Internal Displacement and Elastic Properties of the Silicon Tersoff Model*

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Martin's method, which is used to determine the internal displacement of atomic systems and elastic constants, is applied to the Tersoff potential. The potential is modified to provide an accurate description of the high-temperature elastic properties of silicon. The elastic constants of crystalline silicon were investigated at both low and high temperatures. Results were verified using the statistical thermodynamic method, i.e., 'Fluctuation formula'. It was found that values of elastic constants and the influence of the internal displacement are valid. However, at high temperatures the gap becomes larger owing to the thermal fluctuation. Since the convergence of the Martin's method is faster by about two orders, it is the more effective method. It was also found that the fluctuation term includes the effects of the internal displacement and thermal fluctuation.

Key Words: Molecular Dynamics, Elasticity, Micro Mechanics, Thermodynamics, Internal Displacement, Lattice Dynamics, Elastic Constants

1. Introduction

In the recent development of semiconductors, the size of the evaluation region has reached several score nanometers and is approaching the atomic level. This has strongly necessitated a process simulation for such a nano-scale region. However, the validity and limits of the present continuum-based simulation are remained under debate.

Molecular dynamics, in which the material is not treated as a homogeneous continuum body but as an inhomogeneous atomic ensemble, seems to be a very powerful tool for investigating the difference between macro (continuum body) and micro (atoms) scales. Especially, the calculation of the elastic constants of atomic system is thought to be important. Much success have been achieved in the prediction of the elastic properties of immeasurable materials and inhomogeneous structures such as grain boundaries[1] and analysis of the stability of atomic systems and fractures[2].

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The difficult aspect of calculating elastic constants using molecular dynamics method concerns the problem of internal displacement. In the conventional linear elastic theory, the displacements of material points become linear to deformation. However, in actuality, atomic displacements do not generally become linear to deformation. Each atom moves to its most stable point in response to the deformation in an atomic system. Such a difference between the displacement of continuum body approximation and that of atoms is referred as internal displacement (Fig. 1). Since internal displacement appears in the diamond lattice or in inhomogeneous structures such as grain boundaries and surfaces, such influence must

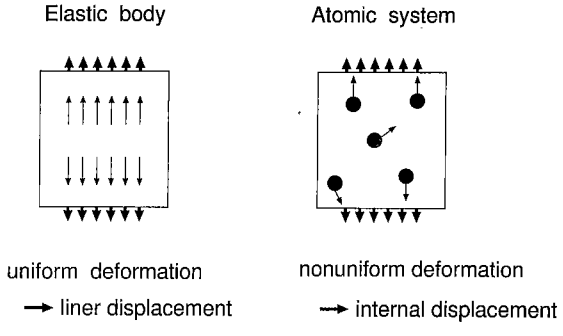

Fig. 1 Internal displacement of the atomic systems

be taken into account in the definition of elastic constants, which adds the complexity of the problem.

Several methods have been proposed to deal with these problems. These methods include that which actually deforms the system[3] and a method that uses the fluctuation formula of the statistical ensemble[4]. However, many problems are yet to be solved. The former method involves three problems. First, a deformation calculation is needed for each component of the elastic constants. Second, it cannot deal with the crystal structures that structural transition causes due to strain. Third, the slow convergence of the strain of constant stress ensemble or the stress of the constant volume ensemble leads to large measurement errors.

Ray and Pearson have formulated statistical thermodynamics methods[4],[5]. While the validity of the result may be guaranteed, there are some limitations in these methods. For example, they cannot be applied to systems other than statistical ensembles and cannot provide the local values around each atom. Since such an application is limited to homogeneous systems having periodic boundary condition, it is difficult to effectively apply it to inhomogeneous systems.

In this paper, we considered Martin's method[6], which provides the internal displacement and elastic constants of atomic systems, could resolve the above problem. This method is applied to the Tersoff potential[7] suitable for the description of silicon which is an indispensable material in the semiconductor field. We selected the Tersoff potential since it is known to express the properties of silicon very well by incorporating the bond angle and coordination dependence that are characteristic in the covalent system and by fitting energies to the ab-inito calculation. By this method, the investigations of elastic constants and the internal displacement at arbitrary inhomogeneous systems such as grain boundaries[1], amorphous structures, and crack tips are realized without applying actual deformation.

In chapter 2, we describe the formulation of the calculations of the elastic constants. In chapter 3, the results of the application of the method to crystalline silicon at low and high temperatures are shown. In chapter 4, in a discussion of the results we compare the results with those obtained by using the fluctuation formula. The validity and efficacy of convergence are discussed. Finally, in a comparison of the terms of both methods, we discuss the physical meaning of the fluctuation terms (statistical fluctuation in phase space).

2. The Method of Calculating Elastic Constants

We describe the definition of strain, internal displacement, and elastic constants and their application to the Tersoff potential.

2.1 Definition of the strain

Due to the existence of internal displacement, defining strain through the use of atomic displacement becomes impossible in the MD system. Therefore, the averaged strain of the whole MD cell (with periodic boundary) is defined for the molecular dynamics of a solid system. The concept of the shape matrix of the MD cell is used for the definition. The coordination of the atoms is represented by a normalized form as Eq. (1), where the shape of the unit cell is regarded as parallelepiped (Fig. 2) with 3 edges of unit vectors $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$. By using this concept, the system can be arbitrarily deformed only by changing the lattice matrix $\boldsymbol{h}$ while fixing $\boldsymbol{\rho}$.

$$r_i^\alpha = a_i\rho_1^\alpha + b_i\rho_2^\alpha + c_i\rho_3^\alpha = h_{ij}\rho_j^\alpha \quad (0<\rho_1^\alpha,\ \rho_2^\alpha,\ \rho_3^\alpha<1) \tag{1}$$

$$\boldsymbol{h}=\begin{pmatrix} a_x & b_x & c_x \\ a_y & b_y & c_y \\ a_z & b_z & c_z \end{pmatrix}=\begin{pmatrix} h_{11} & h_{12} & h_{13} \\ h_{21} & h_{22} & h_{23} \\ h_{31} & h_{32} & h_{33} \end{pmatrix} \tag{2}$$

The atomic coordination in the standard state (stress-free state) is represented by $\boldsymbol{r}_0^\alpha=\boldsymbol{h}_0\boldsymbol{\rho}_0^\alpha$. By replacing $\boldsymbol{h}_0$ into $\boldsymbol{h}$, the atomic coordination displaced by averaged strain becomes $\boldsymbol{r}^\alpha=\boldsymbol{h}\boldsymbol{\rho}_0^\alpha$. From both relationships, it follows that $\boldsymbol{r}^\alpha=\boldsymbol{h}\boldsymbol{h}_0^{-1}\boldsymbol{r}_0^\alpha$. Therefore, the displacement gradient tensor can be defined by $\boldsymbol{F}=\boldsymbol{h}\boldsymbol{h}_0^{-1}$. As a result, Green-Lagrange strain $\boldsymbol{\eta}$ can be represented by Eq. (3) by using $\boldsymbol{F}$,

$$\boldsymbol{\eta}=\frac{1}{2}(\boldsymbol{F}^t\boldsymbol{F}-\boldsymbol{I})=\frac{1}{2}(\boldsymbol{h}_0^{-t}\boldsymbol{G}\boldsymbol{h}_0^{-1}-\boldsymbol{I}),\ (\boldsymbol{G}=\boldsymbol{h}^t\boldsymbol{h}). \tag{3}$$

2.2 Definition of the elastic constants (Martin's method)

In the Molecular Dynamics method, the system energy becomes the function of the included interatomic distance. Martin[6] defined the elastic constants by including the relative displacement (i.e. the internal displacement) of each sublattice, in which the displacement is linear to the deformation, into the interatomic distance.

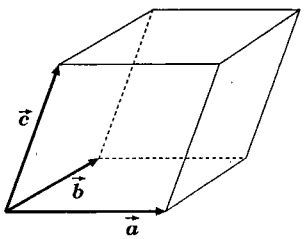

Fig. 2 The defenition of MD cell

In general, several kinds of sublattices whose deformation is homogeneous are contained in the crystal. For example, the diamond structure has two overlapped sublattices of a fcc structure. It can be established that each atom belongs each sublattice. We next define the relative displacement of each sublattice. Expressing the representative point of sublattice p as $\boldsymbol{r}^p$, the center of the gravity of sublattices $(1-m)$ can be defined by $\boldsymbol{R}=\sum_{p=1}^{m}\boldsymbol{r}^p$. Since the distance from the center of gravity can be represented by $\boldsymbol{d}^p=\boldsymbol{r}^p-\boldsymbol{R}$, the relative displacement vector between sublattices can be defined as $\boldsymbol{d}^p-\boldsymbol{d}^m$ ($\boldsymbol{d}^m$ origin). The variation in the relative displacement vector in response to the arbitrary deformation $\boldsymbol{F}$ (deformation gradient tensor) can be represented by the homogeneous deformation term (1st term of the right-hand side of Eq.(4)) and the relative displacement term of sublattice p from m (2nd term), where the subscript 0 symbolizes the state before deformation,

$$\boldsymbol{d}^p-\boldsymbol{d}^m=\boldsymbol{F}(\boldsymbol{d}_0^p-\boldsymbol{d}_0^m)+\boldsymbol{u}^p. \tag{4}$$

If the atoms α and β belong to the sublattice $p(\alpha)$ and $p(\beta)$ respectively, the distance between atom α and β can be easily written by

$$\boldsymbol{r}^{\alpha\beta}=\boldsymbol{F}\boldsymbol{r}_0^{\alpha\beta}+\boldsymbol{u}^{p(\beta)}-\boldsymbol{u}^{p(\alpha)}. \tag{5}$$

Now the internal displacement vector is newly defined by $\boldsymbol{\xi}^p=\boldsymbol{F}^t\boldsymbol{u}^p$ as a rotational invariant variable. By using this definition, the rotational invariant distance $s^{\alpha\beta}=(\boldsymbol{r}^{\alpha\beta})^t\boldsymbol{r}^{\alpha\beta}$ can be represented as follows:

$$s^{\alpha\beta}=(\boldsymbol{r}_0^{\alpha\beta})^t(2\boldsymbol{\eta}+\boldsymbol{I})\boldsymbol{r}_0^{\alpha\beta}+2(\boldsymbol{\xi}^{p(\beta)}-\boldsymbol{\xi}^{p(\alpha)})\boldsymbol{r}_0^{\alpha\beta}+(\boldsymbol{\xi}^{p(\beta)}-\boldsymbol{\xi}^{p(\alpha)})(2\boldsymbol{\eta}+\boldsymbol{I})^{-1}(\boldsymbol{\xi}^{p(\beta)}-\boldsymbol{\xi}^{p(\alpha)}). \tag{6}$$

From Eq.(6), the variation in the interatomic distance in response to the deformation $\boldsymbol{F}$ (averaged strain $\boldsymbol{\eta}$) can be derived. Moreover, under the condition that the internal displacement becomes minimum and the stress is free, the elastic constants can be defined by Eq.(8).

$$\sigma_{ij}=\frac{1}{\Omega_0}\frac{\partial\phi}{\partial\eta_{ij}}\bigg|_{\eta=0,\xi=0}, \tag{7}$$

$$C_{ijkl}=C_{ijkl}^0+C_{ijkl}^*, \tag{8}$$

$$C_{ijkl}^*=-\sum_p\sum_q D_{ijm}^p g_{mn}^{pq}D_{kln}^q, \tag{9}$$

$$C_{ijkl}^0=\frac{1}{\Omega_0}\frac{\partial^2\phi}{\partial\eta_{ij}\partial\eta_{kl}}\bigg|_{\eta=0,\xi=0}, \tag{10}$$

$$D_{ijk}^p=\frac{1}{\Omega_0}\frac{\partial^2\phi}{\partial\eta_{ij}\partial\xi_k^p}\bigg|_{\eta=0,\xi=0}, \tag{11}$$

$$E_{ij}^{pq}=\frac{1}{\Omega_0}\frac{\partial^2\phi}{\partial\xi_i^p\partial\xi_j^q}\bigg|_{\eta=0,\xi=0}, \quad ;\ \sum_q g_{ij}^{pq}E_{jk}^{qr}=\delta_{pr}\delta_{ik}, \tag{12}$$

Where ϕ is potential energy, D_{ijk}^p is piezo elastic constants, E_{ij}^{pq} is the force constants between sublattices, $\Omega_0=\det(\boldsymbol{h}_0)$ is volume, and indexes p, q, r represent the sublattices.

The first term of the right-hand side of Eq.(8) is referred to as the local elastic constants (Born term C_{ijkl}^0) and the second term is the relaxation elastic constants (Relaxation term C_{ijkl}^*). The former is defined by ignoring the effect of internal displacement and corresponds to the stiffness of atomic bonding. The latter corresponds to the softening effect of internal displacement.

Since the independent freedom of the force constants tensor $\boldsymbol{E}(3N\times3N)$ in Eq.(12) is $(3N-3)$, it cannot be solved directly. In order to remove these three dependent freedoms, $\boldsymbol{E}$ must be diagonalized. From the eigen values $\lambda_1, \lambda_2, \cdots, \lambda_{3N}$ ($\lambda_{3N-2}=\lambda_{3N-1}=\lambda_{3N}=0$) and eigen vectors $\boldsymbol{v}_1, \boldsymbol{v}_2, \cdots, \boldsymbol{v}_{3N}$ of $\boldsymbol{E}$, we can define the $\boldsymbol{\Lambda}_{in}$ and $\boldsymbol{L}_{in}$ as shown below,

$$\boldsymbol{\Lambda}_{in}=\begin{pmatrix}\lambda_1 & 0 & 0 & \cdots & 0\\ & \lambda_2 & 0 & \cdots & 0\\ & & & \cdots & \cdots\\ & & & & \lambda_{3N-3}\end{pmatrix} \tag{13}$$

$$\boldsymbol{L}_{in}=(\boldsymbol{v}_1, \boldsymbol{v}_2, \cdots, \boldsymbol{v}_{3N-3});\ (\boldsymbol{L}_{in}^t\boldsymbol{L}_{in}=\boldsymbol{I}). \tag{14}$$

Finally $\boldsymbol{g}$ can be obtained from Eq.(15),

$$\boldsymbol{g}=\boldsymbol{E}^{-1}=\boldsymbol{L}_{in}\boldsymbol{\Lambda}_{in}^{-1}\boldsymbol{L}_{in}^t. \tag{15}$$

The atomistic local elastic constants ($C_{ijkl}^{0\alpha}$) and relaxation elastic constants ($C_{ijkl}^{*\alpha}$) can be defined as a contribution of each atom, which is the same concept as that seen in atomic stress. Here we assume that all atoms have each sublattice ($p(\alpha)=\alpha$). In Eq.(16), we define the atomic elastic constants so that their averages can be equal to the global elastic constants, which is different from Albers' definition[1] since they used 2 body-like property of EAM potential for the definition.

$$C_{ijkl}^{\alpha}=C_{ijkl}^{0\alpha}+C_{ijkl}^{0\alpha}, \left(\frac{1}{N}\sum_{\alpha}C_{ijkl}^{\alpha}=C_{ijkl}\right) \tag{16}$$

$$\Omega_0^{\alpha}C_{ijkl}^{0\alpha}=\Omega_0\sum_{\beta}\frac{\partial\sigma_{ij}}{\partial r^{\alpha\beta}}\frac{\partial r^{\alpha\beta}}{\partial\eta_{ij}}, \left(\frac{1}{N}\sum_{\alpha}C_{ijkl}^{0\alpha}=C_{ijkl}^0\right) \tag{17}$$

$$\Omega_0^{\alpha}C_{ijkl}^{*\alpha}=-\Omega_0\sum_{\beta,n,m}D_{ijm}^{\alpha}g_{mn}^{\alpha\beta}D_{kln}^{\beta}, \left(\frac{1}{N}\sum_{\alpha}C_{ijkl}^{*\alpha}=C_{ijkl}^*\right) \tag{18}$$

Where Ω_0^{α} is atomistic volume, which here is set at $\Omega_0^{\alpha}=\Omega_0/N$.

2.3 Application to the Tersoff potential

The covalent bonding of silicon is represented by four coordination structure as illustrated in Fig. 3. Here, the atoms β and γ are the neighbors of atom α. $r^{\alpha\beta}$ is the distance between atoms α and β. $\theta_{\alpha\beta\gamma}$ is the angle between the bonding $\alpha\beta$ and $\alpha\gamma$.

Tersoff[7] described his three-body potential ϕ as a two-body form of atoms α and β as shown in Eq. (19) and included the three-body effect of atoms α, β, and γ into $\zeta^{\alpha\beta}$ implicitly. The concrete form of potential is shown in Eq.(19) - (27):

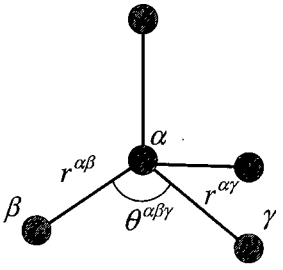

Fig. 3 Covalent bonding of silicon

$$\phi=\frac{1}{2}\sum_{\alpha\neq\beta} V^{\alpha\beta} \tag{19}$$

$$V^{\alpha\beta}=f_C(r^{\alpha\beta})[a^{\alpha\beta}f_R(r^{\alpha\beta})+b^{\alpha\beta}f_A(r^{\alpha\beta})] \tag{20}$$

$$f_R(r)=A\exp(-\lambda_1 r) \tag{21}$$

$$f_A(r)=-B\exp(-\lambda_2 r) \tag{22}$$

$$f_C(r)=\begin{cases}1, & r<R-D\\ \frac{1}{2}-\frac{1}{2}\sin\left[\frac{\pi}{2}(r-R)/D\right], & R-D<r<R+D\\ 0, & r>R+D\end{cases} \tag{23}$$

$$b^{\alpha\beta}=(1+\beta^n\zeta^{\alpha\beta n})^{-1/2n} \tag{24}$$

$$\zeta^{\alpha\beta}=\sum_{\gamma(\neq\alpha,\beta)} f_C(r^{\alpha\gamma})g(\theta^{\alpha\beta\gamma})\exp[\lambda_3^3(r^{\alpha\beta}-r^{\alpha\gamma})^3] \tag{25}$$

$$g(\theta)=1+c^2/d^2-c^2/[d^2+(h-\cos\theta)^2] \tag{26}$$

$$a^{\alpha\beta}\simeq 1 \tag{27}$$

f_R and f_A are the repulsive and attractive potential, respectively. f_C is cutoff function, by which the bonding is smoothly cut off between the 1st and 2nd neighbors. The dependences of coordination number and the three-body effect are incorporated in $\zeta^{\alpha\beta}$. A, B, λ_1, λ_2, λ_3, R, D, c, d, h, n, α, β are potential parameters provided by Tersoff[7].

For calculation of the derivatives of potential with respect to strain, the partial derivative along all dependent paths is necessary. For example, the stress can be obtained from the first order derivative of total energy with respect to the strain, resulting in Eqs. (28) and (29),

$$\Omega_0\sigma_{ij}=\left.\frac{\partial\phi}{\partial\eta_{ij}}\right|_{\eta=0,\xi=0}=\frac{1}{2}\sum_{\alpha\neq\beta}\left.\frac{\partial V^{\alpha\beta}}{\partial\eta_{ij}}\right|_{\eta=0,\xi=0} \tag{28}$$

$$\frac{\partial V^{\alpha\beta}}{\partial\eta_{ij}}=\frac{\partial V^{\alpha\beta}}{\partial r^{\alpha\beta}}\frac{\partial r^{\alpha\beta}}{\partial\eta_{ij}}+\frac{\partial V^{\alpha\beta}}{\partial\zeta^{\alpha\beta}}\left[\frac{\partial\zeta^{\alpha\beta}}{\partial r^{\alpha\beta}}\frac{\partial r^{\alpha\beta}}{\partial\eta_{ij}}+\sum_{\gamma\neq\alpha,\beta}\frac{\partial\zeta^{\alpha\beta}}{\partial r^{\alpha\gamma}}\frac{\partial r^{\alpha\gamma}}{\partial\eta_{ij}}+\sum_{\gamma\neq\alpha,\beta}\frac{\partial\zeta^{\alpha\beta}}{\partial\cos\theta^{\alpha\beta\gamma}}\frac{\partial\cos\theta^{\alpha\beta\gamma}}{\partial\eta_{ij}}\right]. \tag{29}$$

$(\partial r^{\alpha\beta}/\partial\eta_{ij})$ can be derived by using Eq.(6) as shown in Eq.(30), where $(r_0^{\alpha\beta})_i$ means the i-th component of $\boldsymbol{r}_0^{\alpha\beta}$,

$$\frac{\partial r^{\alpha\beta}}{\partial\eta_{ij}}=\frac{1}{2r^{\alpha\beta}}\frac{\partial s^{\alpha\beta}}{\partial\eta_{ij}}=\frac{(r_0^{\alpha\beta})_i(r_0^{\alpha\beta})_j}{r^{\alpha\beta}}. \tag{30}$$

The elastic constants can be obtained using the same procedures. For example, the local elastic constants C^0_{ijkl} of Eq.(10) can be derived by the second order derivative of total energy with the strain, as shown in Eqs.(31) and (32),

$$C^0_{ijkl}=\frac{1}{\Omega_0}\left.\frac{\partial^2\phi}{\partial\eta_{ij}\partial\eta_{kl}}\right|_{\eta=0,\xi=0}=\frac{1}{\Omega_0}\frac{1}{2}\sum_{\alpha\neq\beta}\left.\frac{\partial^2 V^{\alpha\beta}}{\partial\eta_{ij}\partial\eta_{kl}}\right|_{\eta=0,\xi=0} \tag{31}$$

$$\frac{\partial^2 V^{\alpha\beta}}{\partial\eta_{ij}\partial\eta_{kl}}=\frac{\partial^2 V^{\alpha\beta}}{\partial r^{\alpha\beta 2}}\frac{\partial r^{\alpha\beta}}{\partial\eta_{ij}}\frac{\partial r^{\alpha\beta}}{\partial\eta_{kl}}+\frac{\partial V^{\alpha\beta}}{\partial r^{\alpha\beta}}\frac{\partial^2 r^{\alpha\beta}}{\partial\eta_{ij}\partial\eta_{kl}}+\frac{\partial^2 V^{\alpha\beta}}{\partial r^{\alpha\beta}\partial\zeta^{\alpha\beta}}\left[\frac{\partial\zeta^{\alpha\beta}}{\partial r^{\alpha\beta}}\frac{\partial r^{\alpha\beta}}{\partial\eta_{kl}}+\sum_{\gamma\neq\alpha,\beta}\frac{\partial\zeta^{\alpha\beta}}{\partial r_{ac}}\frac{\partial r_{ac}}{\partial\eta_{kl}}+\sum_{\gamma\neq\alpha,\beta}\frac{\partial\zeta^{\alpha\beta}}{\partial\cos\theta^{\alpha\beta\gamma}}\frac{\partial\cos\theta^{\alpha\beta\gamma}}{\partial\eta_{kl}}\right]\frac{\partial r^{\alpha\beta}}{\partial\eta_{ij}}+\cdots\cdots \tag{32}$$

Only the derivative of the first term of the right-hand side of Eq.(29) is shown here and the detailed formulation is shown in Appendix.

3. Application to Crystalline Silicon

The elastic constants of crystalline silicon are investigated using Martin's method. Since Martin's method is defined for static structures, an increase in error is expected as the temperature is increased, especially in the range of anharmonic vibration. In order to evaluate the effect of thermal fluctuation, both low and high temperature calculations are conducted.

3.1 Analysis conditions

The analysis conditions of crystalline silicon are shown in Table 1. For low temperature analysis, $T=$ 300 K is selected since it is low enough in comparison to the Debye temperature (640 K). For high temperature, $T=1\,477$ K, which amounts to about 90% of the melting temperature of the Tersoff potential, is selected. The number of atom is 216. Since the system is homogeneous, that size is enough large to obtain the elastic constants.

For the accurate expression of high temperature properties, we modified the cutoff function shown in Eq.(23). The second derivative of Tersoff's cutoff function with respect to distance r is shown as the dotted line in Fig. 4. It is found that the function is discontinuous. Such a discontinuous function causes the nonphysical discontinuity of energy at high temperatures, where the second nearest atoms frequently invade the cutoff region owing to the large fluctuation.

The damping cutoff function 'tanh' is newly introduced as Eq.(33) so that these discontinuities can be improved. In addition, for the most effective incorporation of the effect of nearest neighbor atoms, the cutoff distance R is changed from 2.85 Å to 3.0 Å. The other cutoff parameter D is not optimized. The second order derivative of the modified cutoff function is shown as the solid line in Fig. 4. For comparison, R is set at 2.85. With the disappearance of the discontinuity, the function becomes continuous.

Table 1 Analysis condition of crystalline silicon

Potential	modified Tersoff
Crystal orientation	x[100], y[010], z[001]
Difference equation	Verlet method Δt=5 fs
Temperature	T=300 K, 1477 K
Number of atoms	N= 6 × 6 × 6=216
Ensemble	Micro canonical (zero stress)

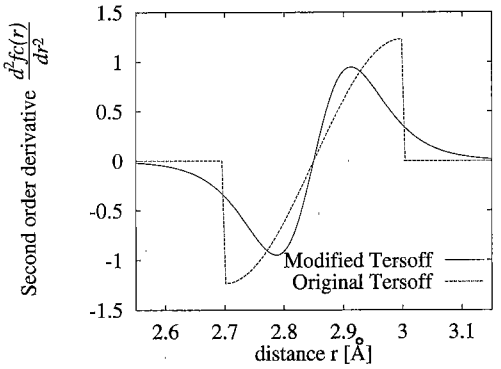

Fig. 4 Second order derivative of original and modified cutoff function f_c

$$f_c(r)=\frac{1}{2}-\frac{1}{2}\tanh\left[\frac{\pi}{2}(r-R)/D\right] \tag{33}$$

As an example of modification, the temperature dependences of C_{11} and C_{12} after and before modification are shown in Figs. 5 and 6, respectively. Experimental results are also shown for comparison.

As for the model before modification, the elastic constants increase unphysically at high temperatures in contrast to the experimental tendency. However, these tendencies have been improved by our modification of the potential. That is, the anharmonic effects can be expressed accurately. While the values of the quantities deviate about 15% from the experimental values, they are the intrinsic properties of the Tersoff potential. According to Tersoff, further fitting is impossible while maintaining the other physical properties such as surface energy[7].

Here we used the fluctuation formula, explained later, for the calculation of elastic constants in order to obtain the accurate values at high temperature.

3.2 Results

Since two overlapped fcc lattices are included in the crystalline silicon, only the relative displacement between two sublattices needs to be taken into account. This makes the problem very simple. Thus, the D_{ijk} tensor of Eq.(11) and the E_{ij} tensor of Eq.(12) can be written as

$$D_{ij}(i=1-3, j=1-6)=\begin{pmatrix} 0 & 0 & 0 & d & 0 & 0 \\ 0 & 0 & 0 & 0 & d & 0 \\ 0 & 0 & 0 & 0 & 0 & d \end{pmatrix}, \tag{34}$$

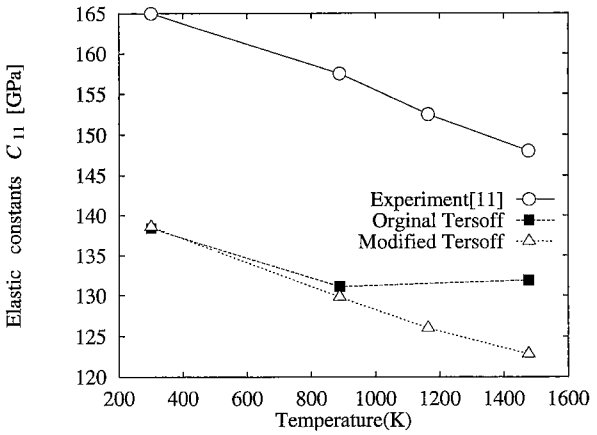

Fig. 5 The dependence of C_{11} on the temperature

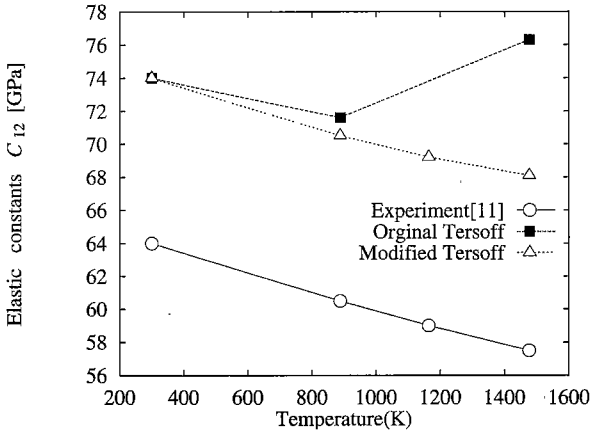

Fig. 6 The dependence of C_{12} on the temperature

and

$$E_{ij}=\begin{pmatrix} e & 0 & 0 \\ 0 & e & 0 \\ 0 & 0 & e \end{pmatrix}. \tag{35}$$

For the notation of D_{ijk}, Voight notation is used[8] in Eq.(34). The relaxation elastic constants can be calculated using the following equation:

$$C_{44}^*=C_{55}^*=C_{66}^*=-\overline{d^2/e}, \tag{36}$$

where 10 000 steps averaging is performed. For example, we obtained $d=5.2\times10^2$ [GPa/nm] and $e=5.7\times10^3$ [GPa/nm^2] at 300 K. Elastic constants at 300 K and 1 477 K are shown in Tables 2 and 3, respectively.

Due to the effect of internal displacement (i.e., relaxation elastic constants), C_{44} decreases. This result coincides with the fact that internal displacement appears and contributes to the elastic properties if the shear stress is applied to the crystalline silicon with [100] - [010] orientation[9].

4. Discussion

The validity and efficacy of the elastic constants are evaluated by comparison with the results of statistical thermodynamics method (Fluctuation Formula)

Table 2 Elastic constants using the Martin's method (300 K)

	Relax.	Born	Total[GPa]
C_{11}	0.0	139.1	139.1
C_{12}	0.0	74.4	74.4
C_{44}	-47.6	114.3	66.7

Table 3 Elastic constants using the Martin's method (1 477 K)

	Relax.	Born	Total[GPa]
C_{11}	0.0	127.0	127.0
C_{12}	0.0	70.3	70.3
C_{44}	-43.4	100.3	56.9

proposed by Ray. In addition, through the comparison of two methods, the physical meaning of the fluctuation formula is clarified, which has not been previously achieved.

4.1 The verification of the values of elastic constants

For verification of Martin's method, the results are compared with those obtained by using the fluctuation formula in the micro canonical ensemble proposed by Ray. Since molecular dynamics realizes the statistical ensemble, it is clear that accurate values can be obtained by using the concept of statistical phase space.

According to Ray, the elastic constants can be represented by Eq.(37). The first term of the right-hand side is referred as the *fluctuation* term. The second term is the second order derivative of Hamiltonian $\hat{H}$ with respect to the strain,

$$V_0 h_{0ip}^{-1} h_{0jq}^{-1} h_{0kr}^{-1} h_{0ls}^{-1} C_{pqrs} = -4\delta(M_{ij}M_{kl})/k_B T + 4\left\langle \frac{\partial^2 \hat{H}}{\partial G_{ij}\partial G_{kl}} \right\rangle. \quad (37)$$

Where h_{0ij} and V_0 are the lattice matrix and volume in the standard state (stress-free), respectively. h_{ij} and V are those of the deformed (present) state and $V=\det(\boldsymbol{h})$. $G_{ij}=h_{ik}h_{kj}$ and δ means fluctuation ($\delta(AB)=\langle AB\rangle-\langle A\rangle\langle B\rangle$, $\langle\ldots\rangle$ means ensemble average). $M_{ij}=\partial\hat{H}/\partial G_{ij}$ and T is temperature. The partial derivatives of potential with $\boldsymbol{G}$ can be obtained by using Eq.(3). $\langle\ldots\rangle$ represents ensemble average, and σ_{ij} is Cauchy stress.

Substituting the Hamiltonian of Eq.(38) into the second term of Eq.(40), Eq.(39) is obtained, where m_a is the mass of atom a, $\boldsymbol{v}_a$ is the velocity of atom a, and N is total number of atoms:

$$\hat{H}=\sum_a^N \frac{1}{2} m_a \boldsymbol{v}_a{}^2 + \phi, \quad (38)$$

Table 4 Elastic constants using the fluctuation formula (300 K) [GPa]

	Fluct.	Kin.	Born	Total	Exp.[11]
C_{11}	-1.1	0.8	139.1	138.8	(167.4)
C_{12}	-0.2	0.0	74.4	74.2	(65.2)
C_{44}	-47.4±13.8	0.4	114.3	67.3±13.8	(79.6)

Table 5 Elastic constants using the fluctuation formula (1 477 K) [GPa]

	Fluct.	Kin.	Born	Total	Exp.[11]
C_{11}	-8.0	3.8	127.0	122.8	(148.0)
C_{12}	-2.2	0.0	70.3	68.1	(57.5)
C_{44}	-43.1±1.0	2.0	100.3	59.2±1.0	(70.0)

$$\left\langle \frac{\partial^2 \hat{H}}{\partial G_{ij}\partial G_{kn}} \right\rangle = \frac{1}{2} N k_B T (G_{in}^{-1}G_{jk}^{-1} + G_{ik}^{-1}G_{jn}^{-1}) + \left\langle \frac{\partial^2 \phi}{\partial G_{ij}\partial G_{kn}} \right\rangle. \quad (39)$$

The first term of right-hand side of Eq.(39) is referred to as the kinetic term, which is the derivative of kinetic energy with strain. The second term is referred to as the Born term, which is the derivative of potential energy with strain. The form of the Born term is the same as the local elastic constants of Martin's method.

In the case of zero stress, the definition can be written in simple form as shown by Eq.(40),

$$C_{ijkl} = -\frac{V_0}{k_B T}\delta(\sigma_{ij}\sigma_{kl}) + \frac{2Nk_B T}{V_0}(\delta_{il}\delta_{jk}+\delta_{ik}\delta_{jl}) + \frac{1}{V_0}\left\langle \frac{\partial^2 \Phi}{\partial \eta_{ij}\partial \eta_{kl}} \right\rangle. \quad (40)$$

Elastic constants at 300 K and 1 477 K are shown in Tables 4 and 5, respectively. The experimental values are also shown for comparison[10]. As explained in the previous section, an intrinsic error appears between the experiment and the Tersoff potential.

At 300 K, since the deviation of Martin's method is less than 1%, the validity of Martin's method at low temperature is proven. In addition, it is found that the relaxation elastic constant C_{44} closely correlate with the fluctuation term. Ray speculated that the effect of internal displacement was included in the fluctuation term. Our results have proved the validity of his idea quantitatively. Inversely, the fluctuation formula can estimate the effect of internal displacement without considering its physical meaning.

At 1 477 K, though the deviation increases as compared with that of 300 K and reaches about 5%, closely similar values were still obtained.

The deviations of C_{11} and C_{12} are induced (originated) mostly by the fluctuation term. That is thought to be due to the effect of thermal fluctuation. Thus, although Martin's method cannot deal with the

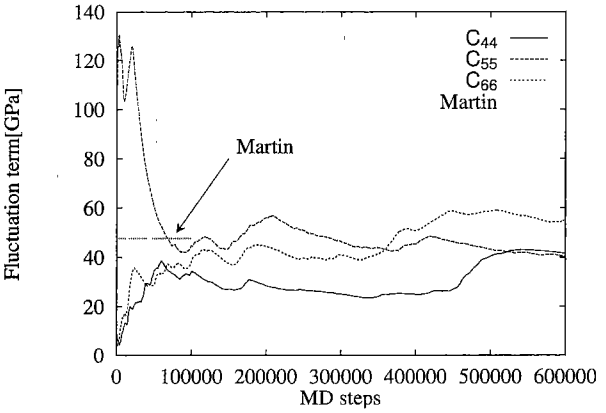

Fig. 7 The convergence curve of the fluctuation term (300 K)

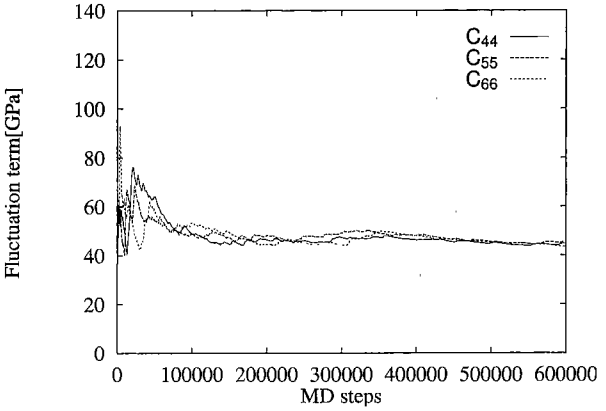

Fig. 8 The convergence curve of the fluctuation term (1 477 K)

thermal fluctuation, the fluctuation formula can predict both internal displacement and thermal fluctuation effect indirectly.

4.2 The evaluation of convergence

In order to show the efficacy of Martin's method, the convergence curves of the fluctuation term of C_{44}, C_{55}, and C_{66} are shown in Fig. 7. The convergence is very slow and much scattering remains after several hundred thousands averaging steps. Therefore, 600 000 steps and three-component averaging are necessary in order to reduce the measurement error. The ± scatterings shown in Table 4 are the standard deviations of three components averaged by 600 000 steps. On the other hand, the convergence curve of the relaxation elastic constants is also shown in Fig. 7. The curve converges through several thousand steps and appears straight due to small variation. Thus, the convergence is significantly fast as compared with that of the fluctuation formula. Since the accurate values can be obtained effectively, it is found that Martin's method is greatly effective for the calculation of elastic constants at low temperature.

Following the same procedure, the convergence curves of the fluctuation term at 1 477 K are shown in Fig. 8. The curves arrived at using Martin's method becomes straight line as well at 300 K, similar to that shown in Fig. 7. It is found that the convergence is improved as compared with that of low temperature. Since the fluctuation is relatively small at low temperatures, the second-order moment with respect to stress fluctuation $\delta(M_{ij}M_{kn})$ becomes difficult to obtain[11]. At high temperatures, since the accuracy of Martin's method decreases and the convergence of the fluctuation formula increases, the statistical thermodynamics method shows a relative increase in efficacy.

5. Conclusions

Martin's method, which is used to obtain the internal displacement of atomic systems and elastic constants, is applied to the Tersoff potential. The elastic constants of crystalline silicon were investigated at both low and high temperatures. The results were verified using the statistical thermodynamic method, i.e., the 'Fluctuation formula'.

(1) Martin's method is very effective at low temperatures, since it provides accurate values and good convergence. At high temperatures, while the thermal fluctuation causes an error of several %, it is nonetheless an effective method.

(2) It is clarified that the fluctuation term of the fluctuation formula includes the effects of internal displacement and thermal fluctuation.

(3) Since the convergence of fluctuation formula increases as the temperature is increased, it is effective at high temperature.

In this paper, we applied Martin's method to crystalline silicon, which includes only two sublattices. However, the significant advantage of Martin's method is its applicability to arbitrary crystal structures. We will further develop our research in this area by focusing next on thin silicon films.

Appendix

Detailed formation of the second-order derivative of $V^{\alpha\beta}$ with the strain is shown in Eq.(41). Other derivative forms are available at our web site[12].

$$\frac{\partial^2 V^{\alpha\beta}}{\partial\eta_{ij}\partial\eta_{kl}}=\frac{\partial^2 V^{\alpha\beta}}{\partial r^{\alpha\beta 2}}\frac{\partial r^{\alpha\beta}}{\partial\eta_{ij}}\frac{\partial r^{\alpha\beta}}{\partial\eta_{kl}}+\frac{\partial V^{\alpha\beta}}{\partial r^{\alpha\beta}}\frac{\partial^2 r^{\alpha\beta}}{\partial\eta_{ij}\partial\eta_{kl}}$$
$$+\frac{\partial^2 V^{\alpha\beta}}{\partial r^{\alpha\beta}\partial\zeta^{\alpha\beta}}\left[\frac{\partial\zeta^{\alpha\beta}}{\partial r^{\alpha\beta}}\frac{\partial r^{\alpha\beta}}{\partial\eta_{kl}}+\sum_{\gamma\neq\alpha,\beta}\frac{\partial\zeta^{\alpha\beta}}{\partial r^{\alpha\gamma}}\frac{\partial r^{\alpha\gamma}}{\partial\eta_{kl}}\right.$$
$$\left.+\sum_{\gamma\neq\alpha,\beta}\frac{\partial\zeta^{\alpha\beta}}{\partial\cos\theta^{\alpha\beta\gamma}}\frac{\partial\cos\theta^{\alpha\beta\gamma}}{\partial\eta_{kl}}\right]\frac{\partial r^{\alpha\beta}}{\partial\eta_{ij}}$$
$$+\frac{\partial^2 V^{\alpha\beta}}{\partial\zeta^{\alpha\beta}\partial r^{\alpha\beta}}\left[\frac{\partial\zeta^{\alpha\beta}}{\partial r^{\alpha\beta}}\frac{\partial r^{\alpha\beta}}{\partial\eta_{ij}}+\sum_{\gamma\neq\alpha,\beta}\frac{\partial\zeta^{\alpha\beta}}{\partial r^{\alpha\gamma}}\frac{\partial r^{\alpha\gamma}}{\partial\eta_{ij}}\right.$$
$$\left.+\sum_{\gamma\neq\alpha,\beta}\frac{\partial\zeta^{\alpha\beta}}{\partial\cos\theta^{\alpha\beta\gamma}}\frac{\partial\cos\theta^{\alpha\beta\gamma}}{\partial\eta_{ij}}\right]\frac{\partial r^{\alpha\beta}}{\partial\eta_{kl}}$$
$$+\frac{\partial^2 V^{\alpha\beta}}{\partial\zeta^{\alpha\beta 2}}\left[\frac{\partial\zeta^{\alpha\beta}}{\partial r^{\alpha\beta}}\frac{\partial r^{\alpha\beta}}{\partial\eta_{kl}}+\sum_{\gamma\neq\alpha,\beta}\frac{\partial\zeta^{\alpha\beta}}{\partial r^{\alpha\gamma}}\frac{\partial r^{\alpha\gamma}}{\partial\eta_{kl}}\right.$$

$$+\sum_{\gamma\neq\alpha,\beta}\frac{\partial\zeta^{\alpha\beta}}{\partial\cos\theta^{\alpha\beta\gamma}}\frac{\partial\cos\theta^{\alpha\beta\gamma}}{\partial\eta_{kl}}\Bigg]$$
$$\times\Bigg[\frac{\partial\zeta^{\alpha\beta}}{\partial r^{\alpha\beta}}\frac{\partial r^{\alpha\beta}}{\partial\eta_{ij}}+\sum_{\gamma\neq\alpha,\beta}\frac{\partial\zeta^{\alpha\beta}}{\partial r^{\alpha\gamma}}\frac{\partial r^{\alpha\gamma}}{\partial\eta_{ij}}$$
$$+\sum_{\gamma\neq\alpha,\beta}\frac{\partial\zeta^{\alpha\beta}}{\partial\cos\theta^{\alpha\beta\gamma}}\frac{\partial\cos\theta^{\alpha\beta\gamma}}{\partial\eta_{ij}}\Bigg]$$
$$+\frac{\partial V^{\alpha\beta}}{\partial\zeta^{\alpha\beta}}\Bigg[\frac{\partial^2\zeta^{\alpha\beta}}{\partial r^{\alpha\beta 2}}\frac{\partial r^{\alpha\beta}}{\partial\eta_{ij}}\frac{\partial r^{\alpha\beta}}{\partial\eta_{kl}}+\frac{\partial\zeta^{\alpha\beta}}{\partial r^{\alpha\beta}}\frac{\partial^2 r^{\alpha\beta}}{\partial\eta_{ij}\partial\eta_{kl}}$$
$$+\sum_{\gamma\neq\alpha,\beta}\frac{\partial^2\zeta^{\alpha\beta}}{\partial r^{\alpha\beta}\partial r^{\alpha\gamma}}\frac{\partial r^{\alpha\beta}}{\partial\eta_{ij}}\frac{\partial r^{\alpha\gamma}}{\partial\eta_{kl}}$$
$$+\sum_{\gamma\neq\alpha,\beta}\frac{\partial^2\zeta^{\alpha\beta}}{\partial r^{\alpha\beta}\partial\cos\theta^{\alpha\beta\gamma}}\frac{\partial r^{\alpha\beta}}{\partial\eta_{ij}}\frac{\partial\cos\theta^{\alpha\beta\gamma}}{\partial\eta_{kl}}\Bigg]$$
$$+\frac{\partial V^{\alpha\beta}}{\partial\zeta^{\alpha\beta}}\sum_{\gamma\neq\alpha,\beta}\Bigg(\frac{\partial^2\zeta^{\alpha\beta}}{\partial r^{\alpha\gamma}\partial r^{\alpha\beta}}\frac{\partial r^{\alpha\gamma}}{\partial\eta_{ij}}\frac{\partial r^{\alpha\beta}}{\partial\eta_{kl}}$$
$$+\frac{\partial^2\zeta^{\alpha\beta}}{\partial r^{\alpha\gamma 2}}\frac{\partial r^{\alpha\gamma}}{\partial\eta_{ij}}\frac{\partial r^{\alpha\gamma}}{\partial\eta_{kl}}+\frac{\partial\zeta^{\alpha\beta}}{\partial r^{\alpha\gamma}}\frac{\partial^2 r^{\alpha\gamma}}{\partial\eta_{ij}\partial\eta_{kl}}$$
$$+\frac{\partial^2\zeta^{\alpha\beta}}{\partial r^{\alpha\gamma}\partial\cos\theta^{\alpha\beta\gamma}}\frac{\partial r^{\alpha\gamma}}{\partial\eta_{ij}}\frac{\partial\cos\theta^{\alpha\beta\gamma}}{\partial\eta_{kl}}\Bigg)$$
$$+\frac{\partial V^{\alpha\beta}}{\partial\zeta^{\alpha\beta}}\sum_{\gamma\neq\alpha,\beta}\Bigg(\frac{\partial^2\zeta^{\alpha\beta}}{\partial\cos\theta^{\alpha\beta\gamma}\partial r^{\alpha\beta}}\frac{\partial r^{\alpha\beta}}{\partial\eta_{kl}}$$
$$+\frac{\partial^2\zeta^{\alpha\beta}}{\partial\cos\theta^{\alpha\beta\gamma}\partial r^{\alpha\gamma}}\frac{\partial r^{\alpha\gamma}}{\partial\eta_{kl}}+\frac{\partial^2\zeta^{\alpha\beta}}{\partial\cos\theta^{\alpha\beta\gamma 2}}\frac{\partial\cos\theta^{\alpha\beta\gamma}}{\partial\eta_{kl}}\Bigg)$$
$$\times\frac{\partial\cos\theta^{\alpha\beta\gamma}}{\partial\eta_{ij}}+\frac{\partial V^{\alpha\beta}}{\partial\zeta^{\alpha\beta}}\sum_{\gamma\neq\alpha,\beta}\frac{\partial\zeta^{\alpha\beta}}{\partial\cos\theta^{\alpha\beta\gamma}}\Bigg(\frac{\partial^2\cos\theta^{\alpha\beta\gamma}}{\partial\eta_{ij}\partial\eta_{kl}}\Bigg) \tag{41}$$

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