

## MICROCRYSTALLINE AND NANOCRYSTALLINE SILICON: SIMULATION OF MATERIAL PROPERTIES

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### ABSTRACT

We have simulated nano-crystalline silicon and microcrystalline silicon structures with varying crystallite volume fractions, using molecular dynamics simulations. The crystallite regions reside in an amorphous matrix. We find the amorphous matrix is better ordered in nanocrystalline-Si than in the homogenous amorphous silicon networks, consistent with the observed higher stability of H-diluted films. There is a critical size above which the crystallites are stable and may grow. Sub-nm size crystallites in the protocrystalline phase are found to reduce the strain of the amorphous matrix. We simulated micro-crystalline silicon with a substantial crystallite volume fraction. Microcrystalline structures exhibit a crystalline core surrounded by an amorphous shell with similarities to silicon nanowires. We find a relatively uniform H distribution in the amorphous region and a crystal-amorphous phase boundary that is not well-defined.

### INTRODUCTION

Mixed phase semiconductors near the phase boundary of amorphous and micro-crystalline growth are a very active area of current research. These include two broad classes of new materials. One is microcrystalline silicon ( $\mu\text{c}$ ), grown on the crystalline side of the phase boundary (Fig. 1) containing a large volume fraction of crystalline grains. The coalesced crystalline grains are separated by amorphous tissue. Microcrystalline silicon is being employed as a stable low bandgap solar cell material [1,2] and is stable to light exposure.

The other class of material is grown on the amorphous side of the  $\text{a-}\mu\text{c}$  phase boundary, in a silane-hydrogen gas mixture with high H dilution ratio (R). Under H-dilution conditions small nano-crystallites with dimensions of a few nm are formed in a background  $\text{a-Si:H}$  matrix [3,4,5]. As the film grows in thickness, the crystallites grow in size and eventually coalesce at a critical film thickness into the micro-crystalline phase [3,4]. Higher H-dilution decreases the onset of the crystallinity. Most current  $\text{a-Si:H}$  solar cells employ thin layers of H-diluted materials grown before the onset of microcrystallinity. H-diluted material is markedly more stable to light-induced degradation [6,7,8]. This material is close in electronic properties and band gap to  $\text{a-Si:H}$  and has a crystallite volume fraction typically less than  $\sim 10\%$ . Transmission electron microscopy has imaged the nm size crystallites dispersed in an amorphous matrix [9]. Among the key questions is why such nano-crystalline silicon material has improved stability to light-soaking, and whether the material has superior order over traditional  $\text{a-Si:H}$ . Fluctuation electron microscopy [10] of sputter-deposited unhydrogenated  $\text{a-Si}$  and  $\text{a-Ge}$  shows medium range order originating from a paracrystalline network of buried crystallites in an amorphous

network.

A number of studies have identified a phase boundary defining the transition from amorphous to amorphous and  $\mu c$  growth- or the mixed phase (Fig. 1). Below this  $a \rightarrow a + \mu c$  boundary the material is considered protocrystalline [3,4] and nanometer size nuclei have just started to spontaneously nucleate. Using molecular dynamics simulation we address the possible structure and stability of this protocrystalline region. An intriguing aspect is the dependence of the phase boundary on film thickness and why the transition to microcrystalline occurs earlier for larger H dilution. In our present work we simulate microcrystalline silicon, nano-crystalline silicon and the proto-crystalline region and study the progression of the crystallite size.

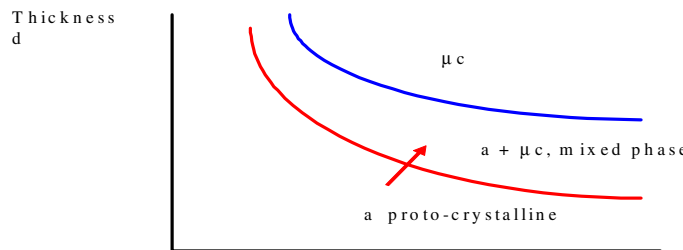


Fig. 1. Schematic phase boundary between the microcrystalline phase, mixed phase and the protocrystalline phase as a function of film thickness and H-dilution ratio.

## NANO-CRYSTALLINE SILICON MODEL

Molecular dynamics has been very popular in simulating bulk amorphous semiconductors, film growth and recently the simulation of mixed phases [11,12]. Our first approach was to generate and analyze nano-crystalline structures with an embedding approach that we described previously [13]. This approach utilized existing bulk a-Si:H structures that have been most successful in describing metastability, structure and H-motion [14,15]. These structures are free of coordination defects and midgap electronic states. Starting from an a-Si:H model we remove a central portion of this structure, and then replace it with a crystalline seed with approximately the same volume and shape as the removed region. Different crystallite sizes can be embedded. A classical molecular dynamics scheme [16] was used for larger models and tight-binding for smaller ( $N < 600$  atom models) [13].

The relaxation and annealing of this cell initially yields coordination defects. The mixed phase cell is then systematically annealed to remove these defects. Weak silicon bonds are removed by H-passivation. H is introduced to anneal the over-coordinated sites. Dangling bonds are individually saturated with H atoms. The addition of H atoms throughout the annealing phase is analogous to processes occurring in H-dilution growth. Resulting models (Fig. 2) have no coordination defects- which is essential if one is to realistically model device-quality material with dangling bond densities of  $< 10^{17} \text{ cm}^{-3}$  or less than 1 atom in  $10^5$ .

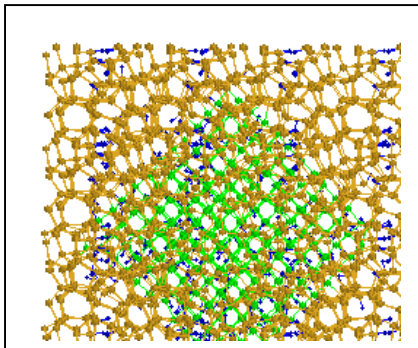
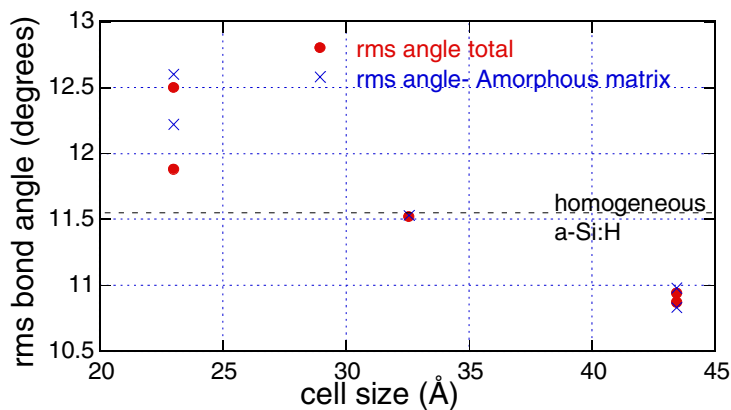


Fig. 2 Model of mixed phase nano-crystalline silicon with 4059 atoms. Nanocrystallite are inner spheres.

We have extensively analyzed the structure of the nc-Si model [13]. The radial distribution function for the entire structure shows the characteristic sharp first neighbor peak expected for a-Si:H and a broader second neighbor peak. These features are very similar to the bulk amorphous structure because the crystallite volume fraction is small. The nano-crystallites have an excess density of H at the crystallite surfaces, due to the passivation of defects in the interfacial region between the crystallite and the amorphous matrix. In previous work [17] we found that this region of high H density was responsible for a low temperature H evolution peak that is commonly seen in H-diluted materials at 400-450 C [18]. The H from the bulk amorphous region is responsible for the usual higher temperature H-evolution peak at 550-600 C [17,18].

One of the most important results is that in nc-Si the nanocrystallites have a beneficial effect in improving the ordering of the material. This result can be seen by calculations of the root mean square (rms) bond angle (Fig. 3) in the mixed phase model averaged over all the atoms, as a function of the cell size (or the number of atoms). We separated the bond angle strain into its contribution from all the atoms in the cell (including the crystallite) and the portion of the angular distribution from the amorphous matrix. We find (Fig. 3) that the small cells (with size  $a < 25$  Å) are severely distorted with strained rms bond angle distributions exceeding  $11.5^\circ$ . The bond-angle strain decreases with cell size and is markedly reduced for larger cells. For the larger cells ( $a > 4$  nm) we find the average rms bond-angle variation in the amorphous region is below that ( $11.5^\circ$ ) of the homogenous a-Si:H network that we started with.



This suggests beneficial ordering of the amorphous matrix, induced by the crystallite. This feature is suggested by the narrowing of the TO Raman line-width in mixed phase samples. A corresponding decrease in the rms bond lengths is also found as a function of cell size. The lower strain and lower density of weak bonds in the a-Si:H matrix improves the stability of nc-Si to light

soaking.

Fig. 3 Rms bond-angle values as a function of the cell size for the different mixed phase models. The rms angle for the homogeneous network is marked.

Nucleation and growth theory can be applied to nc-Si. There is a bulk free energy gain from the lower energy of the nanocrystallite that is balanced by the surface energy cost between the nano-crystallite and the amorphous matrix. From nucleation and growth theory this leads to a critical radius  $R^* \sim 1$  nm [13]. For nanocrystallites with  $R > R^*$ , the nuclei are stable and should exhibit grain growth. For  $R < R^*$  the nuclei are unstable and should dissolve into the amorphous matrix. Using molecular dynamics we have observed[13] this occurring at considerably higher temperature ( $> 600^\circ\text{C}$ ), where H motion is significant. Thus at typical operating temperatures the nano-crystallites are in a metastable state.

## MICROCRYSTALLINE SILICON

We now focus on microcrystalline silicon on the higher side of the a- $\mu$ c phase boundary. We simulate  $\mu$ c-Si with higher crystallite volume fractions than nc-Si. We start with a silicon crystal (c-Si) of  $\sim 10,400$  atoms. We inhomogeneously heated the cell and maintained a temperature differential within the cell so that the atoms of the boundary were heated slightly above the melting temperature, whereas the interior atoms were at a cooler temperature below melting. Heat flows from the exterior to the interior. Periodic boundary conditions were used. The boundary of the cell began to disorder and after simulations varying from 20K-80K steps we cooled the system back to low temperature. This effectively avoided the complete melting of the boundary region but succeeded in progressively disordering the amorphous boundary layer with increasing simulation time.

The resulting structures (Fig. 4) consist of a crystallite within an amorphous matrix with crystallite volume fraction exceeding 60% similar to experimental volume fractions for  $\mu$ c silicon. Such  $\mu$ c-Si is used as the stable low band gap cell in the multi-junction stacks. We are not in the regime of coalesced microcrystallites. There is no well defined boundary between the crystallite and the amorphous matrix (Fig. 4) and boundary layer strain is absent. We substantially reduced the number of dangling bonds by insertion of H atoms at under-coordinated silicon sites (Fig. 4). The structure is considerably improved although it still contains a significant density of over-coordinated defects.

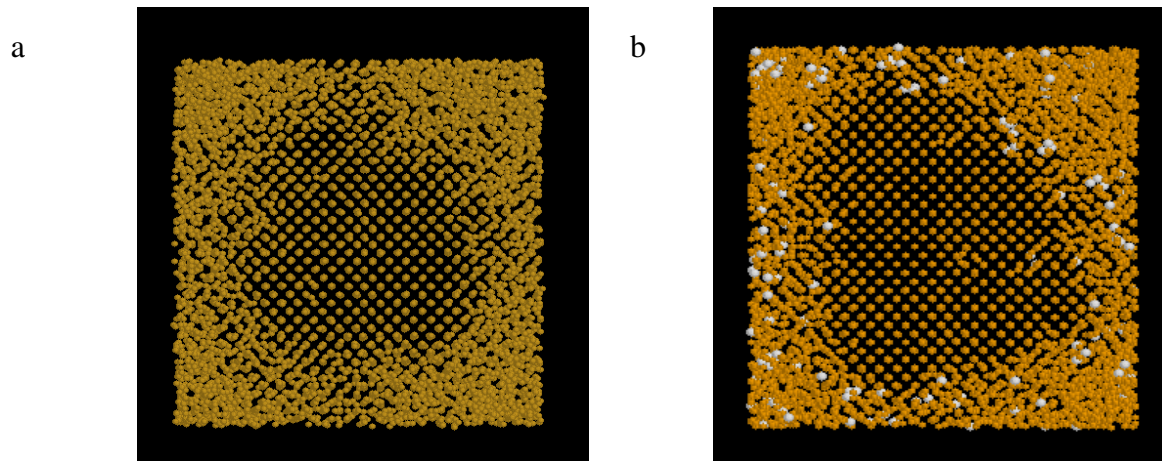
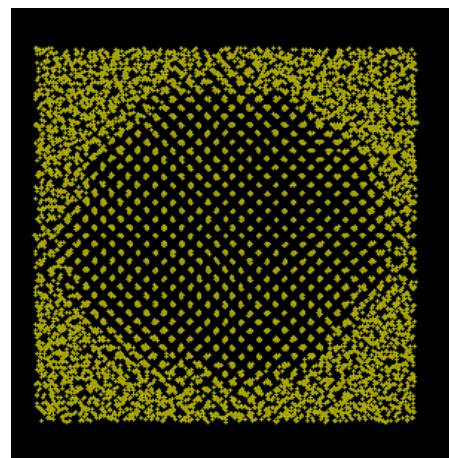


Fig. 4. Microcrystalline silicon cell simulated by melting and disordering the outer portion of the cell. a) A microcrystalline cell without H atoms b) a Microcrystalline cell where H atoms have been added in the amorphous region to remove dangling bonds. H atoms are in white.

We have also performed a complementary set of simulations where a cylindrical region of material in the x-y plane is kept at a cooler temperature whereas the region outside the cylindrical region is heated to the higher temperature above melting. The cell is uniform along the z direction. When this cell is cooled it leads to an inner cylindrical region that has a crystalline structure and an outer shell that is amorphous in nature (Fig. 5).

Fig. 5 A simulated cell with a tube of crystalline material surrounded by the amorphous matrix. The structure has similarities to nanowires.



Such material has similarities to the mixed phase material where crystalline cones have lengthened in the growth direction. This material also has intriguing similarities to the silicon nanowires, which also have crystalline cores surrounded by amorphous outer shells.

## PROTO-CRYSTALLINE SILICON SIMULATIONS

We now focus on the extreme of very low crystallite volume fraction or protocrystalline phase which occurs prior to the mixed phase. In order to gain insight into the formation processes underlying proto-crystalline and nano-crystalline silicon, we simulate the ordering processes in the amorphous silicon matrix. It is likely that very small crystalline nuclei form during growth in this proto-crystalline phase.

We selected locally strained silicon sites in the a-Si:H matrix. We introduced crystalline regions of ~5 silicon atoms into the amorphous matrix, by removing a locally strained silicon atom and its 4 neighbors (Si1-Si5) and replacing it with a 5-atom fragment of crystalline silicon. This generates some dangling bonds at the boundary of the 5-atom unit. We then introduce additional H atoms to passivate these dangling bonds, analogous to H-annealing reactions occurring during growth in a H-rich environment. Complete relaxation and annealing of all the atoms then generates a structure with a distorted tetrahedral unit Si1-Si5 and no dangling bonds.

The essential result is the generation of an ordered region of silicon sites. On several sites, the rms bond-angle at the central silicon atom (Si1) is considerably lower than the value in the original amorphous network (Fig. 6). In one case  $\theta_{\text{rms}}$  is initially  $12.24^\circ$  and is reduced to  $7.16^\circ$  after the ordering, considerably smaller than that in the amorphous network. There is no disordered grain boundary or region of strained bond-angles, between the crystallite and the amorphous matrix.

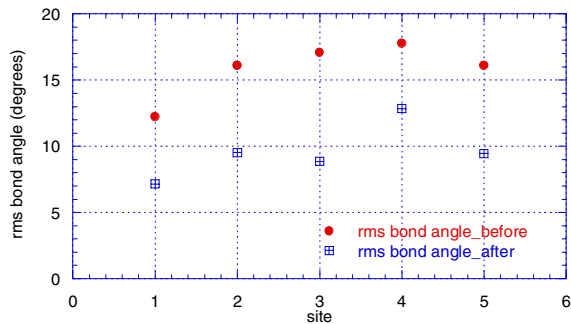


Fig. 6. Rms bond angles on strained silicon sites before and after the introduction of crystallite fragments, showing an improved ordering.

We repeated this ordering procedure for a central Si-atom (Si1) and its two neighboring shells, equivalent to 17 atoms. After relaxation and incorporation of additional H we achieved cells with no dangling bonds but with considerable strained bonds. There was a disordered boundary region between the 17-atom crystallite and the amorphous matrix with large  $\theta_{\text{rms}}$ .

The simulations indicate that it is likely that the proto-crystalline phase nucleates through the generation of sub-nanometer size crystalline regions of approximately 5 atoms in size. As the film grows in thickness the proto-crystalline nuclei increase in density and improve the ordering of the film. A film thickness is reached when the nuclei are dense enough that they grow in size to form nano-crystallites with  $> 1\text{nm}$  dimensions. This is the onset of the  $a \rightarrow a + \mu c$  transition. The growth rate is faster in the crystalline region than in the amorphous region, causing increase of crystallite sizes [13] and formation of crystallite cones. The sub-nanometer scale ordering is

to be contrasted with the H-induced ordering proposed from molecular dynamics studies [19] where H inserts into the bond of amorphous silicon reorders a local region, after diffusing away.

## CONCLUSIONS

In conclusion we have generated realistic models of nano-crystalline silicon and microcrystalline silicon with molecular dynamics simulations. Nanocrystallites improve the ordering of the amorphous matrix. We have analyzed the ordering mechanisms in proto-crystalline silicon, where sub-nm crystallites can improve the ordering of the material.

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