

## Voids in Hydrogenated Amorphous Silicon: A Comparison of *ab initio* Simulations and Proton NMR Studies

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### ABSTRACT

Recently, a new hydrogen NMR signal has been observed in a number of PECVD prepared hydrogenated amorphous silicon (a-Si:H) films of varying quality. It is speculated that the signal is the consequence of a dipolar-coupled hydrogen pair separated, on average, by  $1.8 \pm 0.1$  Å. To elucidate the possible bonding configurations responsible for the NMR data of ref. [1], we have used *ab initio* simulation methods to determine a set of relaxed structures of a-Si:H with varying void sizes and H-concentrations. Models containing two isolated hydrogen atoms indicate a preferred H-H distance of approximately 1.8 Å when the two atoms bond to nearest neighbor silicon atoms. This separation also occurs for models containing small, hydrogenated voids, but the configurations giving rise to this H-H distance do not appear to be unique. For larger voids, a proton separation of about 2.4 Å is seen, as noted previously [2]. There appears to be consistency between the computed structures and the NMR data for configurations consisting of isolated hydrogen pairs or for clusters of an even number of hydrogen atoms with the constraint that the average H-H distance is 1.8 Å. In this paper, we will discuss the most probable bonding configurations of clustered hydrogen based upon the extent of the NMR data and simulated structures.

### INTRODUCTION

The microstructure of hydrogenated voids in a-Si:H, and their potential role in the Staebler-Wronski effect, are not well understood. Early nuclear magnetic resonance (NMR) studies on films prepared by plasma enhanced chemical vapor deposition (PECVD) revealed that hydrogen occurs in isolated and clustered environments with a small fraction of H<sub>2</sub> molecules existing in larger voids [3]. The intuitive idea of a hydrogenated divacancy gained support when multiple quantum NMR studies on PECVD films showed evidence of clusters of six hydrogen atoms [4]. Recently, a new hydrogen NMR signal has been observed by Bobela *et al.* in a number of PECVD prepared a-Si:H films [1]. It is speculated that the signal is the consequence of a dipolar-coupled hydrogen pair separated, on average, by  $1.8 \pm 0.1$  Å. However, more complex hydrogen configurations, such as those resulting from hydrogenated voids or polysilane like chains, (SiH<sub>2</sub>)<sub>n</sub> can also explain the sometimes unusual dipolar-dipole powder patterns that have consistently emerged in a number of a-Si:H films. To elucidate the possible bonding configurations responsible for the NMR data of Ref. [1], we have used *ab initio* simulation methods to determine an ensemble of structures of a-Si:H with varying void sizes and H-concentrations. Studies are still underway as to whether or not the configuration responsible for this H-H separation is associated with the Staebler-Wronski effect (SWE).

This work also addresses the preliminary results for the kinetics of hydrogen molecules,  $H_2$ , when they form in voids. Recent studies by C. Longeaud have linked the interstitial  $H_2$  trapped in the voids of a-Si:H with metastability [5]. Although the existence of  $H_2$  in a-Si:H has been well-documented by NMR experiments, Ref [6], the exact location of these entities within the network and its relation to the SWE is still a mystery.

## MODELS AND METHODS

We studied different configurations of a-Si:H models with varying concentrations of hydrogen and void sizes in them. Starting with two defect free CRN models of amorphous silicon of 216 atoms and 64 atoms, silicon atoms are removed and spheres of radii of about 2-6 Å are cut and voids are created which results in dangling Si bonds in the interface of the void and the CRN. These bonds are then terminated with hydrogen atoms at a Si-H distance of 1.5 Å and then the system is annealed at a temperature of 700°K and 300°K. Finally, a conjugate gradient relaxation is applied to reduce the forces to almost zero. The model of a-Si:H with a divacancy is created by removing two silicon atoms which are nearest neighbors and terminating the resulting dangling Si bonds with hydrogen. We generated 4 models with a divacancy at different sites in a network with 62 Si atoms and 6 H atoms and 214 Si atoms and 6 H atoms. Models of a-Si:H with larger voids are created by cutting spheres of radii 4-6 Å and removing 8, 16, 32 and 64 Si atoms. The interface Si dangling bonds are then passivated with hydrogen.

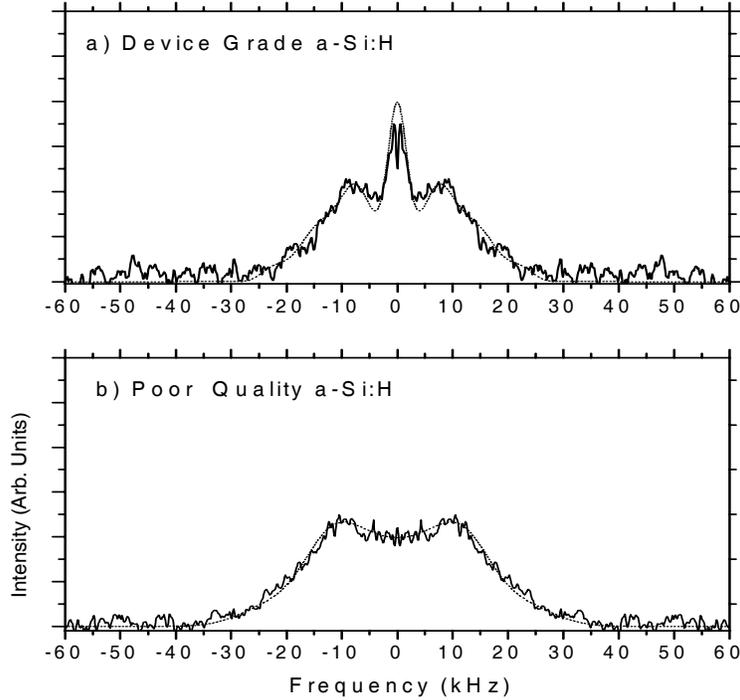
Another set of models was generated where the H atoms are put at a distance of  $\sim 3$  Å from each other and at a distance of at least  $\sim 2$  Å from the silicon atoms so that they are not bonded to the silicon atoms. These hydrogen atoms would be referred to as mobile H atoms and are introduced to study how the network evolves with the introduction of the H atoms and to study how Si-H bonds are formed. All the models are equilibrated at temperatures of 300°K and 500°K for 3ps.

In our simulations, we used SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) which is a DFT based first principles pseudopotential method based on Linear Combination of Atomic Orbitals (LCAO) [7]. SIESTA uses norm-conserving Troullier-Martins pseudopotentials [8] in its fully non-local (Kleinman-Bylander) [9] form. In this work, self consistent Kohn-Sham functional in the General Gradient Approximations (GGA) with the parametrization of Perdew, Burke and Ernzerhof [10] is used. Both double- $\zeta$  polarized basis sets (DZP) for silicon and hydrogen are used with two s and three p orbitals for the H valence electrons and two s, six p and five d orbitals for Si valence electrons.

## RESULTS AND DISCUSSIONS

Representative proton NMR spectra of dipolar coupled hydrogen pairs are shown in Fig. 1 for “device” grade (Fig. 1a) and “poor” quality (Fig. 1b) a-Si:H. The spectra differ only by the intensity of the central region, which constitutes the best clue as to the identity of the H system contributing to the lineshape. From the form of the spin-spin interactions of the dipolar coupled hydrogen system, the spectrum in Fig. 1 is most likely due to a cluster of hydrogen atoms whereby the nearest neighbor H atoms are separated by 1.8 Å and are less strongly coupled to their neighbors. An intuitive candidate is the hydrogenated divacancy, since the geometry allows for H separations of up a few angstroms, which would constitute a “loosely” coupled H-pair when compared to the nearest neighbor spacings. The dotted line represents a simulation of such

a geometry and does well to match the gross features of the NMR data. Other geometries cannot be ruled out. However evidence from multiple quantum NMR experiments do support the preferred cluster size of six atoms [4]. Figure 1b is reminiscent of the spectra presented in Ref. [1], where the interpretation of the data required the H-H distance to be 1.8 Å regardless of the broadening affects. For spectra with this characteristic shape, it is likely that the H-H pair is isolated from other clusters.

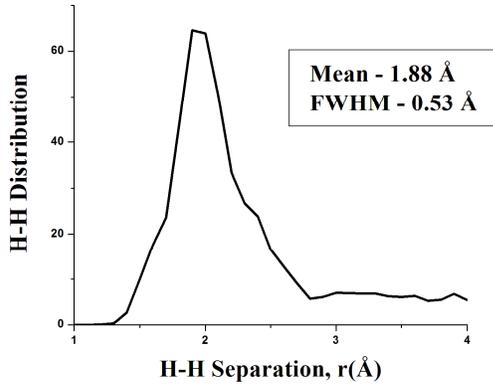


**Figure 1.** Proton NMR spectra of dipolar coupled hydrogen atoms in a) device grade and b) poor quality a-Si:H. Dotted lines denote simulations of the spectra, see text for details.

For the models with a divacancy with no dangling bonds present, the H-H distance is tracked for a Molecular Dynamics (MD) run for 3 ps. We observed a peak at a H-H distance of  $1.8 \pm 0.2$  Å for all the models. Although dihydride, ( $\text{SiH}_2$ ), structures giving a H-H separation of 2.4 Å as reported earlier [2] is present in some of the models, a mean H-H distance of  $\sim 1.8$  Å is obtained from two distinct scenarios: hydrogen connected to silicon atoms that are next nearest neighbors, a monohydride ( $\text{SiH HSi}$ ) configuration, and hydrogen clustering at the interface of the voids. The void surface comprises either  $\text{Si-H}_2$  or  $\text{Si-H}$  bonding configurations. Not only do ( $\text{Si-H H-Si}$ ) configurations contribute to a H-H distance of  $\sim 1.8$  Å, but H atoms from these configurations separated from H atoms in the adjacent dihydride configurations are responsible. However, there is no unique configuration responsible for the H-H distance of  $\sim 1.8$  Å.

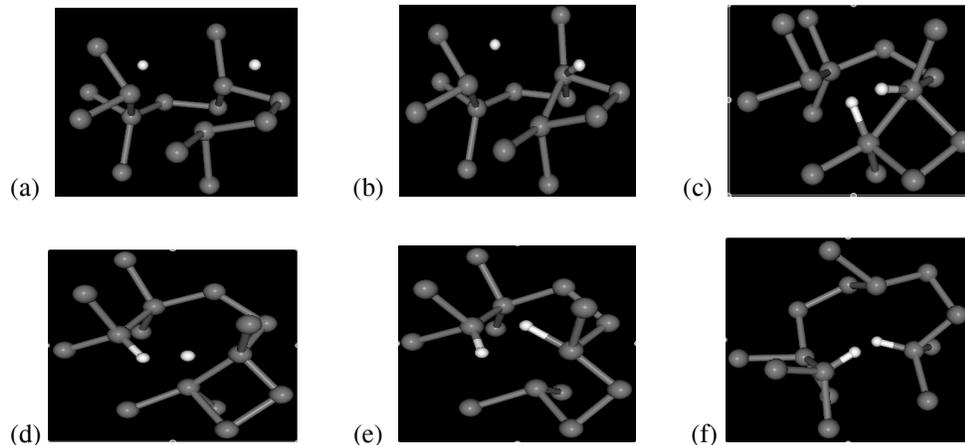
We performed similar studies on the models with larger voids. In these scenarios, a H-H separation of 2.4 Å consistently emerges where both complexes are formed. This result supports the physically intuitive idea that space constraints restrict the H atoms from assuming their natural separation of 2.4 Å. The reduced H-H distance is simply a consequence of clustering in small divacancy-like voids. A representative result for the distribution of H-H separation is shown in the Fig.2. The H-H separation is distributed about 1.8 Å with an FWHM of 0.53 Å.

This agrees very well with the proton- proton separation extracted from the NMR data in Fig. 1b by Bobela *et al.* [1].



**Figure 2.** Plot of H-H distribution vs. H-H separation for a divacancy like void with 214 Si atoms and 6 H atoms. MD simulation temperature is 700°K.

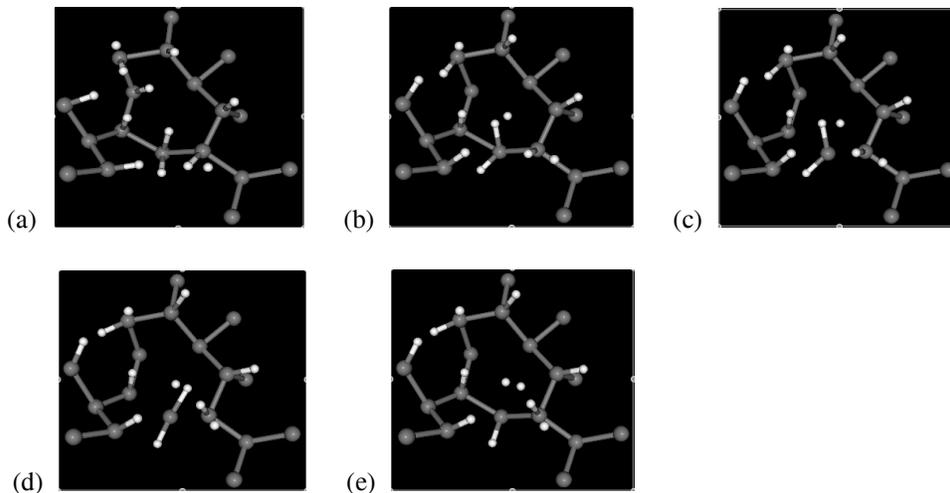
Similarly, for the models with unbonded H, a MD simulation is performed at 300°K and 500°K for 3 ps to let the H atoms form bonds on their own. We observed that the unbonded hydrogen atoms tend to form monohydride configurations in pairs. Four out of the six hydrogen atoms form monohydrides and cluster together whereas the other two are isolated Si-H bonds. In small voids like divacancies, it is observed that there is a tendency to form more monohydride configurations than dihydrides. Another complex where hydrogen bonded to silicon that are nearest neighbors is also formed. In these models, the H-H distance of  $1.8 \pm 0.2 \text{ \AA}$  is confirmed. Snapshots of the MD simulation showing the formation of a monohydride configuration is shown in Fig. 3. The hydrogen atom comes into the bond center whereby it breaks the Si-Si bond and sticks to one silicon. A dangling bond remains after the monohydride configuration has formed.



**Figure 3.** Creation of dangling Si bonds and formation of monohydride (SiH HSi) complexes at a particular site in a-Si:H with 62 Si atoms and 6 H atoms with a divacancy from *ab initio* MD simulation. H atoms are denoted by white color and Si atoms by dark color. (a) Mobile hydrogen atoms come towards a dangling bond, (b) one mobile H terminates the Si dangling Bond, (c) Si atoms become fivefold coordinated, (d) H comes between the bond center, (e) H atom breaks Si-Si bond and hops between Si, (f) H finally forms the (SiH HSi) complex.

In these models, the mobile hydrogen atoms play an important role in creating dangling bonds. In the a-Si models with a divacancy-like void consisting of 6 dangling bonds, the interface of the void reconstructs to leave 2 dangling bonds upon relaxation. Now, when unbonded H atoms are included in the network, the mobile H atoms tend to form Si-H bonds. When hydrogen comes within a 2 Å radius of a silicon atom which has 4 nearest neighbors, it bonds with the silicon making it 5 fold coordinated. Hence, the bond between two silicon atoms breaks and results in a dangling bond at a distance of ~4-5 Å from the H atom. A Si-H bond is formed and as a result one or more dangling bonds are created. In all the models, H atoms hop between two Si atoms till it chooses one.

Formation of H<sub>2</sub> molecule inside the voids is also seen in some cases. When two unbonded hydrogen atoms come in close proximity (~2 Å) to each other, they tend to form molecules instead of forming Si-H bonds. In certain cases, as shown in the Figure below, the diffusive mobile H atom come close to a bonded H atom and break Si-H bond. These atoms then switch bonds and finally form a H<sub>2</sub> molecule. These molecules tend to get trapped inside the voids. After the formation of the H<sub>2</sub> molecule, the bond breaking and bond switching mechanism slows down. Snapshots of the formation of a hydrogen molecule inside the void are shown in Fig. 4.



**Figure 4.** Formation of H<sub>2</sub> molecules inside a big void in a-Si:H with 152 Si atoms and 67 H atoms from *ab initio* MD simulations. H atoms are denoted by white color and Si atoms by dark color. (a) H atoms become mobile, (b) H comes between bond center, (c) H breaks Si-Si bond, (d) while in between the bond center, the H atom comes closer to another bonded H atom, (e) the H atom breaks Si-H bond and finally forms H<sub>2</sub> molecule.

## SUMMARY

We have studied the various bonding configurations and the dynamics of hydrogen in a-Si:H with various sizes of voids. Our results are indicative of a proton-proton distance of  $1.8 \pm 0.2$  Å that consistently emerges for all models with a divacancy. For models with dangling Si bonds around the divacancy decorated with hydrogen, this H-H distance appears to result from monohydride configurations as well as from hydrogen clustering in the inner surfaces of the divacancy. For models with unbonded hydrogen, it is observed that hydrogen tend to form

monohydride configurations in pairs which is an indication of hydrogen clustering. However, for large voids a proton-proton separation of  $\sim 2.4 \text{ \AA}$  is observed. In some cases, formation of  $\text{H}_2$  molecules is also observed. Whether these structures are relevant to SWE is still unclear.

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