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Surface energy, stress and structure of well-relaxed amorphous silicon: A combination approach of ab initio and classical molecular dynamics

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Abstract

In this study, a combined method of a classical molecular dynamics calculation with the Tersoff potential and an ab initio calculation based on density functional theory has been performed. 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 method, a surface energy of 1.05 ± 0.14 J/m² and a surface stress of 1.5 ± 1.2 N/m are obtained. This calculation also leads to a new discovery of the microscopic characteristic of a-Si surfaces, which is not revealed through the use of an empirical potential. It is shown that there are two types of threefold coordinated atoms at the surface region; one with p³-like bonding and the other with sp²-like bonding. In addition, the investigation indicates that the microstructures of these defects are different from those of a threefold coordinated atom observed in the bulk structure.

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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 in gaining a better understanding of the growth mechanism during the deposition process of thin films [1]. Despite a-Si being one of the most fundamental thin film materials, little is known about the microscopic details of a-Si surfaces.

Other properties of particular interest are physical properties, such as surface energy and surface

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stress. More recently, Floro et al. [2] have pointed out that these two quantities 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, which is a parameter-free quantum-mechanical calculation. This approach has successfully reproduced a (111) 7×7 dimer-adatom-stacking-fault (DAS) structure [3], a (111) 2×1 π-bonded structure [4] and a (100) 2×1 asymmetric dimer structure [5] confirmed by experimental observation [3,6]. 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 initio molecular dynamics approach, Stich et al. [7] 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 classical molecular dynamics (CMD) approach. As demonstrated in previous works, a CMD method can realize nano-second simulation, which is sufficient to completely relax the amorphous bulk [8,9] and surface [10] 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) [11]. In the present work, this combination method gives quantitative values of the surface energy and surface stress of wellrelaxed a-Si. In addition, the structural analyses reveal the remarkable difference in surface microstructure between the model obtained from the classical simulations and that from the simulations based on quantum mechanics.

2. Computational methods

2.1. Combination method

The first step is to prepare well-relaxed amorphous structures by a CMD method. The Tersoff potential [12] was chosen to compute the interatomic forces among silicon atoms. In general, the Tersoff potential can reproduce the structural and physical properties regarding bulk crystal phase, bulk amorphous phase and the surfaces of both phases [8,13,14].

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 (VASP) [15,16] based on pseudopotential and plane-wave techniques. The ultra-soft Vanderbilt pseudopotential [17] was employed to describe the interaction between ions and electrons. The approximation associated with the exchange-correlation energy was the generalized-gradient approximation (GGA), suggested by Perdew and Wang [18]. For the Brillouin-zone (BZ) integrations, various k-grids of Monkhorst-Pack special points [19] were used together with the Methfessel-Paxton technique [20]. In order to find the minimum-energy structure, the entire system is first allowed to dynamically relax at a finite temperature for several picoseconds and is then cooled down to 0 K. In this dynamical scheme, only the Γ -point for BZ integration was used and the plane-wave cut-off was set to 150 eV. After quenching, we perform the structural optimization using the DFT calculation involving the more kpoints and larger value of cut-off energy than those in the dynamical calculations. These detailed conditions would be mentioned in the next section.

2.2. Calculation of surface energy and surface stress

The surface energy and surface stress are defined in the same manner suggested in Ref. [21]. It should be noted that, because the size of the systems that can be 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.

2.2.1. Bulk calculation

CMD calculations start with a cubic cell system containing 64 atoms. Periodic boundary conditions are used in the all three directions. An amorphous network was generated by direct quenching from liquid silicon. This quenching method produces a highly defective structure with about 15% non-fourfold coordinated atoms (coordination defect) [8]. Thus, by annealing this sample at 1600 K for 10 ns, a well-relaxed structure with coordination defects less than 5% is obtained [9]. Subsequently, the results of the CMD calculations are used as starting points for DFT calculations. First, the system is annealed at 1200 K for 1 ps. As a result, the total energy shows convergence to a constant value. This fact indicates that the fully structural relaxation has been already accomplished through the pre-annealing with a CMD scheme. Next, the resulting geometries are optimized with a plane-wave cutoff energy of 225 eV and $(2 \times 2 \times 2)$ k-grids to calculate the total energy and the equilibrium lattice size. The system is optimized until the total energy is converged to within 1 meV per atom.

In order to examine the degree of structural relaxation in this amorphous model, two major structural parameters are measured; the excess energy of amorphous phase relative to crystal phase, Δg_{ac} , and the bond angle deviation, $\Delta \theta$. Our amorphous model results in a Δg_{ac} of $0.15 \pm 0.02 \text{ eV}/$ atom and a $\Delta \theta$ of $10.2^{\circ} \pm 1.0^{\circ}$, which are in good agreement with experimental results ($\Delta g_{ac} = 0.13 \text{ eV}/\text{atom}$ [22], $\Delta \theta = 9.7^{\circ}$ [23]). Comparison with the results of a previous model of the ab initio molecular dynamics ($\Delta g_{ac} = 0.28 \text{ eV}/\text{atom}$, $\Delta \theta = 15.5^{\circ}$) [7], 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 [14]. In order to allow these atoms to reconstruct, the surface model is annealed at 1200 K for 2 ns within the framework of a CMD method [21]. This long annealing resulted in the complete disappearance of the twofold coordinated atoms and the increase of the three and fourfold coordinated atoms. In addition, the recent detailed diffusion analysis [10] also made it clear that the annealing of the simulation time of one nano-seconds can provide the well-relaxed surfaces of a-Si.

The subsequent DFT calculations are performed in the following way. For surface calculations, a supercell system is employed; a slab and a vacuum layer are periodically repeated toward the z-direction as shown in Fig. 1. The samples are heated at 840 K for 1 ps, and then statically optimized to calculate the total energy and stress. In such a calculation it is necessary to ensure that the results are converged with respect to the thickness of the vacuum layer, the k-grids and the plane-wave cutoff energy [24,25]. For this purpose, we carried out test calculations for a (100) 1×1



Fig. 1. Side view of a unit cell employed in the DFT calculation. Threefold-, fourfold- and fivefold-coordinated atoms are shown as black, open and gray circles, respectively.

surface model with 128 atoms and determined these optimum conditions. Consequently, it was found that the surface energy converged to within 1 meV per atom for a vacuum layer of 6.8 Å with a plane-wave cutoff energy of 225 eV and $(2 \times 2 \times 1)$ *k*-grids. Thus, these conditions are applied to the a-Si surface calculation.

3. Results

3.1. Surface energy and surface stress of a-Si

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 121 Å² (Each sample contains two surfaces on the top and bottom.). The results of a Si(100) 2 × 1 and Si(100) p(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	(J/m^2) and	surface	stress f	(N/m) of a	a-Si

	γ (J/m ²)	f_{xx}, f_{yy} (N/m)
a-Si		
CMD-DFT ^a	1.05 ± 0.14	1.5 ± 1.2^{b}
CMD ^a	1.13 ± 0.09	0.7 ± 1.0^{b}
Si(100) 2×1		
DFT ^a	1.40	0.73, -1.06
DFT [26]	_	0.81, -2.08
DFT [27]	_	0.75, -1.19
CMD ^a	1.48	0.40, -1.34
$Si(100) p(2 \times 2)$		
DFT ^a	1.28	1.24, 0.60
DFT [27]	-	1.33, 0.51
Si(100) 2×1		
Exp. [28]	1.36	_
Exp. [29]	_	$1.12 \pm 0.16^{\circ}$
Exp. [30]	-	0.56 ^c
Exp. [31]	-	$1.28 - 2.08^{\circ}$

The experimental and theoretical data for Si(100) crystal surfaces are also shown for comparison. The *x* and *y* directions run along the dimer bond and the rows of dimers, respectively.

^a This work.

^b Averaged values of f_{xx} and f_{yy} .

^c Values of anisotropy; $f_{xx} - f_{yy}$.

The values presented in Table 1 indicate that the surface energy of a-Si is lower than those of (100) surfaces. No significant difference can be seen between the surface energy of the CMD-DFT 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. It is also noticeable that our DFT results, the surface energy and stress of 2×1 and $p(2 \times 2)$, agree well with the experimental results [28–31]. In addition, we find the excellent agreement of the surface stresses of 2×1 and $p(2 \times 2)$ obtained from our DFT calculations with the other DFT results [26,27].

3.2. Surface structure of a-Si

The physical properties of surface strongly depend on its microscopic features. Therefore, the atomistic details of the surface region were analyzed using coordination statistics, C_n (n = 3-5), ring statistics, R_n (n = 3-7), and bond angle, θ . For these analyses, the width of the surface region is considered to be 5.0 Å. The cut-off bond distance is extracted from the position of the first minimum of the radial distribution function (r = 2.85 Å). Table 2 provides the coordination and ring statistics. Fig. 2 illustrates the bond angle distribution of threefold, fourfold and fivefold coordinated atoms located in the surface region. In Table 2 and Fig. 2, the results are obtained from 30 surfaces.

As shown in Table 2, in the present model, the surface atoms mainly consist of $22.3 \pm 3.9\%$ of threefold coordination and $73.5 \pm 2.9\%$ of fourfold coordination. The ratio of these coordination defects is very similar to that observed for the (100) 2×1 surface, which reveals 22.8% of threefold coordinated and 77.2% of fourfold coordinated atoms [21]. The typical side view presented in Fig. 1 indicates that the threefold-coordinated atoms are formed at the topmost of the surface region, in contrast to the fivefold-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 \pm 0.01 rings/atom), although the number of rings,

	CMD-DFT surface	CMD surface	CMD-DFT bulk	CMD bulk
C_3	22.3 ± 3.9	25.6 ± 1.7	0.5 ± 1.0	0.0 ± 0.0
C_4	73.5 ± 2.9	70.8 ± 3.7	97.0 ± 2.2	94.4 ± 3.6
C_5	4.2 ± 3.4	3.5 ± 3.6	2.4 ± 2.0	5.6 ± 3.6
R_3	0.05 ± 0.04	0.00 ± 0.01	0.00 ± 0.01	0.01 ± 0.01
R_4	0.08 ± 0.04	0.08 ± 0.03	0.02 ± 0.03	0.04 ± 0.03
R_5	0.52 ± 0.07	0.54 ± 0.08	0.40 ± 0.11	0.42 ± 0.11
R_6	1.05 ± 0.12	1.07 ± 0.13	0.97 ± 0.15	1.00 ± 0.15
R_7	1.12 ± 0.16	1.13 ± 0.16	0.96 ± 0.21	0.99 ± 0.19

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

The results of bulk model are also shown for comparison.



Fig. 2. Bond angle distributions $g(\theta)$ of (a) threefold-, (b) fourfold- and (c) fivefold-coordinated atoms located in the surface region. Solid line: CMD-DFT scheme, dotted line: CMD calculation.

larger than three-membered, in both models gives similar values. On the other hand, in the bulk model, few three-membered rings $(0.00 \pm 0.01$ rings/atom) were observed. This result would suggest that three-membered ring is one of the predominant structures in a-Si surface. Fig. 2(a) reveals significant differences in the bond angle distribution of threefold coordinated atoms between the CMD-DFT model and the CMD model; specifically the CMD-DFT model has a more wide-spread distribution and its peak is slightly shifted to lower bond angle values, as compared with the CMD model. The distribution of bond angle of the fourfold coordinated atoms (Fig. 2(b)) has the same tendency for both models. In Fig. 2(c), it appears that the bond angles of fivefold-coordinated atoms are widely distributed in both cases.

4. Discussions

4.1. Coordination defect of the a-Si 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 angle 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. 3. The data of θ_{ave} was taken from all the threefold coordinated atoms located in 30 surfaces.

Interestingly, Fig. 3 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



Fig. 3. Distribution function $g(\theta_{ave})$ of averaged bond angle θ_{ave} defined for threefold coordinated atoms in the surface region. Solid line: CMD-DFT scheme, dotted line: CMD calculation.

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 atom, and peak 2 as a P2 atom. In Fig. 4, we provide 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. 4.

Clearly, the local geometries of these two types of atom are different; the P1 atom has back bonds forming a sharp pyramidal geometry, while the P2 atom has those lying on a plane. The respective geometries of the P1 and P2 atoms deviate from the sp³ tetrahedral bond angle ($\theta_{ave} = 109.5^{\circ}$). These deviations reflect the rehybridization of the orbitals at each of the atoms, that is, the back bonding of the P1 atom is p³-like bonding and that of the P2 atom is sp²-like bonding. This configuration is similar to that of the Haneman's buckling model for Si(111) [32] and the Chadi's buckling dimer model for Si(001) 2×1 [33]. Assuming that the stabilization mechanism proposed in Refs. [32,33] also hold in the a-Si case, it is expected that the rehybridization accompanies with the charge transfer from the P2 atom to the P1 atom. 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



Fig. 4. Typical snapshot of the a-Si surface containing two characteristic threefold coordinated atoms (P1 atom) with p^3 -like bonding and (P2 atom) with sp^2 -like bonding (bottom). Local geometries of (middle: left) the P1 and (middle: right) P2 atoms. 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 shown (top). For reference purpose, in both contour plots, the contour lines where the density has the same value are drawn by dotted and thick solid lines, respectively.

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 [34] 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 sp² and sp³ 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 surface

The CMD-DFT well-relaxed bulk model of this study contains 0.5% of threefold coordinated atoms, which are not observed in the CMD bulk model (Table 2). Therefore, we clarify the micro-structure of this defect located in the bulk and compare it with that in the surface. Fig. 5(a) presents the detailed atomic geometries of the threefold coordinated atom (left) and the corresponding contour plots of the valence electronic charge density (right). For comparison, those of the fourfold coordinated atom are also shown in Fig. 5(b).

In Fig. 5(a), the atom C presents one of the four atoms lying near the atom A. But, unlike the other three atoms, 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



Fig. 5. (Left) Local geometries and (right) corresponding contour plots of the valence electronic charge density on a plane defined by three atoms (A, B, C). The contour plots are drawn in the same manner as shown in Fig. 4. (a) Threefoldand (b) fourfold-coordinated defects in the well-relaxed bulk a-Si.

electronic charge is distributed between them. This electronic feature is evidence that atom A in Fig. 5(a) 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° (averaged value of the three defects), slightly less than the tetrahedral bond angle. This indicates that the back bonding of the defect tend to be sp³-like bonding. By comparing the results of the surface defect mentioned above, it is demonstrated that there exists differences in the structural and electrical properties of threefold coordination defects between bulk and surface of a-Si.

5. Conclusions

Using a combination method of classical molecular dynamics and ab initio calculation, a quantitative evaluation of the surface energy and surface stress of well-relaxed amorphous silicon (a-Si) has been demonstrated. This approach resulted in a surface energy of $1.05 \pm 0.14 \text{ J/m}^2$ 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, which are not obtained through the use of the Tersoff empirical potential. It has been shown that there are two types of threefold coordinated atoms at the surface region; one with p3-like bonding and the other with sp^2 -like bonding. It is also demonstrated that the structural and electrical properties of these coordination defects are different from those observed in the bulk structure.

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