STRUCTURAL AND MECHANICAL PROPERTIES OF AMORPHOUS SILICON: *AB-INITIO* AND CLASSICAL MOLECULAR DYNAMICS STUDY

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ABSTRACT

Understanding the surface properties of amorphous silicon (a-Si) is extremely important for effective application of a-Si in its wide usage as a thin film material. Several theoretical works using *ab-initio* molecular dynamics schemes have been performed to investigate this subject. However, due to the limited time scale accessible to the *ab-initio* scheme, the resulting a-Si structure has not been subject to sufficient relaxation. One possible way to resolve this time scale problem is to employ classical molecular dynamics (CMD), because this method can handle the large time scale required to relax the amorphous structure. In this study, a combined method of a CMD calculation with the Tersoff empirical potential and an *ab-initio* calculation based on density functional theory has been performed. The main role of the CMD method is to sufficiently relax the amorphous structure. Subsequently, the results of the CMD calculations are used as starting points for *ab-initio* calculations. As a result, this combination method can provide quantitative evaluation of the surface energy and surface stress of well-relaxed amorphous silicon in addition to its structure. Using this combination method, a surface energy of 1.05±0.14 J/m^2 and a surface stress of 1.5±1.2 N/m were obtained. This calculation also led to a new discovery of the microscopic characteristic of a-Si surface, which was not revealed through the use of an empirical potential. It was shown that there are two types of threefold coordinated atoms at the surface region; one with p^3-like bonding and the other with sp^2-like bonding. In addition, the investigation indicated that the microstructures of these defects were different from those of a threefold coordinated atom observed in the bulk structure.

1 INTRODUCTION

The surface properties of amorphous silicon (a-Si) have attracted much attention in recent years. Particularly, the structural properties of surfaces at an atomistic level are of great interest. Despite a-Si being one of the most fundamental thin film materials, little is known about the microscopic details of a-Si surfaces. Other surface properties of particular interest are mechanical properties, such as surface energy and surface stress, which play a key role in the theoretical prediction of film stresses. However, the present authors note that there is still a lack of experimental data regarding the surface energy and surface stress of a-Si.

At present, the most sophisticated technique available to evaluate these properties is an *ab-initio* approach. This approach has successfully reproduced a (111) 7×7 DAS structure and a (001) 2×1 asymmetric dimer structure confirmed by experimental observation. However, creating an a-Si surface model that provides results comparable to experimental results is still a matter of debate. For example, using an *ab-inito* molecular dynamics approach, Stich et al. [1] directly created the bulk a-Si through the rapid quenching of liquid silicon, followed by a thermal annealing within the range of a few picoseconds. The resulting structure involved a high bond-angle deviation, compared with the experimental value. The origin of this disagreement arises from the insufficient thermal annealing for structural relaxation due to its heavy computational burden. One possible way to resolve this time-scale problem is to employ a CMD approach. A CMD method can realize nano-second simulation, which is sufficient to completely relax the amorphous structure.

The approach taken here is to use a combination method of a CMD calculation and an *ab-initio* calculation. The main role of the CMD method is the full relaxation of a-Si. Subsequently, the results of the CMD calculations are used as starting points for *ab-initio* calculations based on density functional theory (DFT). In the present work, this combination method gives quantitative values of the surface energy and surface stress of well-relaxed a-Si. In addition, the structural analyses reveal the marked difference in surface microstructure between the model obtained from the classical simulations and that obtained from the simulations based on quantum mechanics.

2 METHOD

2.1 *Combination method*

The first step is to prepare well-relaxed amorphous structures by a CMD method. The Tersoff potential [2] was chosen to compute the interatomic forces among silicon atoms. In the next step, DFT calculations are carried out to relax the atomic geometries obtained from CMD simulations. The present calculations are performed using Vienna *ab-initio* simulation package [3] based on pseudopotential and plane-wave techniques. We employed the ultra-soft Vanderbilt pseudopotential. The approximation associated with the exchange-correlation energy was the generalized-gradient approximation (GGA), suggested by Perdew and Wang. In order to find the minimum-energy structure, the system is first allowed to dynamically relax at a finite temperature for several picoseconds and is then cooled down to 0 K. In this scheme, only the Γ-point for BZ integration was used and the plane-wave cut-off was set to 150 eV. After quenching, the structural optimization was performed.

It should be noted that, because the size of the systems that is handled with the *ab-initio* scheme is considerably limited, the spatial-related scattering of these two quantities cannot be neglected. Therefore, in the present work, we performed a total of 15 simulations in order to evaluate these two quantities with a high accuracy.

2.2 *Calculation of surface energy and surface stress*

2.2.1 *Bulk calculation*

CMD calculations start with a cubic cell system containing 64 atoms. Periodic boundary conditions are used in the all three directions. Through the annealing procedure reported in Ref. 4, a well-relaxed a-Si structure with coordination defects less than 5% is obtained. Subsequently, the results of the CMD calculations are used as starting points for DFT calculations. After annealing the system at 1200 K for 1 ps, the resulting geometries are optimized with a plane-wave cutoff energy of 225 eV and (2×2×2) ***k***-grids.

In order to examine the degree of structural relaxation in this bulk model, two structural parameters are measured; the excess energy of amorphous phase relative to crystal phase, Δg_{ac}, and the bond angle deviation, $\Delta\theta$. The amorphous model results in a Δg_{ac} of 0.15±0.02 eV/atom and a $\Delta\theta$ of 10.2±1.0°, which are in good agreement with experimental results (Δg_{ac} = 0.13 eV/atom [5], $\Delta\theta$ = 9.7° [6]). Comparison with the results of Stich et al.'s model [1] of the *ab-initio* molecular dynamics (Δg_{ac} = 0.28 eV/atom, $\Delta\theta$ = 15.5°), makes it apparent that our model has achieved sufficient relaxation.

2.2.2 *Surface calculation*

A large bulk model containing 128 atoms is first prepared by stacking the two identical small bulk models containing 64 atoms each. Following this, two surfaces are produced by removing the periodic boundary condition in one direction. The absence of periodicity leads to an unrelaxed surface state with many undercoordinated atoms. In order to allow these atoms to reconstruct, this surface model is annealed at 1200 K for 2 ns within the framework of a CMD method. The subsequent DFT calculations are performed in the following way. For surface calculations, a supercell system is employed; a slab (2.18 nm) and a vacuum layer (0.68 nm) are periodically repeated toward the *z* direction. The whole system is dynamically annealed at 840 K for 1 ps, and then is optimized by using a plane-wave cutoff energy of 225 eV and (2×2×1) *k*-grids.

3 RESULTS

3.1 *Surface energy and surface stress of amorphous silicon*

The surface energy, γ, and the surface stress, $f=(f_{xx}+f_{yy})/2$, of a-Si are listed in Table 1. These results are averaged over 30 surfaces whose each surface area is equal to 1.21 nm^2 (Each sample contains two surfaces on the top and bottom.). The results of a *s*(001) 2×1 and *p*(001) 2×2 crystal surface calculations are also provided for comparison. The f_{xx} and f_{yy} values for surface stress correspond to the component of the dimer bond and the dimer row direction, respectively.

Table 1: Surface energy γ (J/m^2) and surface stress f (N/m) of a-Si.

	γ (J/m^2)	f_{xx}, f_{yy}(N/m)
a-Si		
CMD-DFT$^{(*)}$	1.05 ± 0.14	1.5 ± 1.2
CMD	1.13 ± 0.09	0.7 ± 1.0
s(001)2×1		
DFT$^{(*)}$	1.40	0.7, -1.1
DFT[7]	-	0.8, -2.1
DFT[8]	-	0.8, -1.2
CMD$^{(*)}$	1.48	0.4, -1.3
p(001)2×2		
DFT$^{(*)}$	1.28	1.2, 0.6
DFT[8]	-	1.3, 0.5

This work(*)

The values presented in Table 1 indicate that the surface energy of a-Si is lower than those of (001) surfaces. No significant difference can be seen between the surface energy of the combination model and the CMD model. It is noted that the surface stress of a-Si is positive and the scatter of surface stress is a factor of one higher than that of the surface energy. The surface stresses of *s*(001) 2×1 and *p*(001) 2×2, obtained from DFT calculations, show good agreement with the other DFT results [7, 8].

3.2 *Surface structure of amorphous silicon*

The physical properties of surface strongly depend on the microscopic features. Therefore, the atomistic details of the surface region (0.5 nm) were analyzed using coordination statistics, $C_{n,}$, ring statistics, R_n. Table 2 provides the coordination and ring statistics.

As shown in Table 2, in the present model, the surface atoms mainly consist of 22.3±3.9% of threefold coordination and 73.5±2.9% of fourfold coordination. The ratio of these coordination defect is very similar to that observed for the (001) 2×1 surface, which reveals 22.8% of threefold

Table 2: Coordination statistics C_n (%) and ring statistics R_n (rings/atom) of a-Si surface.

	C_3	C_4	C_5	R_3	R_4	R_5	R_6	R_7
CMD-DFT surface	22.3	73.5	4.2	0.05	0.08	0.52	1.05	1.12
CMD surface	25.6	70.8	3.5	0.00	0.08	0.54	1.07	1.13
CMD-DFT bulk	0.5	97.0	2.4	0.00	0.02	0.40	0.97	0.96
CMD bulk	0.0	94.4	5.6	0.01	0.04	0.42	1.00	0.99

coordinated and 77.2% of fourfold coordinated atoms. The results also show a remarkable difference in the number of three-membered rings R_3 between the CMD-DFT surface model (0.05±0.04 rings/atom) and the CMD surface model (0.00±0.01 rings/atom), although the number of rings, larger than three-membered, in both models gives similar values. In the bulk model, few three-membered rings (0.00±0.01 rings/atom) were observed. This result would suggest that three-membered ring is one of the predominant structures in a-Si surface.

4 DISCUSSION

4.1 *Coordination defects of the surface*

The present calculations suggest that the threefold coordinated atom is the predominant coordination defect located in the surface region. Thus, further focus is directed to its microstructure. In order to characterize the local structure of an individual threefold coordinated atom, the averaged value of three bond angles around the atom, θ_{ave}, was defined as a new structural parameter. This parameter quantifies the sharpness of the vertical angle formed by the three back bonds. The distribution of θ_{ave} is plotted in Fig. 1.

Interestingly, Fig. 1 shows a distinct difference between the CMD-DFT model and the CMD model. In the CMD-DFT model, two main peaks at approximately 100° and 120° (peak 1 and peak 2) are observed, while in the CMD model only one peak, at approximately 113°, is observed. The threefold coordinated atom associated with peak 1 will be referred to as a P1 type atom, and peak 2 as a P2 type atom. Fig. 2 provides a typical snapshot of the surface model containing both types of atom. The atomic geometries and contour plots of the valence electronic charge density are also presented in Fig. 2.

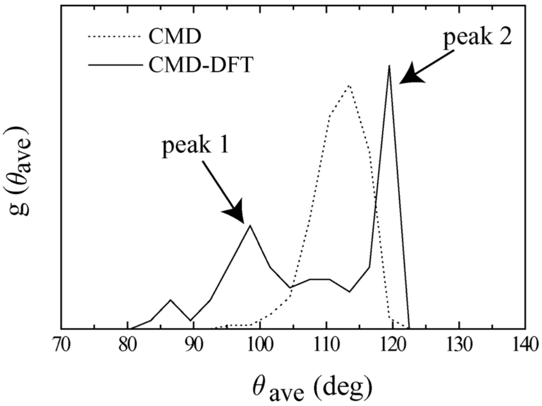

Fig. 1: Distribution function of averaged bond angle defined for threefold coordinated atoms in the surface layer. Solid line, CMD-DFT scheme; dotted line, CMD simulation.

Clearly, the local geometries of these two types of atom are quite different; the P1 type atom has back bonds forming a sharp pyramidal geometry, while the P2 type atom has those lying on a plane. The respective geometries of the P1 and P2 atoms deviate from the sp^3 tetrahedral bond angle (θ_{ave} = 109.5º). From an evaluation of the atomic geometries, it is proposed that the back bonding of the P1 atom is p^3-like bonding and that of the P2 atom is sp^2-like bonding. The difference in these bonding characteristics can be deduced from the electronic structure shown in Fig. 4. The observation indicates that, in the case of P1 atom, more charge is localized on the dangling bond site, as compared with the case of P2 atom. On the other hand, the CMD calculation cannot distinguish between these two types of atom. Brenner [9] pointed out that the Tersoff potential has a disadvantage in the intermediate bonding situation. Specifically, when the threefold coordinated atoms is bonded to the fourfold coordinated atoms, this potential yields the unphysical bond characteristics which is intermediate between sp^2 and sp^3 bonding. The appearance of only one peak would result from this disadvantage. As a result, the use of the combination method provides new findings of the microscopic features of a-Si surface.

4.2 *Comparison of coordination defects between the bulk and the surface*

The well-relaxed bulk model of this study contains 0.5% of threefold coordinated atoms. Here, we compare the microstructure of this defect in the bulk with that in the surface. Fig. 3 presents the detailed atomic geometries of the threefold coordinated atom and the corresponding contour plots of the valence electronic charge density.

In Fig. 3, the atom C presents an atom located at the fourth nearest site from the atom A. The distance between atoms A and C (3.07 Å) is longer than the cutoff distance used to define the bonding (2.85 Å). Correspondingly, less electronic charge is distributed between them. This is evidence that atom A in Fig. 3 is the threefold coordinated defect with one missing neighbor (dangling bond). We evaluated the averaged bond angle θ_{ave} of this threefold coordinated atom. The value obtained was 108°, slightly less than the tetrahedral bond angle. This indicates that the

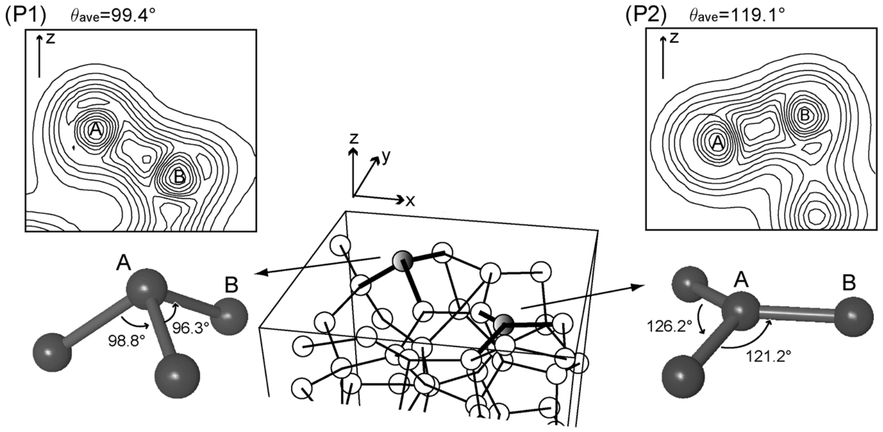

Fig. 2: Detailed diagram of two characteristic threefold-coordinated atoms (P1) with p^3-like bonding and (P2) with sp^2-like bonding. The corresponding contour plots of the valence electronic charge density on a plane, which is perpendicular to the surface and contains both A and B atoms, are also shown.

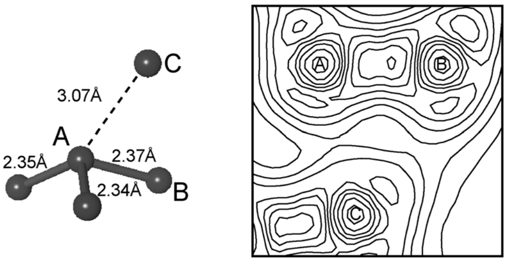

Fig. 3: Local geometry of the threefold coordinated atom in the bulk and corresponding contour plots of the valence electronic charge density on a plane defined by three atoms (A, B, C).

back bonding of the defect tend to be sp^3-like bonding. By comparing the results of the surface defect mentioned above, it is concluded that there exists differences in the structural and electrical properties of threefold coordination defects between bulk and surface of a-Si.

5 CONCLUSION

A combination approach of classical molecular dynamics and *ab-initio* calculation resulted in a surface energy of 1.05±0.14 J/m^2 and a surface stress of 1.5±1.2 N/m. The combination surface model provides new findings of the microscopic features of a-Si surface. It has been shown that there are two types of threefold coordinated atoms at the surface region; one with p^3-like bonding and the other with sp^2-like bonding.

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REFERENCES

[1] Stich, I., Car, R. and Parrinello, M., “Amorphous silicon studied by ab initio molecular dynamics: Preparation, structure, and properties”, Phys. Rev. B 44, 11092-11104 (1991).

[2] Tersoff, J., “Empirical interatomic potential for silicon with improved elastic properties”, Phys. Rev. B 38, 9902-9905 (1988).

[3] Kresse, G., and Hafner, J., “Ab initio molecular dynamics for liquid metals”, Phys. Rev. B 47, 558-561 (1993).

[4] Izumi, S., Hara, S., Kumagai, T., and Sakai, S., “Classification of amorphous-silicon microstructures by structural parameters: Molecular dynamics study”, Comput. Mater. Sci. 39, (in press) (2004).

[5] Fortner, J., and Lannin, J., “Radial distribution functions of amorphous silicon”, Phys. Rev. B 39, 5527-5530 (1989).

[6] Laaziri, K., Kycia, S., Roorda, S., Chicoine, M., Robertson, J. L., Wang, J., and Moss, S. C., “High-energy x-ray diffraction study of pure amorphous silicon”, Phys. Rev. B 60, 13520-13533 (1999).

[7] Payne, M. C., Roberts, N., Needs, R. J., Needels, M., and Joannopoulos, J. D., “Total energy and stress of metal and semiconductor surfaces”, Surf. Sci. 211/212, 1-20 (1989).

[8] Miyamoto, Y., “Comparative study of Si(100) surface stresses with dimerized group-IV adatoms”, Phy. Rev. B 49, 1947-1951 (1994).

[9] Brenner, D. W., “Empirical potential for hydrocarbons for use in simulating the chemical vapor deposition of diamond films”, Phys. Rev. B 42, 9458-9471 (1990).