of the supercell structure with an unit cell of somewhat smaller size for saving computing time.

Results of the grain boundary energies and the optimum rigid-body translations of the two reconstructed models of the Σ=5 (130) boundary in Si calculated using the present various methods are summarized in Tables 4 and 5. Figure 1 shows the stable atomic geometry of the two models obtained by the semiempirical tight-binding method.

Of the theoretical schemes used in this paper, the most quantitatively reliable one is the semiempirical tight-binding method. Main results by this method are summarized as follows. The calculated boundary energies of models A and B are 0.42 and 0.26 J/m², respectively. These values are reasonable as compared with the theoretical values of the reconstructed model of the Σ=9 (221) twin in Si, 0.32 J/m² by the similar method⁴⁾ and 0.29 J/m² by the first principles density functional theory.⁵⁾ The calculation has shown that the structural model by Bacmann *et al.*¹⁷⁾ consisting of zigzag arrangement of the 5–3 units (shown in Fig. 1(b)) is more energetically favored than that by Hornstra¹⁵⁾ consisting of straight arrangement of the 5–3 units (shown in Fig. 1(a)). The optimum rigid-body translation of model B has two components, a slight dilatation along the <130> direction and a translation a little larger than $\frac{1}{8}a_0$ along the <001> direction. Although there have been no detailed experimental observations of this type of boundary in Si, this result is in good agreement with the experimental observation of a germanium bicrystal¹⁷⁾ where the contrast of α-fringes consistent with a rela-

Table 4. Calculated boundary energies of the two models of the Σ=5 (130) boundary in Si. (J/m²)

Theoretical schemes	Calculated boundary energy	
	Model by Hornstra (model A)	Model by Bacmann <i>et al.</i> (model B)
Original Keating potential	0.938	0.924
Modified Keating potential	0.910	0.900
Keating potential with the parameters by Baraff <i>et al.</i>	0.368	0.338
Bond orbital model	1.088	0.952
Semiempirical tight-binding method	0.415	0.259

Table 5. Calculated optimum rigid-body translations of the two models of the Σ=5 (130) boundary in Si.

Theoretical schemes	Calculated optimum rigid-body translation	
	Model by Hornstra (model A)	Model by Bacmann <i>et al.</i> (model B)
Original Keating potential	$\vec{t}_\perp = 0$	$\vec{t}_\perp = \frac{1}{243}a_0[1\bar{3}0]$ $\vec{t}_\parallel = \left(\frac{1}{8} + \frac{1}{56}\right)a_0[00\bar{1}]$
Modified Keating potential	$\vec{t}_\perp = \frac{1}{91}a_0[1\bar{3}0]$	$\vec{t}_\perp = \frac{1}{66}a_0[1\bar{3}0]$ $\vec{t}_\parallel = \left(\frac{1}{8} + \frac{1}{56}\right)a_0[00\bar{1}]$
Keating potential with the parameters by Baraff <i>et al.</i>	$\vec{t}_\perp = 0$	$\vec{t}_\perp = \frac{1}{215}a_0[1\bar{3}0]$ $\vec{t}_\parallel = \left(\frac{1}{8} + \frac{1}{49}\right)a_0[00\bar{1}]$
Bond orbital model	$\vec{t}_\perp = \frac{1}{183}a_0[1\bar{3}0]$	$\vec{t}_\perp = \frac{1}{104}a_0[1\bar{3}0]$ $\vec{t}_\parallel = \left(\frac{1}{8} + \frac{1}{56}\right)a_0[00\bar{1}]$
Semiempirical tight-binding method	$\vec{t}_\perp = \frac{1}{429}a_0[1\bar{3}0]$	$\vec{t}_\perp = \frac{1}{156}a_0[1\bar{3}0]$ $\vec{t}_\parallel = \left(\frac{1}{8} + \frac{1}{49}\right)a_0[00\bar{1}]$

$t_\perp, t_\parallel$: The components of rigid-body translation normal and parallel to the boundary plane, respectively

The coordinate system: the same as that shown in Fig. 1
In model A, all the calculated structures contain the same rigid-body translation parallel to the boundary plane, $\vec{t}_\parallel = \frac{1}{20}a_0[310]$, with respect to the coincidence structure shown in Ref. 17).

tive translation of $\frac{1}{8}a_0$ along the <001> direction was observed.

About the stable geometry of the two models shown in Fig. 1, bonds are formed at the interface accompanied by the bond-length and bond-angle deviations and the formation of odd-membered rings in both models. Pentagons and triangles at the interface in the [001] projection are not five-membered and three-membered rings but parts of seven-membered and five-membered rings, respectively. In model A, the bond-length deviations range from −1.59 to 2.23 %

Fig. 1. Relaxed atomic geometry of the two models of the $\Sigma=5$ ($\bar{1}30$) boundary in Si calculated by the semiempirical tight-binding method. A figure inside circles indicates the height of the atomic site along the $\langle 001 \rangle$ direction expressed in units of $\frac{1}{4}a_0[001]$.

and the bond-angle deviations range from -14.52 to 18.84° . In model B, the bond-length deviations range from -1.43 to 2.08 % and the bond-angle deviations range from -15.08 to 15.04° . The present values of the bond-length and bond-angle deviations are not so large as compared with the calculated values of the $\Sigma=9$ (221) twin in Si.⁴⁾ As compared with model B, the number of largely deformed bonds are larger in model A and this is possibly the main reason of the difference in the boundary energy.

As shown in Tables 4 and 5, the common features in the results by the respective theoretical schemes used in this paper are summarized as follows. Firstly, all the calculations have shown that the structural model by Bacmann *et al.* (model B) is more energetically favored than that by Hornstra (model A). Secondly, the optimum rigid-body translations calculated by all the present methods are similar to each other. All these results are in good agreement with the experimental observation of a germanium bicrystal as mentioned above.

The noticeable differences in the results by the respective methods exist in the absolute values of calculated boundary energies in Table 4. The energy values by the original Keating potential, the modified Keating potential and the bond orbital model are in the same range but are overestimated as compared with those by the semiempirical tight-binding method. On the other hand, it is noticeable that the values by the Keating potential with the parameters by Baraff *et al.* are comparable with those by the semiempirical tight-binding method.

The present results indicate that valence force fields with parameters fitted to the long wave length modes of lattice distortion, *i.e.*, the elastic constants possibly overestimate the change in the total energy induced by localized distortions around lattice defects and it is more appropriate to use the parameters fitted to the finite wave vector modes of lattice distortion. The

main difference between the two sets of parameters exists in the bond-bending parameter β . As shown in Table 1, the value of β of the former set of parameters is about three times as large as that of the latter set, though the bond-stretching parameters α are not so different from each other. In addition, the present reconstructed boundary structures have large bond-angle deviations as compared with the bond-length deviations. Therefore, it can be understood that the difference in the energy values calculated using the two sets of parameters are considerably large.

In the bond orbital model, the method of fitting the parameters shown in Eqs. (4) and (5) is not so essential, because these parameters are mainly concerned with the energy changes by the bond-length deviations and this type of parameters are not considered to be changed so largely by the methods of fitting as well as the valence force potentials. The present overestimation of the boundary energies by the bond orbital model is considered to be caused by the fixed sp^3 configuration of the hybrid basis set and the neglect of the nonzero matrix elements between neighboring bonding and antibonding orbitals.²³⁾ As already pointed out,²³⁾ this problem is more serious in systems with large bond-angle deviations. Similar overestimation was seen in the calculation of the core energy of dislocations in semiconductors.²⁶⁾

IV. Conclusion

The structure and energy of the $\Sigma=5$ ($\bar{1}30$) symmetrical tilt grain boundary in Si, one of the coincidence $\langle 001 \rangle$ tilt grain boundaries, were calculated theoretically. The valence force fields, the bond orbital model and the semiempirical tight-binding method were used and the computed results were compared with each other.

All the calculations by the present methods have shown that the structural model by Bacmann *et al.* is

more energetically favored than that by Hornstra and that the optimum rigid-body translation of the former model is characterized by a translation of about $\frac{1}{3}a_0$ along the $\langle 001 \rangle$ direction. These results are in good agreement with the experimental observation of a germanium bicrystal.

However, there are noticeable differences in the absolute values of calculated boundary energies. The energy values calculated by the original and modified Keating potentials and the bond orbital model are overestimated as compared with those by the semiempirical tight-binding method. In the valence force field model, it is more appropriate to use the parameters fitted to the finite wave vector modes of lattice distortions such as those given by Baraff *et al.* In the bond orbital model, it is necessary to include the effects of the nonzero matrix elements between neighboring bonding and antibonding orbitals²³⁾ in order to give more quantitative energy values.

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