Nano-scale Control of Light-Induced Degradation in Amorphous Silicon

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ABSTRACT

Recently, a remarkable technique to overcome the problem of light-induced degradation in amorphous silicon solar cells using a cyanide (CN) treatment has been developed. A theoretical study on the structural and bonding characteristics of CN in amorphous silicon was carried out using *ab initio* molecular dynamics simulations, placing an emphasize on nano-scale control of defects in simiconductors. It was found that CN incorporation results in more than just the termination of dangling bonds. The connectivity of the covalent random network increases because the CN changes from triply bonded, which is a common form in molecular CN, to the singly bonded form. This may be the mechanism by which CN incorporation produces significant reductions in light-induced degradation.

Keywords: amorphous silicon, Staebler-Wronski effect, CN treatment, impurity

1 INTRODUCTION

After success of valence control of amorphous silicon (a-Si) by hydrogenation, a problem of the light-induced degradation, the so-called Staebler-Wronski (SW) effect, has been as a major obstacle for commercial use of a-Si to the application of solar cells. Although numerous studies were accumulated, there was virtually no significant improvement in this problem more than 20 years. Very recently, a remarkable technique to overcome this problem has been proposed by Prof. Kobayashi *et al.* [3]. In this method, a-Si is immersed in a cyanide solution, in some cases, with help of electrical biases. This simple treatment yields a surprising effect on suppression of the light-induced degradation. So far, no microscopic theory exists.

In this paper, the structure of cyanide ions incorporated in a-Si has been studied by *ab initio* molecular dynamics simulations (MDS) aimed at clarifying the microscopic mechanisms that suppress the light-induced degradation of a-Si. This study would shed a new light on nano-scale control of defects in amorphous silicon. When the mechanism is clarified, we can design the nanoscale structure of a-Si to avoid coordination defects. This was not achieved by introducing single-species dopants, such as H, C, F, etc, alone. Pairing different species is much more important.

2 METHOD

An *ab initio* pseudopotential method is used in the calculations. We have used a pseudopotential code called Osaka2000. [4] The basic elements of this code are local-density approximation, plane-wave expansion, and direct minimization of the Kohn-Sham Hamiltonian. [5] The pseudopotentials used are the Troullier and Martins [6] type, along with the Kleinman and Bylander fully separable form [7]. The plane wave cut-off energy ($E_{\rm cut}$) was 316.7 eV (17461 plane waves). Only the Γ point was used as a k-sampling point. A super cell containing 64 Si atoms was used.

3 RESULT

3.1 Structural model of amorphous silicon

Before studying cyanide incorporation, appropriate modeling of amorphous structures is required. Samples of pure a-Si were prepared from liquid silicon by simulated quenching method, with a cooling rate 1015 K/s. This method becomes a standard for modeling amorphous structures, because no empirical parameters are assumed [8].

An example of pure amorphous silicon sample obtained in this way is shown in Fig. 1. In order to evaluate the extent to what the obtained sample simulates the real structure of amorphous solid, comparison is made of the radial distribution function (RDF). The calculated RDF is in good agreement with the experiment. The first peak is located at 2.34 Å, which is almost the same as that of crystal (2.35 Å). In addition to the nearest neighbor peak, the presence of distant peaks, up to of forth nearest neighbor, is apparent. Clear separation of the first peak from the second allows us to define the coordination number even for amorphous solids.

In our sample, most of Si atoms exhibit four-fold coordination. These normal coordinated bonds form the continuous random network (CRN). Beside normal coordinated atoms, two atoms are found to have three-fold coordination (dangling bond), two atoms have five-fold

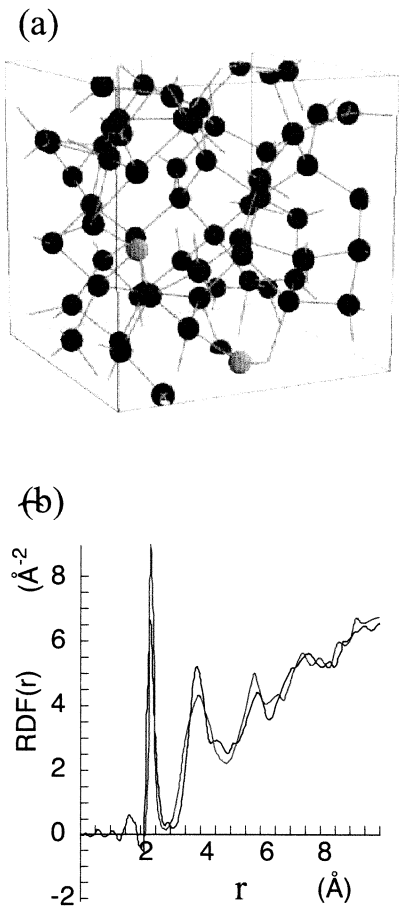


Figure 1: (a) Structure of a calculated sample of pure a-Si. Most of Si atoms are fourfold-coordinated, which are indicated by blue. The cell contains two fivefold-coordinated (red) and two threefold-coordinated Si atoms (yellow). (b) The RDF of a calculated a-Si (red line) and of an experiment (black line) [9].

coordination (floating bond). These wrong-coordinated bonds are primal defects in a-Si, and yield gap states in the electronic structure.

3.2 CN incorporation

Next, a CN ion was introduced in the vicinity of a dangling bond. The initial bond length between C and N is chosen to be 2.0 Å, which is much larger than that of triple bond C≡N in the molecule (∼1.16 Å[10]). Molecular dynamics simulations were performed over several ps. The time step was 0.96 fs. After incorporating a CN ion, no thermo-control was applied.

Because *ab initio* MDS is computationally very demanding, it is difficult to achieve true equilibrium in the feasible computation time. Hence, rough scans with a small number of plane waves were often employed to

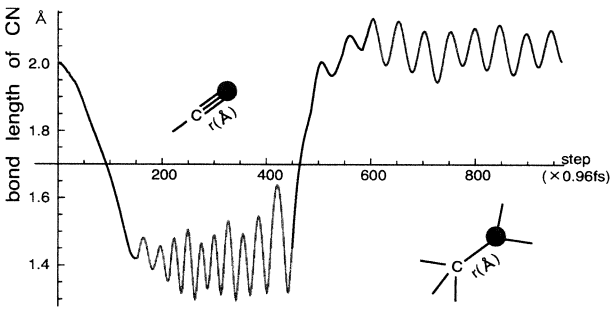


Figure 2: Time evolution of the bond length of CN in a dynamical simulation of a-Si. The bond length is initially oscillated around the bond length of the triple bond. After that, the bond length approaches that of the single bond, which is indicated by a red line.

grasp atomic processes quickly. Figure 2 is such a example of rough scan ($E_{\rm cut}$ = 130.0 eV).

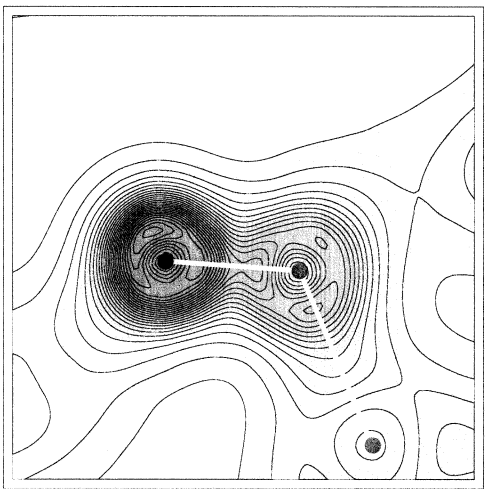
The time evolution of the CN bond length is shown in Fig. 2. Initially, the bond length is decreased to around 1.4 Å. Judging from the charge distribution, this configuration is identified as the triple bond in molecular analogy, even though the bond length is larger than that of molecules. The C site terminates the dangling bond, as a H atom does in a-Si:H. This is what we expected before. In this case, the N atom has no bonding to the nearest neighbor Si atoms.

However, it was our surprise to see that this configuration was not absolutely stable. On the course of time, the amplitude of the oscillation of the triple bond is increased. This implies instability. At 460th time step, the bond length is abruptly increased, reaching about 2.1 Å. After that, the oscillation of the CN is stabilized. In this configuration, the N atom has bonds to two nearest neighbour Si atoms, in addition to the original bond to the C atom. We identified this form as the single bond C−N from the charge distribution, even though the bond length is largely deviated from that of molecule (∼1.47 Å[10]). The charge distribution around this CN bond is shown in Fig. 3. This figure clealy shows the covalent character of N-Si bond as well as C-Si and C-N bonds.

The value of bond length is evaluated more accurately by increasing the cutoff energy for planewave expansion. By increasing the cutoff energy to 316.7 eV, we obtained those values listed in Fig. 4. These values of the bond length are much closer to those of molecular analogues.

In addition to the single bond, we found another form, the double bond C=N by starting from the triple bond. In this form, the bond length is 1.32 Å. The energy gain of the double bond is relatively small, 0.146

(a)



(b)

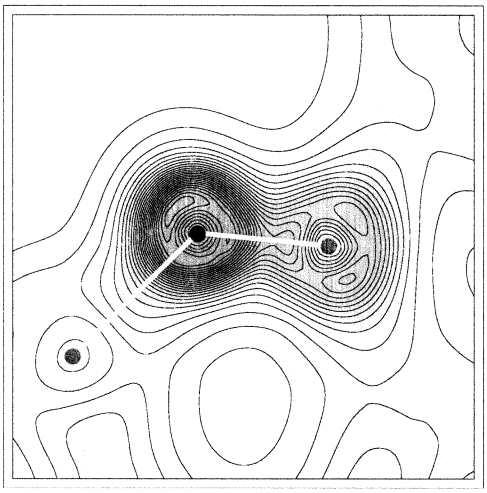


Figure 3: Charge distribution of the single bond C−N. A green circle represents Si, a violet circle C, and a red circle N. The charge density is plotted in a range from 0 to 3.58 $el/\text{Å}^3$ with dividing by 30. (a) shows a cut plane containing a link Si-C-N, while (b) shows a cut plane containing a link Si-N-C.

eV, but is still more than the numerical uncertainty.

In Fig. 4, the features of these three bonds appearing in *a*-Si are compared to the original pure *a*-S. The energy difference is evaluated by taking the energy of the triple bond as the reference. The original pure *a*-Si has four gap states, which are originated from four defects of wrong bonds. All of three configurations of CN incorporation reduce the gap states by one, from which the role of passivation is evident.

Among three forms of CN bond, our calculation shows that the single bond is most stable. At the first glance, this is an unexpected result, because there is a prejudice from the chemical viewpoint that the triple bond C≡N should be very strong. However, in solids, not only the strength of individual bond but also the number of bonds involved influence the stability of the bonding configuration.

In the case of transition to the single bond C−N, at the expense of converting the strongest bond C≡N to a relatively weak bond C−N, the solid gains energy by forming new bonds to its nearest neighbors; two Si−C and two Si−N, bonds. The actual transition process involves further complications beyond the nearest neighbor region. Although many elemental processes are involved there, the net balance of processes is elimination of two Si−Si bonds. A simple evaluation of the energy balance by standard values of the bonding energies used in chemistry [10], shows that the configuration of single bond C−N gains energy by 1.49 eV. This value is close to the present result, 1.08 eV. A similar evaluation also shows that the energy gain of the double bond C=N is 0.25 eV. From this, it follows that it is energetically favourable for the CN unit to share more chemical bonds to the surrounding in *a*-Si.

4 DISCUSSION

We have seen that in *a*-Si a CN unit form a single bond, and that the bond terminates a dangling bond. More importantly, this CN unit connects a broken network of host atoms.

We should like to stress this new effect of CN incorporation, in contrast to the conventional effect of hydrogen incorporation in *a*-Si:H. The difference may be suitably described by using terminologies, i.e., network former and network modifier, introduced by Zallen [11]. The network former is a constituent of CRN, like Ge impurity in SiO_2 glass, while the network modifier is an atom breaking CRN, like Na ion in SiO_2 glass. In *a*-Si:H, although possessing a desirable role of termination of dangling bond, the H atom has no significance on the bonding configuration of the neighbors. CRN is still left as being broken at the site. In this respect, the H atom can be regarded as network modifier. The role of the CN incorporation is not only termination of a dangling bond, but also to connect the broken network.

Bonding type	bond length ●:Si ●:C ●:N	Energy difference [eV]	model calculation [eV]
Triple	1.25 Å	0	0
Double	1.32 Å	-0.146	-0.25
Single	1.49 Å	-1.083	-1.49

Figure 4: Comparison of three configurations of the CN bond in a-Si. During simulation, three types of CN bond are found, which correspond to single, double, and triple bonds in molecular analogy. The energy is shown by taking the total energy of the triple bond as the reference.

Therefore, in this case, CN can be regarded as network former.

This finding is interesting, in view of controlling the SW effect. One of the present authors, some years ago, proposed a model of this effect [12]. Many people believe that the SW effect is related to hydrogen in a-Si:H [13]. At variance with others, we found that occurrence of the SW effect is irrelevant to the presence of hydrogen. It is originated from the inherent defects of amorphous network.

It is our observation in computer simulations that a dangling bond often causes other defects in the vicinity. This gives rise to structural flexibility at a great deal. The structural flexibility is often associated with bistability of atomic arrangement. This bistability is the cause of light-induced degradation of conductivity [15]. Forming more complete fourfold-coordinated CRN reduces the chance for the bistability to occur. We think that this situation takes place in experiment of light irradiation of a-Si:CN.

5 SUMMARY

In the presented computer simulations, the stability of CN in amorphous silicon was observed to occur by different mechanisms than are generally accepted. Single bonded C−N was found to be more energetically favorable than triple bonded C≡N in an amorphous silicon network. The fourfold-coordination fraction of the CRN was found to increase with the introduction of single bonded C−N. This finding is consistent with our model for the SW effect, in which SW is caused by inherent defects in the CRN, which would be eliminated by a perfect fourfold-coordinated network, as realized in crystalline silicon.

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