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Analysis of single and composite structural defects in pure amorphous silicon: A first-principles study

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ABSTRACT

The structural and electronic properties of amorphous silicon (*a*-Si) are investigated by first-principles calculations based on the density-functional theory (DFT), focusing on the intrinsic structural defects. By simulated melting and quenching of a crystalline silicon model through the Car-Parrinello molecular dynamics (CPMD), we generate several different *a*-Si samples, in which three-fold (T_3), five-fold (T_5), and anomalous four-fold (T_{4a}) defects are contained. Using the samples, we clarify how the disordered structure of *a*-Si affects the characters of its density of states (DOS). We subsequently study the properties of defect complexes found in the obtained samples, including one that comprises three T_5 defects, and we show the conditions for the defect complexes to be energetically stable. Finally, we investigate the hydrogen passivation process of the T_5 defects in *a*-Si and show that the hydrogenation of T_5 is an exothermic reaction and that the activation energy for a H_2 molecule to passivate two T_5 sites is calculated to be 1.05 eV.

1. Introduction

Amorphous materials, which lack long-range structural orders but still keep short-range orders, have been investigated for almost a half century [1–3]. An important problem in the physics of such disordered materials is the understanding of their structural characteristics that incorporates the short-range order in the disordered atomic network and of their influence on the electronic properties. Despite the substantial progress made in the past, our understanding of how the structural characteristics affect the electronic properties of disordered materials is still incomplete.

Amorphous silicon (*a*-Si) is an important example of such amorphous materials. It shows attractive properties that are distinct from crystalline silicon (*c*-Si), such as the high light absorption coefficient and the large bandgap. Its low deposition temperature and low fabrication cost, as well as those physical properties, allow the industry to use this material for thin-film devices including solar cells and transistors. Upon miniaturization of electronic devices, clarification of how the atom-scale structural characteristics influence its electronic properties of *a*-Si is crucial also from a technological viewpoint.

Accurate determination of the local atomic structures of *a*-Si is a prerequisite of any quantitative theoretical approach to its physical properties. In the early days, continuous-random-network models [4,5] were used to consider the local structures of amorphous materials. Then molecular dynamics (MD) [6–8] or Monte Carlo [9] techniques combined with empirical interatomic potentials [10–13] are used to obtain the radial distribution functions of *a*-Si. However, the validity of the empirical potentials is always an issue and a “try and error” approach has been continued.

The MD approach based on the first principles of quantum theory gets rid of the problem of the interatomic potentials. Car and Parrinello invented a scheme in which the electron-electron interaction is treated in the density-functional theory (DFT) [14,15] and Hellmann-Feynman forces are used to track the dynamics of ions [16]. In this scheme, a fictitious mass of the wavefunction (Kohn-Sham orbital) is introduced to perform efficient first-principles MD (Car-Parrinello molecular dynamics, CPMD) simulations. The CPMD scheme has been applied to *a*-Si [17,18] and the obtained radial distributions up to the nearest neighbor distance agree with the experiments [19–21] satisfactorily. Other Born-Oppenheimer MD simulations based on the DFT have been performed for *a*-Si and the nature of the short-range order has been partly clarified [22–25]. These MD simulations show that while the Si atoms mostly form four-fold T_4 configurations, whose bond angles are around 110 deg, there are three kinds of structural defects in *a*-Si as well: The three-fold (T_3), the five-fold (T_5), and the anomalous four-fold (T_{4a}) sites [17,18,23]. The difference between the T_4 sites and the T_{4a} sites is that the bond angles of the latter are strongly distorted than those of the former. These structural defects may induce deep levels in the energy gap and be responsible for the conduction and valence band tails [2,3,26]. The deep levels are indeed observed by the electron

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paramagnetic resonance (EPR) measurements [2,3,27] and identified as either T_3 or T_5 configuration [28].

A problem in the first-principles MD simulations described above is the high defect density appearing in the simulation cell: The density is an order of which is higher by two orders of magnitude than the experimentally determined value [27] 10^{19} cm^{-3}. In the CPMD simulations, *a*-Si is prepared by heating *c*-Si to melt and then quenching the obtained liquid. The discrepancy in the defect density from the experimental situation is mainly due to the unrealistic quenching rate in the CPMD simulations, which is usually more than 100 K/ps. In this work, we cool liquid silicon with the speed of ~ 10 K/ps, which is slower than those used to prepare *a*-Si samples in the past, and show that defect-free structures can be certainly obtained by the CPMD. Furthermore, using the generated samples, we tackle several questions in *a*-Si that have not been understood fully.

Theoretical efforts were made to clarify the relationships between the structural and the electronic properties of *a*-Si [29–32], and it was revealed that the disordered network of Si atoms is a key to understanding its electronic states. In this paper, we make a quantitative analysis of the electronic properties of *a*-Si and make a clearer explanation of how the geometric properties of *a*-Si affects its density of states (DOS) in association with its atomic configurations.

One of the important things that characterize the structural property of *a*-Si is the formation of the structural defects. It is commonly assumed that the T_3 defects are prevalent *a*-Si, and previous researches have paid less attention to the other two types of the defects. Moreover, little is known about the complexes that these structural defects possibly compose. Study of defect complexes is important in that they might help us to understand the how defects are spatially distributed or how likely they are to be stable in a particular configuration. To give further insights into these problems, we perform calculations focusing on the defect complexes found in our *a*-Si samples.

Another topic relevant to the defects is the effect of hydrogenation. Defects in *a*-Si are the origins of deep levels in the mid-gap, which contribute to lowering the mobility of *a*-Si and thus to degrading its quality as a material for semiconductor devices. Therefore, industrially fabricated *a*-Si contains a large number of H atoms which passivate the defects in the structure with. The deep levels are known to be made up of two electronic states: the dangling bonds and the floating bonds, the latter of which is a state derived from the T_5 defects [33]. While H atoms are believed to mostly passivate the T_3 defects, not much attention has been paid to the passivation of T_5 defects. As some researchers have mentioned earlier [28,34], however, the T_5 defects might be prevalent in *a*-Si and play a major role in forming the deep levels. We provide discussions on how likely the T_5 defects are to be passivated by H atoms from an energetic point of view.

The outline of this paper is as follows. In Section 2, the calculation methods and the process of generating *a*-Si samples are described. In Section 3, the structural properties of the obtained samples are investigated. In Section 4, we analyze the correspondence between the DOS and the structural properties of *a*-Si. In Section 5, we take a closer look at the electronic states near the Fermi energy, particularly focusing on the defect levels. In Section 6, the stabilities of the defects are studied. In Section 7, hydrogenation effect of the T_5 sites are discussed. A summary and conclusions are given in Section 8.

2. Computational details

We have used our RSDFT (Real Space Density Functional Theory) package [35–37], in which the Kohn-Sham equation based on the DFT [14] is calculated under the real-space scheme [38]. In the real-space scheme, discrete grid points are introduced in the real space, and the wavefunction is expanded on the mesh in the real space. To simulate the structures of *a*-Si, CPMD calculations have been done using RS-CPMD (Real-Space Car-Parrinello Molecular Dynamics) code, which is incorporated in RSDFT package. In this work, we have set the mesh size as 0.41 Å, which corresponds to the cutoff energy of 31.7 Ry. We have used PBE exchange-correlation functional [39] and norm-conserving pseudopotential in both static and dynamic calculations. Brillouin zone (BZ) sampling has been done for the Γ point. We have confirmed that the total energy of the system *a*-Si converges within 0.2 eV/cell with our calculational settings.

Amorphous samples have been obtained by melting and quenching a crystalline structure through the CPMD simulations. As for the initial structure, we have prepared a $3 \times 3 \times 3$ supercell containing 54 Si atoms/cell. The volume of the supercell has been fixed as 1.08 [nm^3], which is consistent with the experiments. The time step in the simulations has been set to be 0.1 fs, and the temperature has been controlled by velocity scaling.

We have started heating the system from 500 K and increased the temperature with the heating rate of 125 K/ps until it reaches 1700 K. We have then kept heating the system at 1700 K for another 5.8 ps, in which process we have confirmed that the system has been sufficiently liquified by checking its radial distribution, shown in Appendix. We have subsequently cooled the system until the temperature has reached 500 K. Here, we have employed four different cooling rates separately: 20.0, 16.7, 14.3, and 12.5 K/ps. We note that these speeds are slower than what have ever been applied for the CPMD simulation of *a*-Si reported by other groups. Finally, we have relaxed the structures of the final step of the cooling to obtain the stable atomic configurations. We refer to the samples obtained from each cooling rate 20.0, 16.7, 14.3, and 12.5 K/ps as *a*-Si20, *a*-Si16, *a*-Si14, and *a*-Si12, respectively. After the relaxation, each sample has been heated at 300 K for 2.0 ps to calculate the radial distribution and the angle distribution, both of which are time-averaged functions of the atomic positions.

3. Structures of the obtained samples

The radial distribution g_r and the bond angle distribution g_a of each sample are shown in Fig. 1. All the four calculated plots of g_r are in good agreement with the experimental result [21]. The sharp peaks are located at 2.31, 2.33, 2.32, and 2.36 Å for *a*-Si20, *a*-Si16, *a*-Si14, and *a*-Si12, respectively. Considering the experimentally obtained first-neighbor distance in *c*-Si, 2.35 Å, these indicate that the short-range order is preserved in every amorphous sample. Furthermore, we can clearly observe the second and third peaks near $r = 3.8$ and 5.8 Å. These broad peaks reflect the deviation in the bond length and the bond angle.

Every plot of g_a shown in Fig. 1 (b) has a broad peak around 100°. The peak position is close to the bond angle in *c*-Si, 109.5°, which indicates that the majority of the Si atoms in the samples retain the nearly-tetrahedral bonds.

Fig. 1 (c) shows the distribution of the rings composed of n ($n = 3, \ldots, 8$) Si atoms in each sample. We find that dominant rings are those composed of five or six atoms in every sample. We also notice that three-membered rings are found only in *a*-Si20 and *a*-Si12, which can be associated with the small peaks around 60° in Fig. 1 (b).

Defects found in the three samples are illustrated in Fig. 3. In this paper, we define a $T_{4\mathrm{a}}$ site as one which satisfies the following inequality

$$\Omega = \sum_{(i,j,k)} \Omega_{ijk} < 4\pi. \tag{1}$$

Here, Ω is the "solid angle" [sr] at the $T_{4\mathrm{a}}$ site which can be described using Fig. 2. Fig. 2 schematically shows a T_4 site, named O, and the four neighboring sites A_1,A_2,A_3, and A_4. P_i ($i = 1,2,3$) is the point where a vector $\overline{OA_i}$ passes through the unit sphere S, represented by the dashed circle. Ω_{123} is the area of the spherical triangle $P_1P_2P_3$, colored by orange. Ω is the sum taken over for all the combinations of the four neighboring sites. By this formulation, for those that retain nearly-tetrahedral bonds, such as the one illustrated in Fig. 2, Ω is equal to 4π. On the other hand, those that contain heavily distorted bonds, such as the

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