

Structural and Mechanical Properties of Amorphous Silicon Surfaces: A Combination Study of *ab-initio* and Classical Molecular Dynamics

S. Hara, T. Kumagai, S. Izumi and S. Sakai

Department of Mechanical Engineering, The University of Tokyo, 7-3-1 Hongo,
Bunkyo-ku, Tokyo, 113-8656 JAPAN, E-mail: harasho@fml.t.u-tokyo.ac.jp

ABSTRACT

Despite amorphous silicon (a-Si) being one of the most fundamental thin film materials, little is known about the microscopic details of a-Si surfaces. Several theoretical works using *ab-initio* approach have been performed to investigate this subject. However, creating an a-Si surface model that provides results comparable to experimental results is still a matter of debate. The origin of this difficulty arises from the insufficient thermal annealing for structural relaxation due to its heavy computational burden. To overcome this problem, we use a combined method of a classical molecular dynamics (CMD) and an *ab-initio* calculation based on density functional theory (DFT). 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. This combination method (CMD-DFT) can provide quantitative evaluation of the surface energy and surface stress of well-relaxed amorphous silicon in addition to its structure. 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.

1. Methodology

The outline of the combination method is as follows. The first step is to prepare well-relaxed amorphous structures by CMD calculations with the Tersoff potential. 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 [1] based on pseudopotential and plane-wave techniques. We

employed the ultra-soft Vanderbilt pseudopotential and the generalized-gradient approximation. 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. After quenching, the structural optimization was performed.

To create a surface model, a bulk model containing 128 atoms is first prepared. The detailed procedure to create the bulk model was discussed in Ref. 2. We found that the structural properties of the bulk model are in excellent agreement with experimental results [2]. Following this, two surfaces are produced by removing the periodic boundary condition in one direction. This surface model is annealed at 1200 K for 2 ns within the framework of a CMD to relax the surface atoms. The subsequent DFT calculations are performed using a supercell system; 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 $(2 \times 2 \times 1)$ k -grids. In the present work, we performed a total of 15 simulations.

2. Surface Energy and Surface Stress of a-Si

Using a CMD-DFT method, the surface energy γ of 1.05 ± 0.14 J/m², and the surface stress f of 1.5 ± 0.2 N/m, of a-Si are obtained. These results are averaged over 30 surfaces whose each surface area is equal to 1.21 nm². For comparison, the DFT results of $s(001)$ 2×1 ($\gamma = 1.40$ J/m², $f_{xx} = 0.7$, $f_{yy} = -1.1$ N/m) and $p(001)$ 2×2 ($\gamma = 1.28$ J/m², $f_{xx} = 1.2$, $f_{yy} = 0.6$ N/m) crystal surface are also provided. The f_{xx} and f_{yy} values for surface stress correspond to the component of the dimer bond and the dimer row direction, respectively. We find that the surface energy of a-Si is lower than those of (001) surfaces. 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.

3. Coordination Defects of a-Si Surface

In this section, we characterize the local structure of an individual threefold coordinated atom, which is the predominant coordination defect located in the surface region, by using the averaged value θ_{ave} of three bond angles around the atom. This parameter quantifies the sharpness of the vertical angle formed by the three back bonds. Interestingly, we find a distinct difference of the distribution of θ_{ave} between the CMD-DFT model and the CMD model. In the CMD-DFT model, two main peaks at approximately 100° and 120° are observed, while in the CMD model only one peak, at approximately 113° , is observed. The threefold coordinated atom of 100° will be referred to as a P1 type atom, and 120° as a P2 type atom. Fig. 1 provides a typical snapshot of the

a-Si surface containing both types of atom. The atomic geometries and contour plots of the valence electronic charge density are also presented in Fig. 1.

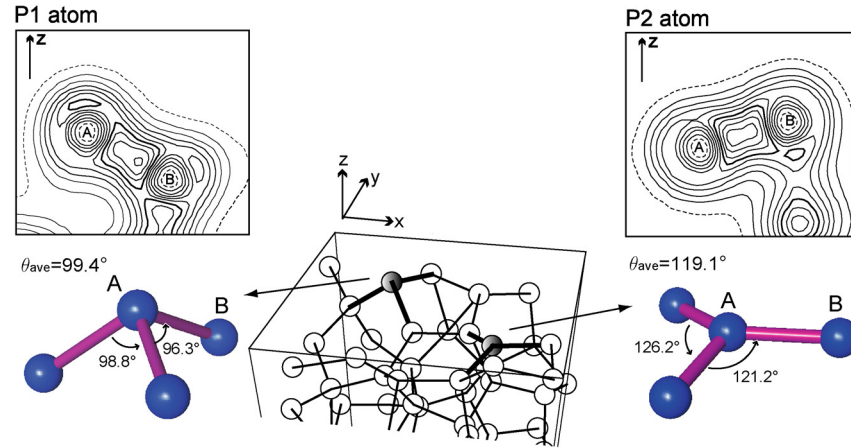


Fig. 1: Detailed diagram of two characteristic threefold-coordinated atoms (P1) with p^3 -like bonding and (P2) with sp^2 -like bonding. The corresponding contour plots of the valence electronic charge density on a plane, which is perpendicular to the surface and contains both A and B atoms, are also shown.

Clearly, it is shown that 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 atomic geometries deviate from the sp^3 tetrahedral bond angle ($\theta_{ave} = 109.5^\circ$). 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. Fig. 1 shows 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 [3] 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 CMD-DFT method provides new findings of the microscopic features of a-Si surface.

References

- [1] Kresse, G., and Hafner, J., "Ab initio molecular dynamics for liquid metals", Phys. Rev. B 47, 558-561 (1993).
- [2] 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).
- [3] 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)