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Structure of hydrogenated amorphous silicon from *ab initio* molecular dynamics

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We have generated a model of hydrogenated amorphous silicon by first-principles molecular dynamics. Our results are in good agreement with the available experimental data and provide insight into the microscopic structure of this material. The calculation lends support to models in which monohydride complexes are prevalent, and indicates a strong tendency of hydrogen to form small clusters.

Hydrogenated amorphous silicon (*a*-Si:H) is an important material for electronic applications, yet its properties to a large extent are not fully understood. Much effort has been devoted to determining its structural properties, which is a prerequisite for further progress. The short-range order of this material has been studied using several experimental techniques including neutron scattering,[1-3] extended x-ray-absorption fine structure,[4] and infrared absorption.[5] In particular, infrared spectroscopy identifies hydrogen in *a*-Si:H as bonded in different complexes. Monohydride (Si-H), dihydride (Si-H_2), trihydride (Si-H_3), and polymeric $(\text{Si-H}_2)_n$ configurations have been detected.[5] Unfortunately, quantitative predictions on the relative concentration of different Si-H_n groups are difficult to extract from vibrational spectroscopy and strongly depend on the hydrogen concentration and preparation conditions. Furthermore, data obtained by different probes can provide inconsistent pictures,[6] leaving room for controversies. Other issues concern the distribution of hydrogen within the sample and the characterization of structural heterogeneity in *a*-Si:H. These questions have been studied mainly by multiple quantum nuclear magnetic resonance (MQ-NMR),[7] and small-angle x-ray scattering.[8]

This experimental effort has not been accompanied by a comparable theoretical understanding, thus our picture of the *a*-Si:H structure is still somewhat controversial. This state of affairs is due, in part, to the lack of a reliable theoretical model of the *a*-Si:H network, since it is difficult to achieve an accurate description of the interatomic interactions and of the delicate chemical competition between the two species. The recent development of *ab initio* molecular-dynamics techniques[9] circumvents these difficulties. One can now calculate interatomic forces from stat-of-the-art quantum-mechanical calculations in a practical manner. This scheme is parameter free and suited to describing systems, such as covalent semiconductors, where chemical bonds may break and form as a consequence of the atomic motion.

In this paper we report the analysis of an *a*-Si:H network generated by means of the computer-simulation approach. We have considered an atomic H concentration of ~11%, typical of a device quality material. The average structural properties of our model are in good agreement with the results of several experimental probes of the short-range order. We also resolve some of the outstanding issues by finding that (1) the most stable H configuration consists of monohydride (Si-H) complexes, in which the H atom is bonded to an otherwise threefold coordinated Si atom. (2) In agreement with the sophisticated MQ-NMR data reported by Baum *et al.*,[7] we find that small clusters of H atoms form. (3) The complex

Si-H-Si with H in a bridging position is found to be metastable.

We represent the interaction of the valence electrons with the ionic cores by first-principles norm-conserving pseudopotentials[10] for both H and Si, while the electron-electron interaction is treated within the local-density-approximation framework.[11] The parameters we used in the present simulation are the same as those previously adopted to study proton diffusion in crystalline Si,[12] apart from an increased energy cutoff of 12 Ry for the plane-wave expansion of the Kohn-Sham orbitals. Such a high cutoff is necessary for an accurate description of the liquid and amorphous phases of pure silicon.[13] We have simulated a system of 64 Si plus 8 neutral H atoms, with simple cubic periodic boundary conditions. The density was fixed at the value of crystalline silicon.[14] We have generated the present a-Si:H structure by rapid quenching from a well-equilibrated liquid, which was obtained by heating a crystalline Si sample containing H atoms originally placed at interstitial tetrahedral positions.

The structural evolution during the quenching process is illustrated in Fig. 1, where the upper pair of panels refers to a liquid at 1800 K, the middle pair to a supercooled system at 1200 K, and the lower pair to an as-quenched amorphous structure at 300 K. Each pair of panels shows the Si-Si and Si-H partial pair-correlation functions $g_{\text{Si-Si}}(r)$ and $g_{\text{Si-H}}(r)$, respectively. The H-H partial pair-correlation function is not shown, since the statistics are very poor, owing to the very limited number of H in the system. At 1800 K the system is a liquid with a marked diffusive behavior.[15] The $g_{\text{Si-Si}}(r)$ closely resembles that of pure liquid Si (Ref. 13) with a coordination number close to 6. The Si-H correlation function exhibits a strong peak with about 1.3 neighbors. This reflects the tendency in the liquid to form quite stable monohydride complexes.

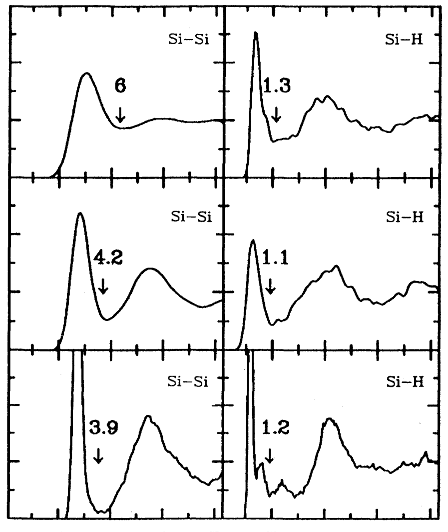

FIG. 1. Si-Si and Si-H pair-correlation functions at different temperatures in the quenching procedure. Upper panel pair: liquid hydrogenated silicon (l-Si:H) at 1800 K. Middle panel pair: supercooled l-Si:H at 1200 K. Lower panel pair: a-Si:H at 300 K. Averages are taken over a simulation time of about 0.2 psec. The coordination numbers shown are obtained by integrating the correlation functions up to the first minimum as indicated by the arrows.

The temperature of the system was successively reduced to 1200 K with a cooling rate of 5×10^{14} K/sec. At this temperature the system is supercooled and the diffusivity was about a factor of 4 smaller than at 1800 K. The $g_{\text{Si-Si}}(r)$ appears to be significantly more structured than at 1800 K with a coordination number of 4.2, which suggests a tendency to form tetravalent bonds even at high T. Finally, after a further and slower cooling at about 2.5×10^{14} K/sec, the system was brought to room temperature. Here diffusion ceases and a very clear fourfold Si-Si coordination emerges, indicating that the Si atoms have formed a tetrahedral network. The Si-H pair-correlation function exhibits some minor structure between the first two main peaks. Correspondingly, the average Si-H coordination is 1.2, i.e., quite close to its value in the liquid state, indicating that not all the H atoms are singly bonded to Si atoms. Indeed, a detailed analysis reveals that in this sample two Si-H-Si bridge configurations with weak Si-H bonds are present, in addition to well-defined monohydrides.

The coordination defects that have been quenched in the Si network by our rather abrupt cooling rate are shown in Table I. These appear to be numerous. After having equilibrated the sample for 1.5 psec, we have performed an additional annealing cycle to reduce the strain. This consisted in taking the system to 1100 K and then after 1 psec of equilibration, cooling it back to 300 K. The rate of temperature change in this process was similar to that used earlier. This additional annealing cycle led to a substantial cohesive energy grain of ~34 meV/atom. The resulting pair-correlation functions are shown in Fig. 2 together with experimental results. The $g_{\text{Si-Si}}(r)$ is hardly changed and shows a coordination number of 3.9 ± 0.1. A Si-Si coordination number slightly smaller than four can be related to the fact that some of the fourfold silicon atoms have one H atom in their first coordination shell. Such a slight reduction, from four, of the Si-Si coordination number in hydrogenated samples is also borne out by the experiment.[4]

More significant changes can be seen in $g_{\text{Si-H}}$, where the first peak becomes more sharply defined and which has

TABLE I. Atomic coordination number for the sample before and after the annealing cycle. T_n ($n=3,4,5$) is the number of silicon atoms with n silicon neighbors. T_n^* indicates that one of the counted bonds is a Si-H bond. The number of Si-Si and Si-H weak bonds (WB) given in the last two columns refers to pairs of neighboring atoms whose relative distance varies so much in time that they can move into and out of the first coordination shell.

	T_3	T_4	T_4^*	T_5	T_5^*	Si-Si WB	Si-H WB
Before annealing	0	45	5	2	2	6	4
After annealing	0	48	6	1	1	6	0

coordination number of exactly 1. This reflects the fact that two Si-H-Si bridge configurations have been annealed out and that now only well-defined monohydride groups are present in the sample. It is tempting to suggest that these metastable states can be populated during the hydrogenation process, with H sitting at weak bond sites, and that these states then decay into more stable Si-H groups after suitable relaxation processes. These metastable configurations are also likely to play a role in the H diffusion process, where they can lower the barrier for migration. These changes in the $g(r)$ also reflect a reduction in the number of defects as shown in Table I. Here we describe the atomic coordination for the as-quenched sample and after the annealing cycle. T_n ($n=3,\ldots,5$) refers to Si atoms and T_n^* includes H in the total count of neighbors. The bonding cutoff distances for Si-Si and Si-H are defined by the first minimum in their respective correlation functions. Weak bonds (WB) refer to pairs of neighboring atoms whose relative distance varies so much in time that they can move into and out of the coordination shell. The table shows that the main effect of the annealing was the disappearance of the Si-H WB associated with Si-H-Si states.

Experimental neutron-diffraction data,[2] are reported in Fig. 2. In contrast to Fig. 1, we also show the theoretical H-H correlation function here, but not the experimental one owing to the very large noise of this set of data. The overall agreement between theory and experiment is very good, the main discrepancy being a small outward shift of the first peak of the the theoretical Si-H correlation function. With our choice for the H pseudopotential, a similar error is also found in the equilibrium separation of the Si-H molecule. Correspondingly, the Si-H bond-stretching frequency is underestimated by $\sim$10%.

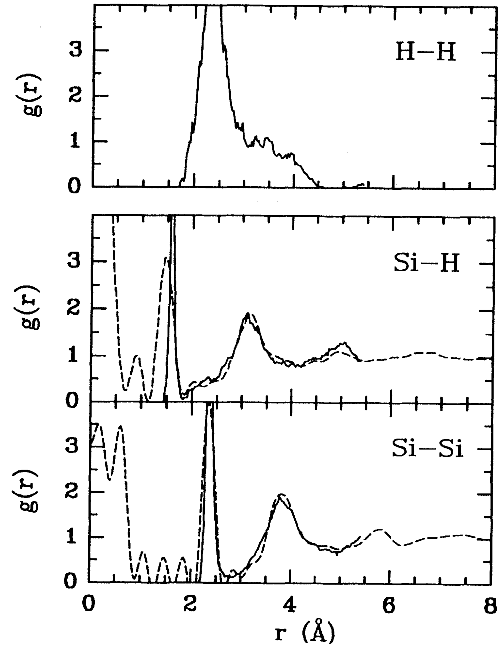

FIG. 2. Theoretical (solid line) and experimental (dashed line) partial pair-correlation functions of *a*-Si:H. The experimental functions correspond to a sample containing 12% atomic H (Ref. 2). The oscillatory behavior shown by experimental curves at small *r* is related to truncation errors in inverting the scattering data.

As we have already remarked, only monohydride groups are present in our annealed sample, supporting the idea that Si-H$_2$ and other polyhydride groups have a rare probability of occurrence in this regime of hydrogen concentrations. Similar conclusions were also drawn from neutron-scattering data.[2,3] Six out of eight Si atoms that take part in the Si-H bonds are in an sp^3 configuration and therefore are coordinated with three other Si, whereas one Si is in a fivefold coordinated state, since it is also bound to four Si atoms (T_5^* in Table I). The remaining Si has three tight and one weak Si-Si bonds.

The H-H correlations in our simulation are affected by large statistical errors associated with the very small number of H atoms present in our sample. However, the pronounced peak around 2.5 Å in the H-H pair-correlation function in Fig. 2 indicates clustering effects. This feature is enhanced by the annealing cycle. A detailed investigation revealed that this peak is related to the presence of two H clusters consisting of four atoms each. One of the two clusters resides in a microcavity where roughly two Si atoms are missing. H clusters of similar size have been detected in experiments performed on device quality *a*-Si:H samples.[7] In Fig. 3 we show a portion of the sample that clearly illustrates this kind of structure.

When comparing our simulation with experiment, one must be cautious in view of the very limited size of our sample and of the preparation conditions which are different from those used in real experiments. Periodic boundary conditions on small samples and rapid quench can induce significant distortions in the distribution of the

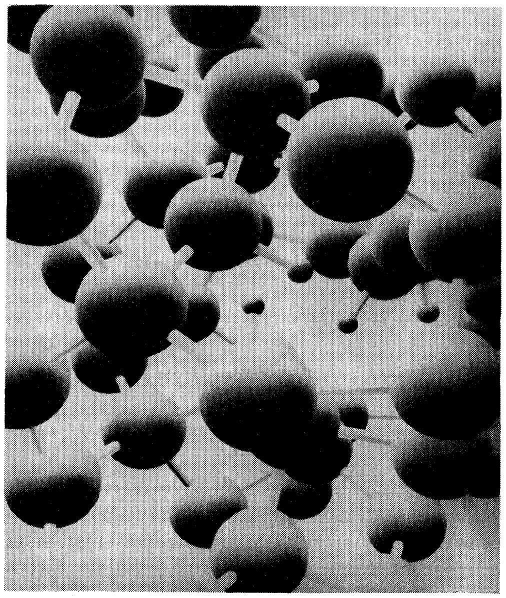

FIG. 3. Instantaneous configuration of the *a*-Si:H computer model. The big balls are silicon, the small ones hydrogen atoms. A microcavity containing a cluster of four hydrogen is clearly visible in this picture.

defects. Nevertheless, the excellent agreement between theory and several experimental findings encourages confidence that we have captured the essential features of the structure. More subtle questions like the exact concentration of the different defects and their role in determining the electrical properties of *a*-Si:H must await further and more extensive calculations.

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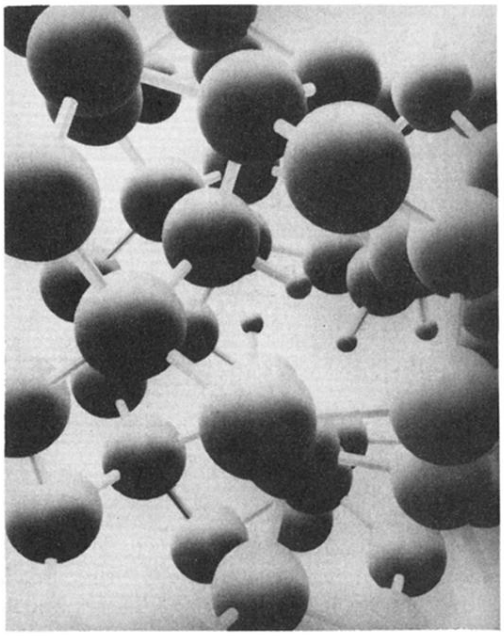
[14] A density of 2.45 g/cm^3 (to be compared with 2.42 g/cm^3 of crystalline silicon) has been reported by A. Menelle in Ref. 2 for an amorphous sample containing 12% H.

[15] The computed self-diffusion coefficient for Si at 1800 K is $D_{\mathrm{Si}} \simeq 1.2 \times 10^{-4}$ cm^2/sec.



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