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journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	39
number	1
page range	33-36
year	1994-03-25
URL	http://hdl.handle.net/10097/28467

Sci. Rep. RITU A39 (1993) pp. 33-36
No. 1, December 1993

Prediction of Intrinsic Defects in Hydrogenated Amorphous Silicon by *ab initio* Molecular Dynamics

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(Received November 30, 1993)

Intrinsic defects in hydrogenated amorphous silicon (a-Si:H) are investigated using *ab initio* molecular-dynamics simulation. It is predicted that the hydrogen-passivated dangling bond (Si-H), the positively-ionized Si-H-Si three-centered bond (Si-H^+-Si), the negatively-ionized three-fold-coordinated dangling-bond (D^-), and the five-fold-coordinated floating-bond (F_5) are the intrinsic defects in a-Si:H. We discuss the role of intrinsic defects and hydrogen related to the origin of the photo-induced defect in a-Si:H based upon the simulation.

KEYWORDS: Hydrogenated amorphous silicon, ab initio molecular dynamics, intrinsic defect

It is well known that the solar cells fabricated by hydrogenated amorphous silicon (a-Si:H) are degraded during the exposure to the visible light. This is so called Staebler-Wronski (SW) effect[1]. SW effect reduces the conductivity and photoconductivity by a few orders of magnitude. Before the exposure of the light, the concentration of the paramagnetic dangling-bonds are very low ($\approx 10^{15}$ cm^{-3}) in the materials for the device application. This result suggests that the number of paramagnetic dangling-bonds are increased by light soaking. Many candidates to explain the origin of SW effect are proposed including the negative effective-U centers of dangling bonds[2], the floating bonds[3], the weak Si-Si back bonds adjacent to the Si-H bond[4], and so on. So far, the role of the hydrogen and the intrinsic defects related to SW effect is not understood microscopically because the microscopic experimental data is not available to identify the defect configuration in a-Si:H. The *ab initio* molecular-dynamics simulation is one of the most promising method to investigate the origin of SW effect. The purpose of the present letter is to predict the role of hydrogen and the microscopic origin of the intrinsic defects related to SW effect in a-Si:H based upon the simulation.

We generate a-Si:H using *ab initio* molecular dynamics which was developed by Car and Parrinello[5]. This method makes us possible to simulate the atomic motion and the stable (or metastable) atomic arrangement based on the *ab initio* electronic structure calculation. Since the concentration of the defects in a-Si:H for a device application is order of 10^{15} cm^{-3}, we need at least 10^7 atoms in a super-cell in order to perform the realistic simulation of the defects. This kind of large-scale simulation is not available up to now (maximum size is still a few hundreds of atoms in a super-cell). In order to get around this problem, we have performed more rapid-quenching procedure to create many metastable defects in a-Si:H with the periodic boundary conditions of super-cells containing 64 silicon (Si) and 8 hydrogen (H) atoms. The metastable defects in the simulation are most possible candidates of the intrinsic defects related to SW effect in a-Si:H to study more carefully because all amorphous materials are frozen in a metastable state and the concentration of the photo-induced defects caused by SW effect is low (order of 10^{18} cm^{-3}) in the real materials. We performed the dynamical simulated-annealing to determine the electronic structure and the metastable atomic coordinates in a-Si:H with rapid-quenching from 1800 K to 300 K by the rate of 2×10^{15} K/sec after keeping it at 1800 K for 0.75 psec to loose the long range order in the atomic arrangement. We have annealed the system for 0.25 psec at 300 K to minimize the local stress and to find more stable atomic arrangement. The displacements of atoms were permitted fully in the super-cells. Atoms are located at a local minimum of the total energy surface (a metastable position) with the force acting on the atoms less than 0.07 eV/A at 300 K.

Calculations of the total energy were performed with the norm-conserving pseudopotential method and the Ceperley-Alder-Perdew-Zunger form of the exchange and correlation energy[6]. We used a set of Bachelet-Hamann-Schlüter type pseudopotentials[7] of Si atom by Kleinman-Bylander's form retaining s nonlocality only[8]. The real potential was used for the hydrogen atoms. Plane waves of up to 163 eV in energy were included in the basis set. The integration over the occupied states in the super-cell Brillouin zone was represented by the summation at the Γ-point. We simulated the system in a constant volume of crystalline silicon (135.0 a.u./atom). The temperature of this system was set by scaling of the velocity of atoms.

Figure 1 shows the perspective of the generated a-Si:H in the present simulation. The partial pair correlation functions of Si-Si, Si-H and H-H in a-Si:H at 300 K compared with the experimental data[9] are shown in Fig. 2 . The overall agreement between the simulation and experiment is reasonable, although the hydrogen concentration is different between simulation (11% atomic hydrogen) and experiment (26% atomic hydrogen). We find a broad first-peak in the Si-H partial pair correlation function which indicates the coexistence of two kinds of Si-H bond of the hydrogen-passivated dangling-bond (Si-H) and the three-centered bond (Si-H-Si) as we will discuss later. We also find two dispersive groups of the peaks in H-H partial pair correlation function. These are due to the separation of the hydrogen-rich and -poor regions which appear in this simulation starting from the uni-

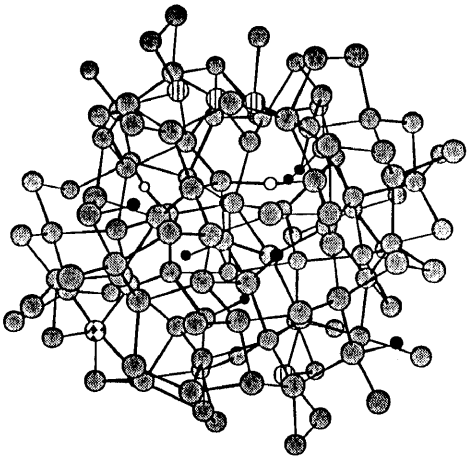

FIG. 1. The perspective of the generated a-Si:H. Bigger circles indicate Si atoms. Hydrogen-passivated dangling-bonds are shown by closed circles. Three-fold-coordinated Si atom which is negatively-ionized dangling-bond (D^-) is shown by vertically-striped circles. Open circles indicate the H atom making the three-centered bond (Si-H-Si). The checked circle is Si atom which has five-fold-coordinated floating bond (F_5).

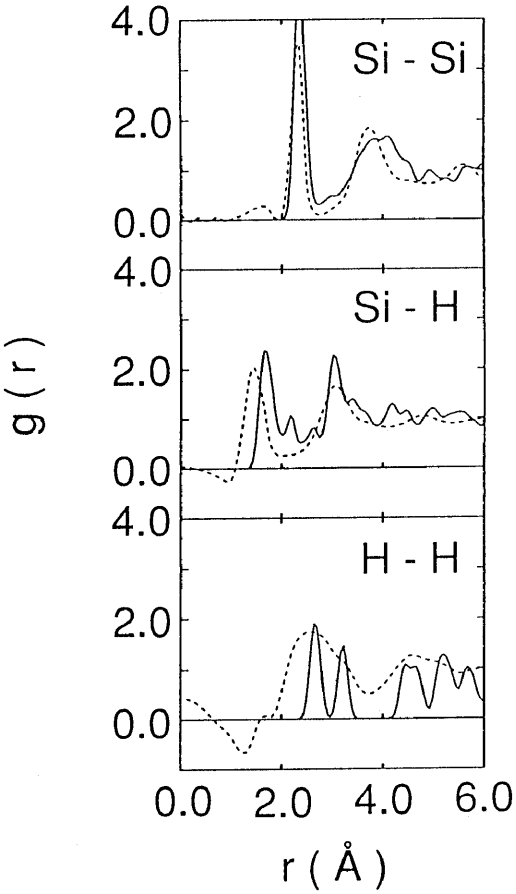

FIG. 2. Theoretical (solid line) and experimental (dashed line) partial pair-correlation function of a-Si:H. The experimental functions correspond to a sample containing 26% atomic hydrogen concentration[9].

form distribution of hydrogen. We find that the most of the dangling bonds are terminated by hydrogen in the hydrogen-rich region. On the other hand, some of the dangling bonds are not terminated by hydrogen in the hydrogen-poor region. Hydrogen accumulation and the creation of hydrogen-rich voids in a-Si:H were studied by Chiarotti *et al.*[10] using the *ab initio* molecular dynamics, and the present result in hydrogen accumulation is consistent with the previous study.

The intrinsic defects we found in the present simulations are (i) the hydrogen-passivated dangling-bond (Si-H) which remove the dangling-bond state from the band gap to the valence band, (ii) the positively-ionized three-centered-bond (Si-H^+-Si) which contains unoccupied gap states (electron spin S=0, Fig. 3) near the conduction band minimum (CBM), (iii) the negatively-ionized three-fold-coordinated dangling-bond (D^-) which contains double-occupied gap states (spin-singlet, S=0, Fig. 4) near the valence band maximum (VBM), and (iv) the five-fold-coordinated floating-bond (F_5) which contains unoccupied gap states (S=0) near the CBM. Comparing these intrinsic defects with ones in crystalline silicon (c-Si), we propose the analogy that the Si-H bond in a-Si:H corresponds to the hydrogen-passivated vacancy-dangling-bond in c-Si, the Si-H-Si bond in a-Si:H does to the hydrogen at the bond-center in c-Si, the D^- bond in a-Si:H does to the negative effective-U center of vacancy in c-Si, and the F_5 bond in a-Si:H does to the self-interstitials in c-Si.

Closed circle in Fig. 1 indicates the hydrogen at the Si-H bond which is the major defect (6 of 8 hydrogen atoms in a super-cell) in a-Si:H. We find no Si-Si weak back-bond adjacent to the Si-H bond because the deviations of the Si-Si bond length is less than 2% at 300 K in the present simulation. The dangling bond is already terminated by hydrogen in the Si-H bond and fully relaxed to reduce the local stress. We find very small charge transfer from the hydrogen to the Si-Si back-bond and no weakening of the Si-Si back-bond. No Si-H_2 bond was also found in this simulation. Open circle in Fig. 1 indicates the hydrogen atom at the Si-H-Si bond which is positively ionized (Si-H^+-Si) with releasing an electron from it. The angles of the Si-H-Si bond are 168.8 and 166.6 deg., respectively (2 of 8 hydrogen atoms in a super-cell are located at the Si-H-Si bond). The Si-H-Si bond is flexible for the rotation and bending ($\sim$ 10 deg.) around the hydrogen atom, therefore Si-H-Si bonds act to reduce the local stress between the four-fold-coordinated clusters in a-Si:H. We find that the roles of hydrogen in a-Si:H are (1) *the termination of dangling bonds to passivate the deep levels in the band gap* and (2) *the reduction of the local stress caused by the bending and rotational Si-H-Si bond.* The Si-H^+-Si bond contains the unoccupied states in the band gap near the CBM. Vertically-striped circle in Fig. 1 indicates the silicon atom at the three-fold-coordinated dangling-bond which is occupied by two electrons in the band gap near the VBM indicating a negatively-charged non-magnetic center (D^-). These results strongly suggest that the D^0 (Si-H^0-Si) is negative effective-U centers with charge disproportion of D^0 into D^+ and D^- (Si-H^0-Si into Si-H^+-Si and Si-H^--Si)

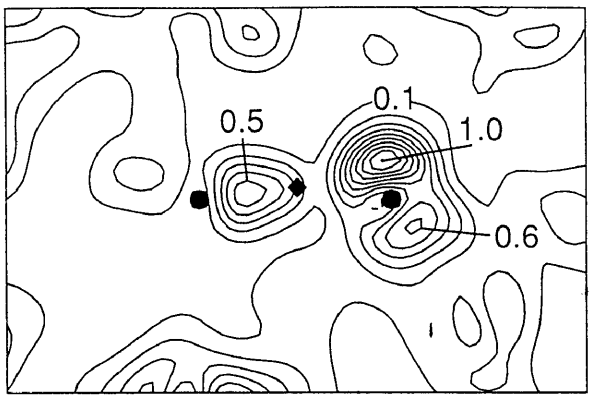

FIG. 3. Charge density of the gap states from the unoccupied Si-H$^+$-Si three-centered bond. Sliced along the plane containing Si-H-Si atoms. Closed circle and diamond indicate Si and H atom, respectively.

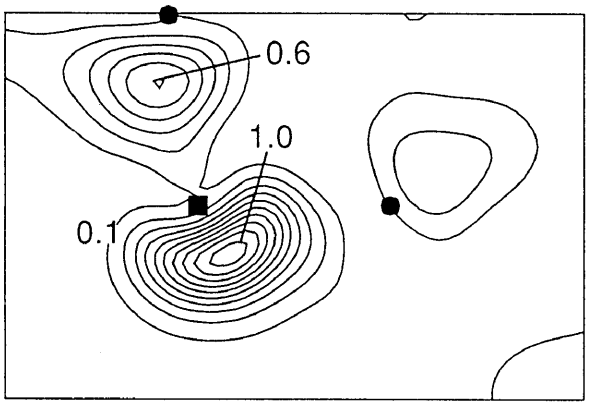

FIG. 4. Charge density of the gap states from the negatively-charged dangling bond (D$^-$). Sliced along the plane containing three-fold-coordinated Si atom (indicated by closed square) and two nearest-neighbored Si atoms (indicated by closed circles).

as p redicted for dangling bond (bond-centered hydrogen) in c-Si[11,12], therefore mostly D$^-$ and Si-H$^+$-Si are realized in the present simulation. The F_5 bond in a-Si:H which was theoretically speculated by Pantelides[13] is found in this simulation and it is floating at 300 K. The bond length to the surrounding silicon atoms are close to the ideal one and the switching the covalent bond is observed during the annealing process. F_5 bond contains unoccupied states near the CBM with non-bonding orbitals.

A defect level in the band gap is necessary to localize the electron-hole pair in SW effect. The possible candidates for the origin of the photo-induced defects in the present simulation are (1) the D^0 bond with S=1/2 caused by the reaction of D$^-$ + (hole) $\Rightarrow$ D^0, (2) the Si-H^0-Si bond with S=1/2 caused by the reaction of Si-H$^+$-Si + (electron) $\Rightarrow$ Si-H^0-Si, and (3) the F_5 bond with S=1/2 trapping an electron. We have a possibility that some of the D^0 bond are negative effective-U centers with large lattice relaxation and the remaining are positive effective-U centers with small lattice relaxation. The sign of effective-U depends on the local environment of the dangling bond as discussed by Bar-Yam and Joannopoulos[12] in amorphous silicon. Actually, we found two types of D-bond, one is sp^2 like and other is sp^3 like, in our simulation. The negative effective-U center of D^0 bond is metastable and observable only at low temperatures by electron spin resonance (ESR), on the other hand, the positive effective-U center of D^0 bond is stable and observable at room temperature by ESR. If photo-induced Si-H^0-Si bond is a negative effective-U center like a hydrogen at the bond center in c-Si[11], Si-H^0-Si bond is realized and observable only at a low temperature because the hydrogen atom is displaced into the interstitial site at the room temperatures with disappearing ESR signal. Above discussion is plausible when we compared these results with the experiments. Knights *et al.* and Yamasaki *et al.*[14,15] observed two kinds of optically induced ESR signals with g=2.004 and 2.01 only at low temperatures (less than 150 K) in addition to the dangling-bond signal (g=2.005) in dark at room temperature in a-Si:H. We identify that metastable negative effective-U centers of Si-H^0-Si and D^0 correspond to the optically induced ESR signals with g=2.004 and 2.01, and the positive effective-U centers of D^0 corresponds to the dangling-bond signal (g=2.005). The hyperfine coupling constant of hydrogen nucleus of Si-H^0-Si is very small because the gap states is almost p-orbital-like non-bonding-character at the hydrogen nucleus[11,16,17]. Isoya *et al.*[18] determined the distance between the photo-induced dangling-bonds related to SW effect and hydrogen atom to be 4.2 Å using the electron-spin-echo envelope-modulation method of pulsed ESR. The present identification is compatible with these experimental data and the origin of SW effect is related to the creation of the positive effective-U centers of D^0 bond from the D$^-$ bond through the photo-excitation. Hydrogen atom in the Si-H bond or Si-H-Si bond is irrelevant to the origin of SW effect in the present simulation, but probably these are relevant to the deactivation of the dangling bond through the annealing at higher temperature (450 K). F_5 bond captures an electron and become a paramagnetic center as discussed by Pantelides[13]. We have not yet finished to investigate F_5 bond very carefully, however, in order to simulate the photo-induced defects in a-Si:H, *ab initio* molecular-dynamics simulations of the electronic excitation by photo-excitation are needed for the above mentioned candidates to simulate SW effect.

In conclusion we have performed *ab initio* molecular-dynamics simulations to predict the intrinsic defects and its relation to SW effect in a-Si:H. It is shown that the hydrogen-passivated dangling-bond, the positively-ionized three-centered bond, the negatively-ionized three-fold-coordinated dangling-bond and the five-fold-coordinated floating-bond are the intrinsic defects in a-Si:H. Based upon the calculated results, we have discussed the role of hydrogen and the possible candidates for the origin of the photo-induced defects in a-Si:H to explain SW effect. The proposed candidates to explain the origin of SW effect are the negatively-ionized three-fold-coordinated dangling-bond. The possibility of the

five-fold-coordinated floating-bond is not excluded for the origin of SW effect, but the weak Si-Si back-bond[14] is irrelevant to SW effect because weak back-bond does not exist in the present simulation.

The authors thank T. Sasaki (NRIM), H. Okushi, K. Tanaka, S. Yamasaki, Y. Toyoshima (ETL) and A. Oshiyama (NEC) for useful discussions. This work is partly supported by grants from the Ministry of Education, Culture and Science of Japan.

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