Structural properties of amorphous hydrogenated silicon using *ab initio* molecular dynamics simulations

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Abstract. We have studied structural properties of amorphous hydrogenated silicon using *ab initio* molecular dynamics simulations. A sample was generated by simulated annealing using periodic boundary conditions with a supercell containing 64 silicon and 8 hydrogen atoms. The radial pair distribution functions for Si–Si, Si–H and H–H have been studied at 300 K and are found to be in good agreement with experimental data. Our results show that hydrogen saturates the dangling bonds and reduces bond strain. We also report existence of Si–H–Si bridge sites which are likely to play an important role in understanding the light induced metastability in this material.

Keywords. Amorphous hydrogenated silicon; radial distribution function; *ab initio* molecular dynamics; bond angle distribution.

1. Introduction

Amorphous hydrogenated silicon (*a*-Si:H) is an important material for the development of photovoltaic devices. However, it suffers from light induced metastable changes (the Staebler-Wronski effect) (Staebler and Wronski 1980) which are believed to lead to an increase in the number of defects and the associated increase in the number of localized states in the gap of the material which shortens the recombination time for electron–hole pairs (Street 1991). In *a*-Si:H hydrogen plays an important role in the passivation of the dangling bonds and reduction of the density of localized states. The light induced metastability seems to be closely linked with the anomalous diffusion of hydrogen and its proper understanding is a topic of much current interest. While several efforts have been devoted to understand this phenomenon, the situation is still far from clear (Yiping *et al* 1995). Here we present results of an *ab initio* molecular dynamics study of the structure of *a*-Si:H which shows the presence of weakly bonded bond centred (BC) H which could play an important role in the anomalous diffusion of H.

2. Method

We have used the Car-Parrinello (1985) method to study the structural properties of *a*-Si:H. The electron–ion interaction for Si was represented by the norm-conserving pseudopotentials of Bachelet *et al* (1982) with *s* and *p* non-locality in the Kleinmann and Bylander (1982) form. However, for hydrogen the actual $1/r$ potential was used. The wave functions were expanded in a plane wave basis with kinetic energy up

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to 12 Ry and $k = 0$ point was used for the Brillouin zone sampling. The equations of motions were integrated using the Verlet algorithm with a time step of 1.209×10^{-16} sec and electronic mass of 200. Periodic boundary conditions were imposed with a simple cubic supercell of side 10.862 Å which was kept constant throughout the simulation. The supercell contained 64 Si and 8 H atoms. The *a*-Si:H sample was prepared using simulated annealing starting with a random displacement of Si atoms on a diamond structure and H atoms on the BC sites. The sample was heated to 2200 K and equilibrated for roughly 5000 time steps. It was then cooled to 1000 K in steps of 200 K with roughly 2000 time steps at each temperature. Then the sample was cooled to 300 K in steps of 100 K with 1000 time steps for each temperature. At 300 K the sample was equilibrated for roughly 5000 time steps. After this the time averaged structural functions were calculated over a time span of about 5000 steps.

3.   Results and discussion '

3.1   *Radial pair distribution functions*

Figure 1 shows the time averaged radial distribution functions for Si–Si, Si–H and H–H. The Si–Si radial distribution function shows a sharp peak centred at 2.37 Å corresponding to the nearest neighbours and a broader peak at 3.72 Å related to next nearest neighbours in close agreement with the experimental values of 2.35 and 3.7 Å (Menelle 1987). The Si–H pair distribution function shows a sharp peak centred at 1.59 Å corresponding to nearest neighbours and broader peaks related to next and next
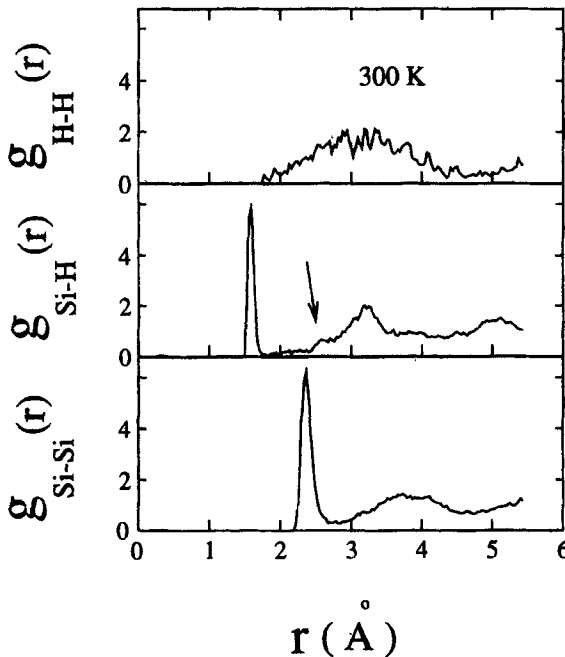

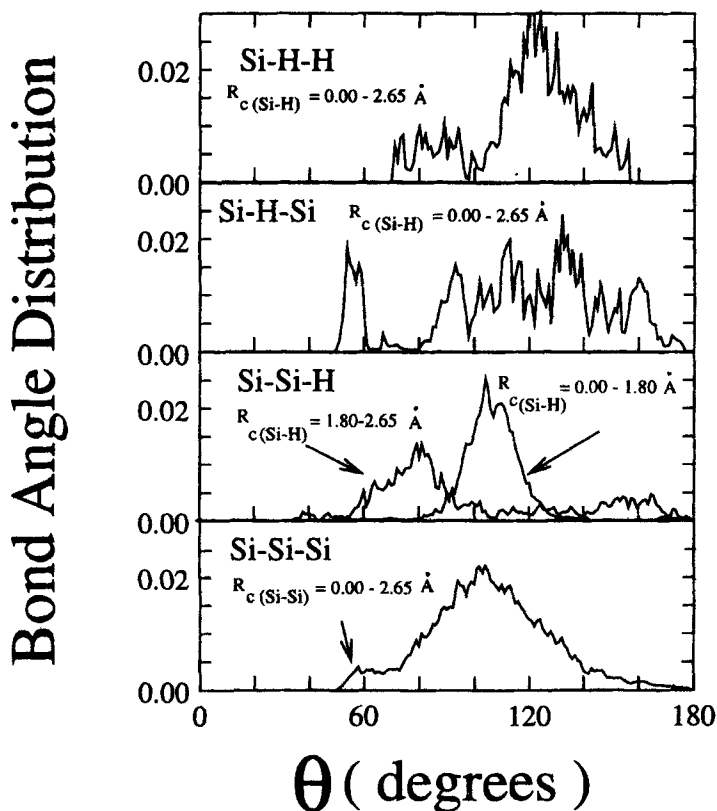**Figure 1.**   Radial pair distribution function for hydrogenated *a*-Si.

Figure 2. Bond angle distribution for hydrogenated *a*-Si.

to next nearest neighbours centred at $3\cdot18$ Å and $5\cdot25$ Å respectively. This also agrees well with the experimental values (Menelle 1987) of $1\cdot59$, $3\cdot1$ and $4\cdot95$ Å and the results of a previous calculation (Buda *et al* 1990, 1991). However, we obtained a shoulder at around $2\cdot50$ Å. This feature corresponds to a floating Si–H bond and is seen in the experimental data (Menelle 1987) but not in the earlier calculation (Buda *et al* 1990, 1991). The H–H distribution function is broad lying between 2 to 4 Å and therefore in our sample we do not have molecular form of hydrogen normally seen in device grade *a*-Si:H.

3.2 *Bond angle distribution*

Figure 2 shows the bond angle distributions. The cut-off radius for Si–Si was taken to be $2\cdot65$ Å i.e. just after the first peak in Si–Si radial distribution function. The cut-off radius for Si–H was also fixed to $2\cdot65$ Å as we were interested in the weak Si–H bonds. For Si–H bonding we used a minimum as well as a maximum cut-off. Only those Si–H pairs which were separated by a distance more than the minimum value and less than the maximum value are counted as bonds. The bond angle distribution for Si–Si–Si shows a broad peak centred around $108°$, showing a 4-fold coordination. But also

present is a shoulder at around 60° which indicates presence of Si atoms which are not 4-fold coordinated. Indeed the average coordination number (CN) of Si atoms is 4·28 when cut-off radius for Si–H bond is taken to be 2·65 Å. When this is reduced to 1·8 Å, the CN reduces to 4·18, but this also is significantly more than 4. Our analysis shows that in addition to 4-fold coordinated sites (71·7%), there are a large number of Si atoms which are 3-fold (3%), 5-fold (20·2%) and 6-fold (5·1%) coordinated. If the Si–H bond length is restricted to 1·8 Å, then the percentage of 4-fold coordinated sites increases to 79 predominantly at the expense of the 5-fold sites. Coordination number for hydrogen is very sensitive to the variation in cut-off radius for Si–H bond. The average CN of hydrogen is 2·10 when R_c(Si–H) is 2·65 Å, but it falls to 1·31 Å when R_c(Si–H) is reduced to 1·8 Å. But even this is significantly more than 1 indicating that H can form bonds with two or more atoms. We find that more than half of H atoms have two nearest neighbours within a radius of 2·65 Å. When R_c(Si–H) was kept at 1·8 Å, this number reduces to 30% but it is still significant. This also means that there are significant number of H atoms which are bound to one Si atom and are within 2·65 Å from another H atom. There are a significant number of Si atoms with 3 Si and one strongly bound H with bond length less than 1·8 Å. Also from figure 2 the distribution of bond angles between Si–Si bond and Si–H bond with bond length less than 1·80 Å is centred around 108°. This peak is relatively sharper than the corresponding peak for the angle between two Si–Si bonds. This indicates that hydrogen not only saturates the dangling bonds but also reduces bond strains. This is likely to lead to an increase in the band gap. The weak Si–H bonds with bond lengths between 1·80 Å to 2·65 Å show two peaks at 83° and 160°, while there are almost no bond angles near 108° showing that these bonds are not 4-fold coordinated. The presence of bond angles near 160° indicates presence of nearly linear Si–Si–H formations. The bond angle distribution for Si–H–Si has several peaks between 80° and 180° and one sharp peak at 60°. The peaks between 80° and 180° indicate that hydrogen has local minimum energy sites between two Si atoms not directly bound. Our simulations show that hydrogen spends more time in these energy pockets. It has been shown (Fedders and Drabold 1993) that the binding energy of H on such bridge sites is about 3 eV less as compared to a dangling bond site. Therefore this Si–H–Si bridge site can play an important role in the light-induced metastability (Street 1991; Prasad and Shenoy, to be published). Also H can have one Si and one H nearest neighbours with angle between the H–H bond and H–Si bond showing a peak at around 120 Å and a small peak near 80°. These H–H bonds are weak with bond lengths more than 1·80 Å as can be seen from figure 1.

4. Conclusions

Hydrogen is observed to play an important role in the saturation of the dangling bonds and in the reduction of bond strain in *a*-Si:H. Also a fraction of H atoms occupies bridge site between two Si atoms which are not directly bound. Such weakly bonded H could be significant in understanding the anomalous diffusion of H and the light induced metastability. Our results of the radial distribution function are in very good agreement with experiments and show an improvement over the previous calculations. The effect of such distribution of H on the electronic properties of *a*-Si:H and the dynamical behaviour of H are currently under study and will be published separately.

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