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Correlations between higher-order rings and microvoids in hydrogenated amorphous silicon

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ABSTRACT

In this paper we report the structure of voids in several thousand atom models of hydrogenated amorphous silicon. The models are produced by jointly employing experimental information from Smets and coworkers [1] and first principles simulations [2]. We demonstrate the existence of a useful correlation between the presence of large irreducible rings and the voids in hydrogenated amorphous silicon networks. Molecular hydrogen is observed in the models, and discussed.

INTRODUCTION

Hydrogenated amorphous silicon a -Si:H is an important material having applications in solar cells [3], thin film transistors [4], position detection sensors [5], light emitting diodes [6], memory switching devices and other uses [7]. The network structure of the material is characterized by the presence of various defects that play a decisive role to determine its electronic and optical properties of the material [7]. While coordination defects are important, so too are extended inhomogeneities, such as voids, which constitute an important part of the network morphology at high concentration of hydrogen. The voids introduce density fluctuations that may be detected experimentally via small-angle X-ray scattering (SAXS) [8] or similar experiments that can probe electronic density fluctuations in the sample. Likewise, the concentration and the evolution of hydrogen in the network can be obtained via secondary-ion mass spectrometry (SIMS) [9]. Experimental methods, such as, calorimetry [10], multiple-quantum nuclear magnetic resonance [11], and infrared absorption spectroscopy [1, 12, 13] provide evidence of the presence of microvoids with diameter in the range of few nanometers (1.0-4.0 nm) depending on the hydrogen content, the history and the method of sample preparation, and the resolution of the measurements. While these measurements provide evidence of the presence of voids and their approximate dimension, the nature and structural features associated with the voids are quite unclear. SAXS data are generally interpreted within the Guinier approximation [14], and is valid for inhomogeneous systems in the dilute limit of the scatterers with a nanometer resolution. Thus, it is instructive to address the problem via direct simulations of voids by developing models involving several nanometers in size using accurate density-functional calculations.

In this short paper, we summarize the results from our recent work on computational modeling of voids at high concentration of hydrogen. To this end, we develop a new hydrogenation scheme by using experimental infrared absorption data on film mass density from Ref. [1], which is then coupled with *ab initio* interactions to generate realistic configurations of

a-Si:H at different concentration. By analyzing the ring structure and the fluctuation of the local (mass) density in the network, we have been able to establish that the presence of large rings and voids is intimately correlated. The approximate size of the voids is obtained by calculating the average ‘radius’ of the irreducible rings that have hydrogen atoms bonded to the ring as mono- and dihydrides. Likewise, the shape of the voids are deduced via the Gaussian approximation of the atomic surfaces near the ring boundary of the atoms

THEORY

Ab initio modeling of voids is difficult due to the nanoscale structure of the voids. For realistic simulation of voids, the size of the system must be at least several nanometers for the voids to form in the network. This translates into a model of several thousand atoms, which is difficult to obtain from direct *ab initio* calculations. Since amorphous silicon is not a glass, the problem is further complicated as the conventional melt-quench approach is unsuitable for simulating amorphous Si:H via molecular dynamics simulations. Most of the current approaches rely on the use of previously built models of amorphous silicon in conjunction with an *ad hoc* hydrogenation scheme to generate hydride configurations [2]. The reliability of *a*-Si:H models obtained from such an approach largely depends on the realism of the hydrogenation scheme, and the extent to which it can incorporate hydride configurations that are consistent with experimental data. At its simplest, this typically involves the addition of H atoms near the dangling bonds (that mimics hydrogen passivation in experiments), and is followed by annealing at moderately high temperature. The latter provides the necessary thermal ‘boost’ that enables the H atoms to migrate through the phase space in search for energetically favorable sites and to produce the characteristic morphology for a given concentration of hydrogen. H is surprisingly mobile in *a*-Si:H [15], and these dynamical effects are especially important in doping [16], but also relevant to voids, and the presence of atomic or molecular H at the internal surfaces or in the free volume of the void.

The hydrogenation scheme that we offer here is based upon experimental information from infrared absorption spectroscopy. In a recent communication, Smets *et al.* [1] have studied *a*-Si:H via infrared absorption spectroscopy. By studying the film mass density of hydride configurations at different concentration, they arrived at the conclusion that the microstructure of *a*-Si:H at high concentration (>14% H) is characterized by the presence of voids, whereas at low concentration vacancies play a dominant role. Based on the analysis of IR data, these authors have proposed the existence of vacancy configurations by introducing a hydrogen incorporation/nanoscale order parameter to explain the variation of film mass density and the high and low frequency vibrational stretch modes (H/LSM) with concentration as observed via infrared absorption spectroscopy. Motivated by this experimental observation, we develop a hydrogenation scheme that is consistent with the observed IR absorption data. We begin by incorporating vacancy configurations as suggested by Smets *et al* [1]. A schematic diagram for each of the configurations is shown in figure 1. Hydrogenation proceeds via the addition of H atoms near the dangling bonds, which is then followed by the incorporation of mono-, di-, and tri-vacancies randomly in a prebuilt *a*-Si network that are consistent with the IR absorption data. The resulting structure is then annealed at 800-1000K for several picoseconds and is brought down to the room temperature. The final structure is obtained via total-energy relaxations of the hydride configurations using the conjugate gradient method. Throughout the calculation, we

have used first-principles density-functional code SIESTA [17]. Below, we present results for a 4756-atom model of *a*-Si:H that consists of 20% H atoms.

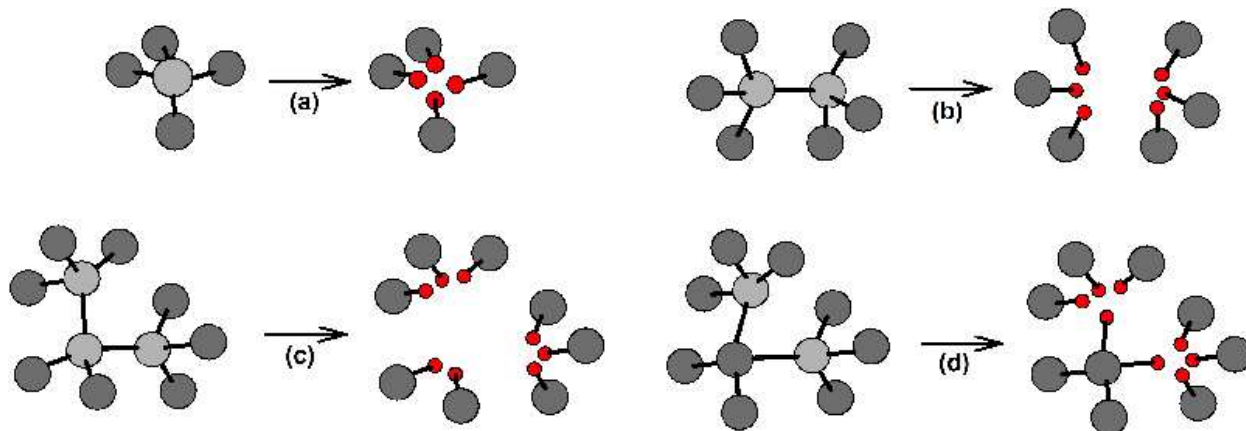


Figure 1. (Color online) Vacancy configurations (VC) used in the hydrogenation scheme for the present work.

DISCUSSION

We begin by presenting the pair distribution functions (PDF) of the amorphous hydride configuration. While the PDFs provide only scalar information at the two-body level, and cannot be used to characterize a three-dimensional structure uniquely, it is necessary to ensure that the incorporation of the vacancy configurations mentioned above do not affect these correlations adversely. In figure 2, the partial pair distributions of Si-H and H-H are presented for the model with 20% H. The results show the typical features of *a*-Si:H. The H-H correlation shows the presence of hydrogen pairs that separated by a distance of about 0.8 Å. For the model with 20% H, 10 such pairs have been realized within a distance of 0.8-0.83Å, which signify the presence of molecular hydrogen (H₂).

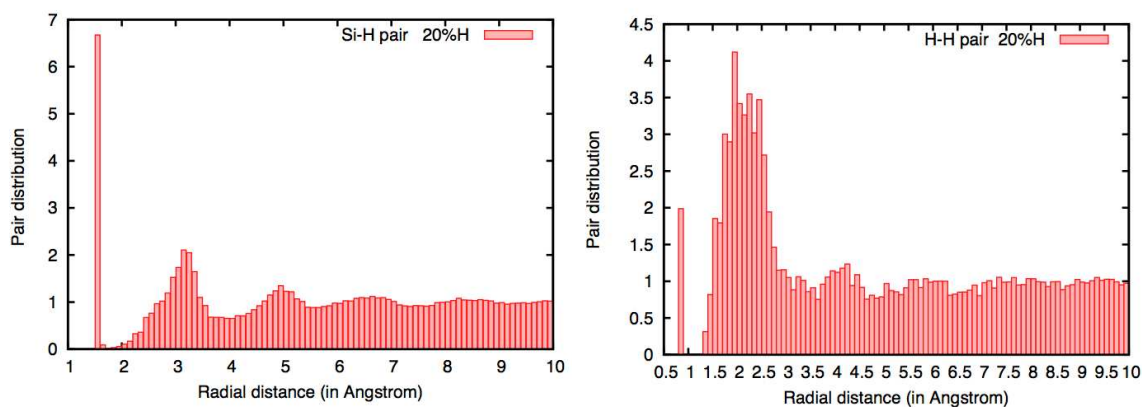


Figure 2. (Color online) Silicon-hydrogen (left) and hydrogen-hydrogen (right) pair distribution functions. The first peak in the H-H pair distribution near 0.8 Å shows the presence of H₂ molecules.

In figure 3L, we plot the fractional number of irreducible rings $N(r)$ versus the size of the rings (r). Irreducible rings represent the topological connectivity of the network and depend on the coordination number of the atomic species (and the dimensionality of the space). An irreducible ring of size n is defined as a minimal, self-avoiding, irreversible path that starts and ends at the same atomic site in n steps. A ring is irreducible in the sense that no shorter paths exist. Stated otherwise, the ring cannot be partitioned into a smaller set of rings [18]. In amorphous silicon, the ring distribution is mostly dominated by the presence of 5-, 6- and 7-member rings. However, the passivation of α -Si by hydrogen changes this distribution due to the terminal nature of the silicon-hydrogen bonding. Experimental data from infrared absorption spectroscopy show that at high concentration of H, a significant number of Si atoms is bonded to H atoms to forming mono-, di- and tri-hydride configurations [19]. This reduces the connectivity of the silicon atoms, which leads to the formation of large ring structure in the network. Infrared absorption experiments [19] and recent theoretical works [20] clearly indicate the presence of long chain structure in α -Si:H, which is characterized by the presence of H atoms bonded to the chain atoms (Si) as mono- and dihydrides. An example of such a configuration is presented in figure 3R that consists of 16 Si atoms with 8 H atoms bonded to the ring atoms. The chain represents a 16-member irreducible ring, and has a root-mean-square (RMS) radius 4.54 Å. A structural analysis of the irreducible rings suggests that the rings with a size of 9-12 atoms with mono- and dihydride bonding configurations attached to the ring atoms are the most likely candidates that encircle the void regions. Thus, the presence of larger rings provide an indicator of open space or void region, which can be used to identify voids and molecular hydrogen in the network.

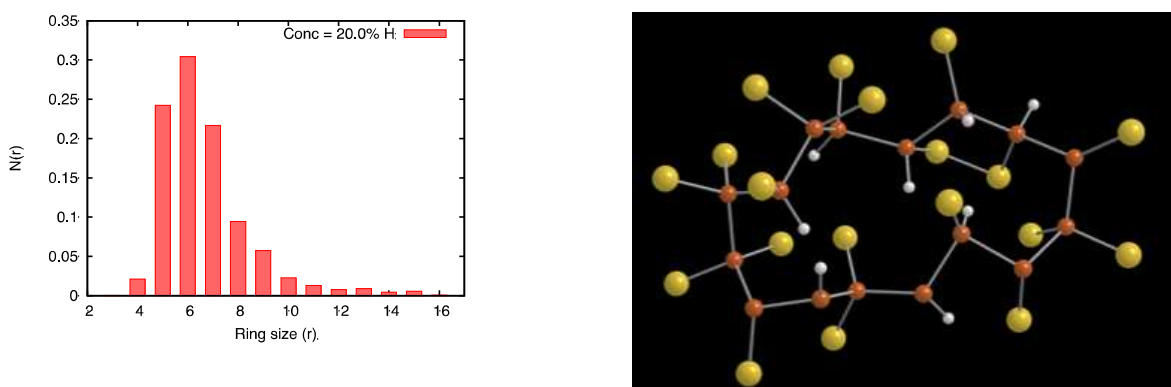


Figure 3. [Color online] (Left) The normalized ring distribution versus ring size for the model with 20% H. (Right) A chain structure representing an irreducible ring consists of 16 Si atoms with several Si-H bonds attached to the ring. The RMS 'radius' of the ring is 4.54 Å with several H atoms nearby. For visual clarity, only the atoms bonded to the chain/ring atoms are shown here.

To illustrate the connection between the microvoids and the long chain structure in a network, in figure 4L we have plotted a 12-member ring structure along with a hydrogen molecule near the center of the ring. The RMS radius of the ring is found to be 3.7 Å, and the surrounding silicon-hydrogen complex shown in the figure has a radius of 5.5 Å. Silicon and hydrogen atoms are shown in yellow/brown (ring Si) and red, respectively. The region

surrounding the H₂ molecule with an outer radius of 5.5 Å constitutes a microvoid region. This is shown in figure 4R by enveloping the atoms within the shell of radii $r=3.7$ Å and $r+dr = (3.7+1.8)$ Å with a three-dimensional Gaussian function. This Gaussian broadening clearly reveals the void structure within the complex with several protruding H atoms on the surface of the voids. The brown patch on the atomic surface in figure 4R indicates the surrounding ring structure as shown in figure 4L. Thus, a void region can be identified by calculating the large ring structure and constructing the region that defines the skin of the ring structure with a skin length $dr = R_{SiH} = 1.5-1.7$ Å.

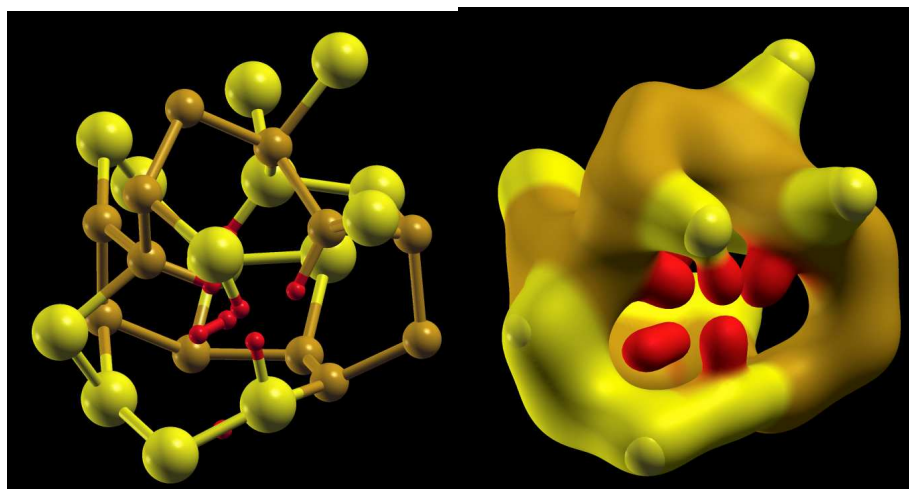


Figure 4. [Color online] (Left) An irreducible ring consists of 12 Si atoms (brown) with a hydrogen molecule near the center of the ring. The RMS 'radius' of the ring is about 3.7 Å. Silicon and hydrogen atoms are shown in yellow/brown and red, respectively. (Right) The void region surrounded by the 12-member ring as shown in the left. The Gaussian isosurface associated with the ring and the neighboring atoms are drawn to visualize the void region.

CONCLUSIONS

We present a new hydrogenation scheme to generate large hydride configurations of amorphous silicon to study the relation between microvoids and large ring structure in a-Si:H. Structural analysis of the irreducible rings at high concentration suggests that the network is characterized by the presence of large chain structure with several hydrogen atoms bonded to the chain atoms as mono- and dihydride configurations. This observation is consistent with the experimental results obtained via infrared absorption spectroscopy. At high concentration, large rings appear in the network. These rings tend to form near the microvoid regions, and have a planer radius of 3.5 Å to 5.0 Å depending on their size. While the presence of a large irreducible ring is not a sufficient condition for the voids to materialize in a network, it is a necessary condition for the voids to exist. Analysis of ring structure thus provides a simple way to identify the regions in a large network where voids or microvoids appear. The approximate shape of the microvoids can be obtained by the Gaussian approximation of atoms near the ring boundary.

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