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Parallel TBMD and Hybrid MD/TBMD Simulations of Nanostructured Materials

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We report results of order-*N* parallel tight-binding simulations and hybrid classical/tight-binding simulations on grain-boundary structures and their stability in nanostructured materials. In the former simulations, we employ the Fermi-operator expansion method (FOEM) for calculations of band-structure energy and Hellman-Feyman forces. The latter method, based on the idea similar to the ONIOM algorithm, is newly developed and implemented on our PC-based parallel system. We apply these methods to analyses on the structural properties and the thermal stability of nanoscale grain boundaries of Si and SiC. The results show that an amorphous-like structure in the (001)Σ5 twist grain boundary of Si is stable, whereas same grain-boundary structure of SiC is rather regular even at high temperature. The hybrid simulation also shows an incipiency toward amorphization of the Si grain boundary.

Keywords: grain boundary, silicon, silicon carbide, tight-binding method, hybrid classical/quantum algorithm

1. INTRODUCTION

Continuous progress in semiconductor technology has relied mainly on the reduction of feature size in electronic devices. Nanocrystalline semiconductors are promising because their structural unit can be reduced to nanoscale keeping their carrier mobility as high as bulk crystal. Such an electronic property is strongly dependent on the grain-boundary (GB) characteristics. So far, only a few investigations on the atomic/electronic level properties of Si grain boundaries have been made. In Ref. [1]. the authors performed molecular-dynamics (MD) simulations on a high-energy grain boundary at high temperature (1000K). They claimed that an amorphous-like structure can be formed and may be stable in the nanoscale GB, while most of the experimental observations show that such a disordered phase of GB exists only in highly impurity-segregated GBs.

In this paper, we investigate structural properties and thermal stability of a twist grain boundary of Si and SiC via large-scale classical and quantum molecular-dynamics simulations based on either a linear-scaling tight-binding algorithm or a hybrid classical/quantum algorithm.

2. NUMERICAL METHODS

We employ a linear-scaling algorithm called the Fermi-operator expansion method (FOEM) [2] for efficient calculations of the band-structure energy and Hellman-Feynman forces in the framework of tight-binding (TB) MD method. The time reversible integrator algorithm for *NPT* ensemble [3] has been used for MD simulations. The TB parameters for Si and for SiC are taken from Ref. [4] and Ref [5], respectively.

Also, we have recently developed a hybrid classical MD/TB-MD method [6], similar to what is called ONIOM method [7], i.e. a quantum region is embedded in the (classical) total system via the "handshake atoms", illustrated in Fig. 1. In the hybrid method, the total Hamiltonian of the hybrid system is defined as:

$$H = H_{\mathrm{MD}}^{\mathrm{system}}(\vec{R}_{\mathrm{all}}, \dot{\vec{R}}_{\mathrm{all}}) + \sum_{\mathrm{TB\ regions}} \left[E_{\mathrm{TB}}^{\mathrm{cluster}}(\{\vec{r}_{\mathrm{TB}}\}, \{\vec{r}_{\mathrm{TB/MD}}^{\mathrm{HS}}\}) - E_{\mathrm{CL}}^{\mathrm{cluster}}(\{\vec{r}_{\mathrm{TB}}\}, \{\vec{r}_{\mathrm{TB/MD}}^{\mathrm{HS}}\}) \right] \quad (1)$$

where the first term represents the Hamiltonian for the whole system modeled by the sum of kinetic energies of the nuclei and a classical interatomic potential [8,9], and the second and third terms of Eq. (1) are the potential energy for "TB cluster", modeled by a semiempirical TB Hamiltonian [4,5], and that for "CL cluster" described by the classical interatomic-potential model [8,9], respectively.

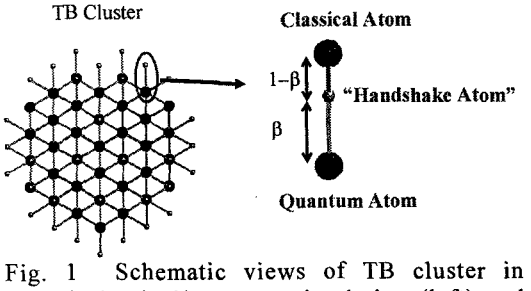

Fig. 1 Schematic views of TB cluster in hybrid classical/quantum simulation (left) and of "handshake atom" between quantum atom and classical atom (right).

In the second and third terms in Eq. (1), the abbreviation "HS" on the atomic position ($\vec{r}^{HS}$) stands for the "Handshake atoms", which bridge between the atoms in the outermost shell of the TB cluster and their nearest neighbor atoms in the original total system (Fig. 1). The positions of the HS atoms are set to be in-between "QM" atom and "Classical" atom in Fig. 1. We have adjusted the relative position (β) of the HS hydrogen atom along the QM-Classical atomic bond by minimizing the discrepancy of atomic forces on the QM atoms bonded with the HS atoms in the case of perfect crystal.

The hybrid method is useful especially when more accurate calculation of interatomic forces on atoms near GB than other methods is required, such as in the case that a reconstruction with large displacement of atoms at the GB plays an essential role on the stability of the GB.

These algorithms have been implemented on parallel PC clusters. Also, the present hybrid algorithm is very suitable for a GRID computation because the data to be exchanged between nodes dedicated to the TB calculations and nodes for the classical calculations are very small. Thus a nearly ideal parallel performance for the present analyses can be achieved on geographically distributed parallel machines [10].

3. RESULTS

3.1 Thermal Stability --- $O(N)$ TBMD Analysis

We first run classical MD codes [8,9] to obtain a well-thermalized structure of the twist GB of Si at 1000K, depicted in Fig. 2(a), and that of SiC at 4000K, in Fig. 4(a). Starting from these configurations, we turn on the $O(N)$ TBMD simulation in order to investigate the stability of the disordered GB structure obtained by the classical MD simulations.

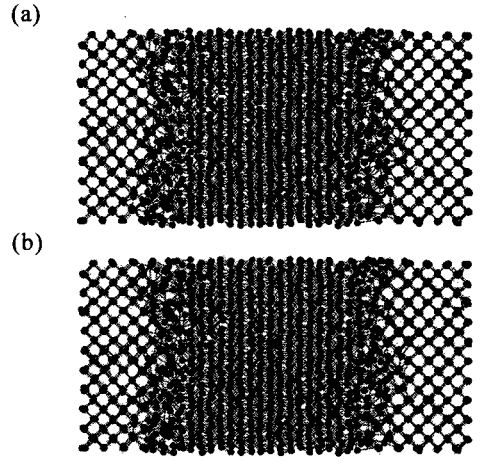

Fig. 2 Snapshots of system with two (001)Σ5 GBs of Si in $O(N)$ TBMD simulation: (a) Initial configuration and (b) configuration after 100ps run at T=1000K.

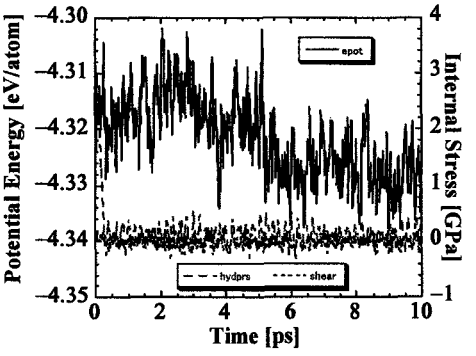

Fig.3 Time evolution of potential energy and internal stresses of the system, illustrated in Fig. 2, in $O(N)$ TBMD simulation.

Figures 2(a) and 2(b) show snapshots of atomic positions before and after the TBMD simulation of the Si GB, respectively. The disordered structure formed near the Σ5 twist GB, prepared by a classical MD run, remains even after 100 ps run with the TB method. Figure 3 shows time evolution of potential energy and internal stresses calculated in the TBMD simulations. It shows that only small relaxation occurs due to a mismatch between the relaxed shape of the MD box for the classical model and that for the TB model.

We thus find the disordered structure formed in the twist GB of Si is, at least, locally stable at high temperature, independent on the interatomic potential model in the MD simulation, confirming the previous analysis based on a classical MD simulation.

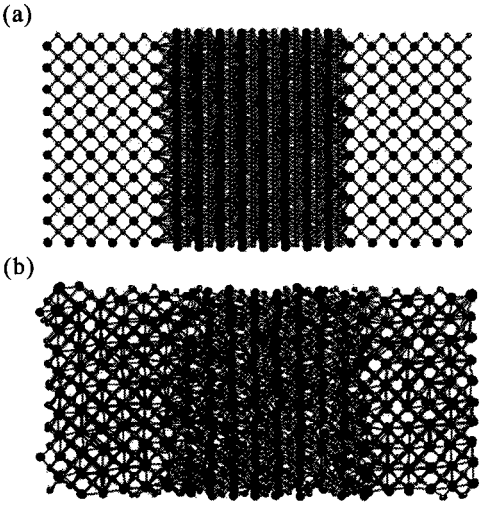

Fig.4 Snapshots of system with two (001)Σ5 GBs of SiC in $O(N)$ TBMD simulation: (a) Initial configuration and (b) configuration after 100ps run at T=1800K.

On the other hand, the (001)Σ5 twist GB of SiC with non-polar atomic-layer alignment shows quite deferent behaviors, despite the geometrical constraint (Σ5) is the same as in the previous case for Si GB. Figures 4(a) and 4(b) show snapshots of the GB of SiC before and after heating to 1800K. Although large displacement of atoms is shown in the heated system (Fig. 4(b)), the atomic-layer alignment is kept regular even in the vicinity of the GB. A visual analysis of atomic trajectories in the TBMD simulation indicates that the atomic bonds between Si and C atoms at the GB are more rigid than those between Si-Si in the previous case for Si GB. Such a strong covalent bonding may be responsible for stabilizing the local atomic structure in the high-energy GB at the high temperature.

3.2 Reconstruction at T=0K --- Hybrid MD/TBMD Analysis

In the previous section, we discussed thermal stability of a high-angle twist GB of Si and SiC using $O(N)$ parallel TBMD method. However, simulating local rearrangement of atoms near the high-energy GB may be quit sensitive to accuracy of forces due to the covalent bonds. We therefore examine the stability of the Si GB using hybrid MD/TB-MD simulation in order to validate and confirm the results obtained in the $O(N)$ TBMD simulations.

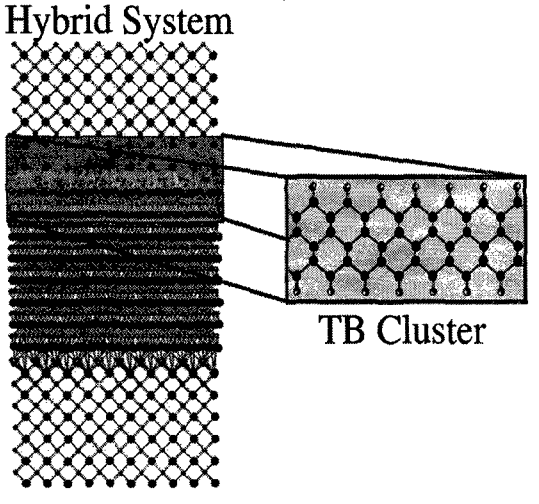

Fig. 5 Schematic representation of hybrid classical/TB-MD scheme for Si system with two (001)Σ5 twist GBs.

Figure 5 illustrates a schematic view of the hybrid system. The atomic forces near one of the twin GB are described by the TB method while others are modeled by a classical interatomic potential [8]. The Si atoms on the boundary between TB region and classical regions are handshaked by H atoms, as depicted in the right-hand side of Fig. 5 and in Fig. 6(a).

The hybrid system is relaxed by the steepest descent method (zero temperature MD). Figure 6 depicts atomic configuration of the TB cluster before and after relaxation. It is shown in Fig. 6(b) that atomic displacements in the TB cluster after relaxation are quite large indicating an incipiency toward disordering of the GB. It can thus be concluded that the (001)Σ5 twist GB of Si is unstable even at zero temperature, and therefore it has tendency to undergo an atomic reconstruction toward a local disordering in the vicinity of the GB.

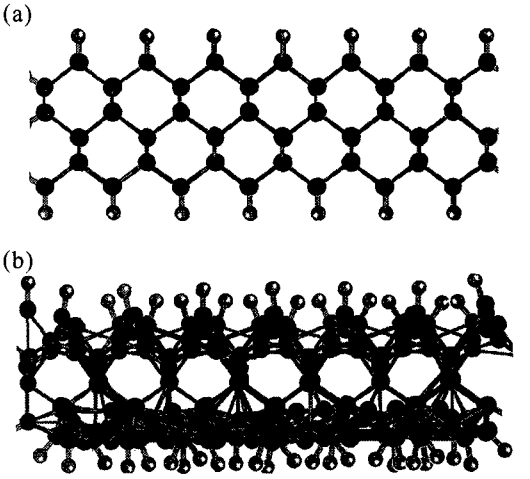

Fig. 6 Atomic configuration of "TB Cluster" near (001)Σ5 GB of Si (a) before and (b) after relaxation by hybrid classical/TB-MD method. Dark-colored and gray-colored balls represent Si atoms and handshaking H atoms, respectively.

4. CONCLUSION

Combining a highly efficient linear-scaling algorithm for electronic structure calculation and a novel algorithm based on a hybrid classical/quantum molecular dynamics method, we have investigated the stability of a high-angle twist grain boundary of nanostructured Si and SiC. While the twist grain boundary of Si undergoes disordering at high temperature (1000K), the twist GB of SiC, with the same Σ value as the Si case, maintains an abrupt interface even at an elevated temperature (1800K). This may be due to the difference between the strengths and characteristics of covalent bonding in these cases, i.e. Si-Si vs. Si-C.

The hybrid MD/TB-MD simulation has been performed to clarify the stability and the local rearrangement of the grain boundary of Si at zero temperature. The result reveals that atomic bonding in the grain boundary is too weak to maintain the abrupt interface structure of the twist boundary, and hence it leads large displacement of atoms near the grain boundary, indicating an incipiency toward the disordering even at the low temperature.

The hybrid simulations for different symmetries of grain boundary at finite temperatures and for study of the effects of impurity atom, such as hydrogen atoms , on the stability of the grain boundaries are in progress.

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The visual analyses for atomic configurations and trajectories in the present study have been performed on our immersive virtual-reality system, consisting of an SGI Onyx300 and a 60inch video projector by BARCO, equipped at the Graduate School of Natural Science and Technology of Okayama University, Japan.

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