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STRUCTURE AND STABILITY OF MICROVOIDS IN a-Si:H

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ABSTRACT

Microvoids appear to be universally present in a-Si:H as demonstrated by small angle X-ray scattering including the presence of microvoids in device quality glow discharge a-Si:H. We have studied the structural properties of these microvoids with molecular dynamics simulations. Using molecular dynamics simulations with classical potentials, we have created microvoids by removing Si and H atoms from a computer generated a-Si:H network. The internal surfaces of the microvoids were passivated with additional H atoms and the microvoids were fully relaxed. Microvoids over a limited range of sizes (5-90 missing atoms) were examined. We obtained a relaxed microvoid structure with no dangling bonds for a microvoid with 17 missing atoms, whereas other sizes examined produced less relaxed models with short H-H distances at the microvoid surface. The strains near the microvoid surface are described. The microvoid model was stable to local excitations on weak bonds in the vicinity of the microvoid.

INTRODUCTION

Microvoids appear to be universally present in a-Si:H including in device quality a-Si:H material as demonstrated by small angle X-ray scattering (SAXS) studies [1,2,3]. The SAXS data [3] exhibit a void volume fraction of about 1% in device-quality a-Si:H films deposited at 300 °C. Deposition of glow discharge material at faster deposition rates (0.62 nm/s) and at the same substrate temperature results in poorer quality material and an increase in the void fraction to about 4% with microvoids of about 1 nm in diameter. In contrast the hot wire films deposited at 300 °C show a larger volume fraction of voids of approximately 4.5% and a significant fraction of larger voids with sizes as large as 20-30 Å.

An excessive density of microvoids has been generally believed to correlate with poorer quality material and an increasing density of hydrogen and also dihydride bonding configurations [4]. An open question is what is the correlation between the microvoid content and electronic quality of the a-Si:H films? Another extremely relevant question is what is the correlation between light induced instability in a-Si:H and the occurrence of the microvoids. Recent measurements [5] indicate a correlation between the initial and degraded efficiencies of solar cells with microstructure. This was evidenced by depositing i layers of p-i-n solar cells at different deposition rates with all other cell conditions remaining the same and measuring the solar cell efficiency. This suggests a correlation between voids and light induced degradation, arguing for the importance in understanding the structure and electronic properties of the microvoids. The structural properties of microvoids are addressed in this paper.

PREVIOUS SIMULATIONS

Our previous molecular dynamics simulations have provided important insights into microvoids in amorphous silicon networks. These studies were performed on pure a-Si without H but they already indicate important features of microvoids. We simulated[5,6] the growth of an a-Si film where clusters of Si atoms were deposited on a cold substrate ($T_s \sim 100$ °C) and the surface diffusion was very limited. The grown film showed the spontaneous formation of a microvoid with a mean radius of gyration between 3.6 and 3.1 Å. The microvoid was somewhat ellipsoidal with a larger radius in the growth plane. A large increase in the structure factor $S(q)$ was found for wave vectors below 1.0Å^{-1} . The a-Si films had significantly lower bond angle and bond length strain than melt quenched a-Si models [5].

The above findings on strain were reinforced by our earlier simulations of microvoids in bulk melt quenched a-Si models[6]. There too we observed the annealing of local bond angle and bond length strain on creating microvoids in bulk a-Si models. This suggests that although a high density of microvoids in amorphous silicon may be undesirable, a certain density of microvoids may in fact help in relieving local strains.

SIMULATION METHODS

In this paper we consider a-Si:H models containing hydrogen, that have many structural features in common with high-quality a-Si:H films. Our starting point was the Guttman-Fong a-Si:H model [7] with 10% H and all H bonded in monohydride bonding configurations. The model initially had 60 atoms, but we repeated the unit cell to create a 480 atom model with periodic boundary conditions and a cube side of 21 Å. This model has a distribution of bond lengths with rms values of 0.10 Å for Si-Si bonds, and 0.01 Å for Si-H bonds together with an rms bond angle distribution of 10.4° in good agreement with experimental estimates. The model was stable to local excitations on weak bonds[8] in the structure indicating that it is a good starting point for the microvoid studies.

Our computational methods are based on molecular dynamics utilizing classical potentials describing Si-Si and Si-H systems [8]. These models have been fitted to experimental information and abinitio calculations and have been found to provide a reasonable description of a Si:H. Very importantly these models are robust enough to be applied to systems with 400-500 atoms and larger in size for long simulation times which is essential for studying microstructure.

We start with identifying an arbitrary silicon site in the a-Si:H network. A microvoid was created by removing shells of Si and H atoms around this central site. The method of removing shells is a natural way to minimize the number of broken bonds in the structure[5] with the number of shells removed determining the microvoid size. After removing the shells we allowed the structure to relax to its lowest energy configuration using a steepest descent relaxation. This allows for surface reconstruction and rebonding at the microvoid surface. This still leaves dangling bonds on the microvoid surface. We then introduced additional

H atoms to passivate these dangling bonds and allowed the new structure with additional H to fully relax. Both steepest descent relaxation and finite temperature molecular dynamics annealing was employed to achieve the relaxation.

RESULTS

We first examined the smallest possible microvoid structures created by removing either a single Si-atom or two Si-atoms (i.e. elimination of a weak Si-Si bond) from the network. The removal of two Si atoms is the analog of creating a divacancy in a crystal. In these cases we had to introduce 4 and 6 additional H atoms to passivate the dangling bonds created. In both of these cases we found that the extra H atoms would come too close to each other with H-H separations of 1.0Å and less. Hence all these H atoms could not be accommodated in the small volume created. We did not obtain a reconstructed divacancy structure with two reconstructed weak Si bonds and four H atoms as observed by Buda et al in ab-initio simulations [8]. This is an electronic effect that also involves significant structural distortion to the amorphous network.

The next case examined was creation of a microvoid by removing 2 shells around a Si atom equivalent to 17 missing atoms. Relaxation of the network relieved local strains but dangling bonds remained at the surface of the microvoid. Then 22 additional H atoms were introduced to saturate the dangling bonds on the microvoid surface. Further relaxation led to a remarkable perfectly saturated structure with no dangling bonds or other types of coordination defects. One dihydride was created in the hydrogenation process. The resulting microvoid structure had 14 % H. All the H-H distances were larger than 1.6 Å.

We calculated the structure factor $S(q)$ for this configuration assuming that the X ray scattering is dominated by the contribution from the Si. The $S(q)$ did demonstrate (Fig. 1) a rise at small q (less than 0.7 \AA^{-1}). The slope of $\log(S(q))$ vs q^2 provided a radius of gyration R_g of $\sim 3.7\text{\AA}$ assuming Guinier scattering ($S(q) = S_0 \exp(-q^2 R_g^2 / 3)$). The radius of gyration is consistent with the second neighbor distance in c-Si.

We next investigated a larger microvoid by removing 3 shells around a Si atom corresponding to 43 missing Si atoms. The relaxation, hydrogenation and relaxation procedure led to a structure with 51 added H and 20 % H. Although no dangling or floating bonds remained after the relaxation we found 4 pairs of unbonded H-H distances less than 1.3Å indicating excessive strain and the difficulty in saturating all the dangling bonds on the microvoid surface. These pairs of hydrogen were already bonded to Si atoms at the microvoid surface so that a close H-H separation is not favored. We also found cases where H formed a bridging bond between two Si atoms. The results for the $S(q)$ calculation (Fig. 1) at small q , revealed a radius of gyration $\sim 5.7 \text{ \AA}$.

Results for microvoids with 4 atomic shells around a Si removed corresponding to 98 missing atoms were similar to the above 3-shell case above with generation of several pairs of close but non bonded H-H distances indicating that the excess density of H near the microvoid surface was not favored.

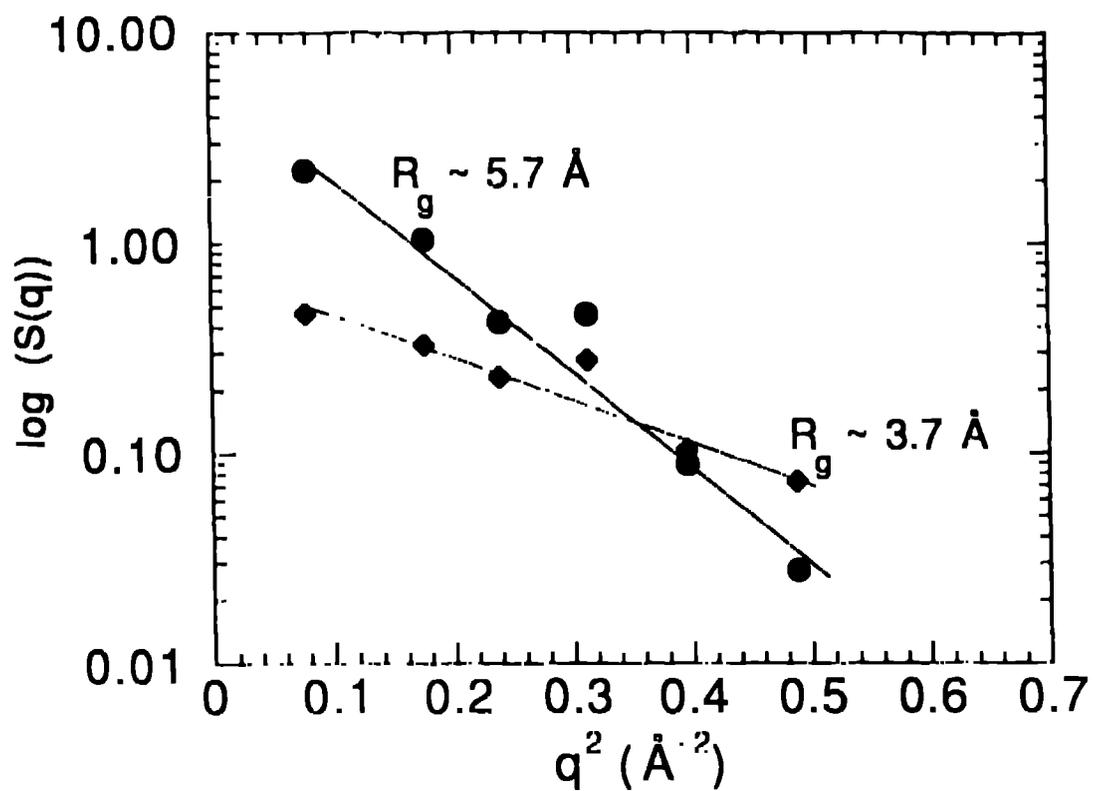


Fig. 1 The logarithm of the structure factor $S(q)$ as a function of the square of the wavevector q , for the two microvoid models, showing evidence for Guinier scattering. Only the small wavevector part is shown. Circles are results with three-shell microvoid (43 missing atoms) and diamonds are for the two-shell microvoid (17 missing atoms). Radii of gyration R_g shown were determined from the slopes of these lines.

The above results for the different size microvoids is very suggestive that there is a certain size microvoid with about 17 missing atoms that may be favored. Accordingly we analyzed in detail the local strains and structure of the 14 % H model created from 17 missing Si atoms. This structure has rms distributions of Si-Si bonds was 0.097 Å and 0.018 Å for Si-H bonds, together with rms bond angle distributions of 10.5° for Si-Si-Si bond angles and 5.1° for Si-Si-H angles. Notably there were two weak Si-Si bonds but these were in the bulk of the microvoid network and not at the microvoid surface. Graphical visualization was used to obtain a detailed picture of the bonding at the microvoid surface.

STABILITY

A persistent unresolved question is the relationship between microvoids and light-induced degradation. To investigate this within a feasible computational framework, we investigated the stability of the a-Si:H network to excitations on the bonds. We have adopted our previous approach [8] of a "hot spot" which models a simple channel for the nonradiative carrier recombination energy to be transferred to the lattice. The microvoid model with no dangling bonds and 14 %H was selected and excitations with an excess kinetic energy of 1.7 to 2.5 eV were made on selected weak bonds in this structure (with bond lengths larger than 2.7 Å). The excess energy was allowed to equilibrate and in all the cases examined we found the structure would rebond to the original bonding configuration with no extra dangling bonds created. This suggests that metastable energy states may not be directly linked to weak Si-Si bond breaking.

These results are consistent with our previous results [8] that the presence of dihydrides (SiH₂) weakens the amorphous network and leads to [8] metastable dangling bond states similar to light-induced defects.

ANALYSIS AND CONCLUSIONS

It should be clarified at the outset that only a limited number of microvoid configurations were examined. To obtain better statistical features microvoids around several Si-sites should be considered. In spite of this statistical uncertainty the results are highly suggestive that microvoids of a certain size corresponding to about 17 missing atoms and radius of gyration about 3.7 Å could be highly favored as a stable microvoid configuration that could exist without any dangling bonds on the microvoid surface. The microvoid configuration determined in this molecular dynamics simulation was stable to simple bond excitations.

It is significant that very small microvoids created from a vacancy or divacancy or a single missing shell around a Si atom in the network did not have sufficient volume to accommodate the extra H needed to passivate the dangling bonds. Similarly a very large microvoid with radius of gyration about 5.7 Å was not favored with close non bonded H-H distances indicating that large H densities at the microvoid surface is not preferred.

It is clear that a future direction will be to examine the electronic properties of these microvoids with models that incorporate the electronic effects. A promising model that has been developed is a molecular dynamics procedure based on tight-binding atomic orbitals that provides very accurate results for the phase diagram of Si, energies of defects in c-Si and the melting of Si. Examining these large microvoid models for electronic properties and stability with this electronic structure model will clearly be needed in further work.

We have generated these microvoids by removing atoms from a bulk network. An alternative procedure that is closer to experiment is to deposit Si and H atoms on a Si-surface or model the decomposition of silane on a substrate and study the spontaneous formation of a microvoid. This is computationally intensive approach that could provide further insight into the size distribution and structure of microvoids.

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