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Coordination number constraint models for hydrogenated amorphous Si deposited by catalytic chemical vapour deposition

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Abstract

We measured structure factors of hydrogenated amorphous Si by x-ray diffraction and analysed the obtained structures using a reverse Monte Carlo (RMC) technique. A small shoulder in the measured structure factor $S(Q)$ was observed on the larger Q side of the first peak. The RMC results with an unconstrained model did not clearly show the small shoulder. Adding constraints for coordination numbers 2 and 3, the small shoulder was reproduced and the agreement with the experimental data became better. The ratio of the constrained coordination numbers was consistent with the ratio of Si–H and Si–H₂ bonds which was estimated by the Fourier transformed infrared spectra of the same sample. This shoulder and the oscillation of the corresponding pair distribution function $g(r)$ at large r seem to be related to the low randomness of cat-CVD deposited a-Si:H.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Amorphous Si (a-Si) has been a very important material over the years, and is widely used in solar cells and thin film transistors for liquid crystal display (LCD) in the commercial world. For practical use, hydrogenated a-Si (a-Si:H) films with stable properties such as a long lifetime during operation are required. The plasma enhanced chemical vapour deposition (PECVD) technique is one of the major processes to fabricate a-Si:H films with good quality. The quality can be estimated from the sharp Urbach tail in the optical absorption spectra and

small amounts of the midgap states with low spin density [1]. Low hydrogen concentration in a-Si:H films leads to little bonded H to pacify the dangling bonds [2, 3]. Although the increase in the concentration of the hydrogen bonded to Si makes the structure stable, it also leads to chain formation of SiH₂ [4], so that micro-voids and inferior electron properties can be easily induced [5–7]. The a-Si:H films produced by PECVD include about 10 at.% H. These films can be easily crystallized because of high H concentrations, which are required to relieve strain. Thus, films with low H concentrations just below the re-crystallization limit [8] are interesting.

The catalytic chemical vapour deposition (cat-CVD) technique has an advantage in this regard. It makes a-Si:H films with a few at.% H content possible [1, 9]. The deposition gases are cracked by catalytic reactions with a heated catalyser placed near the substrate [9]. These films have very promising properties for stability under light soaking and operating current stress. Cat-CVD a-Si:H films have a slightly larger internal stress because of the low H concentration. It is interesting to analyse the structure of the cat-CVD a-Si:H films for the future application of stable a-Si:H devices.

Several structures of a-Si have been investigated from electron diffraction [10], high-energy x-ray diffraction [11], x-ray absorption [12] and neutron diffraction [13] measurements. From a theoretical point of view, model structures for a-Si have been achieved by traditional Monte Carlo simulation [14] and first principle calculations [15, 16]. In experiments, only radial distribution functions $g(r)$ have been estimated and used for a discussion of the structure of a-Si. As there might be many possible structures in the amorphous phase [17], it is important to discuss the structural properties with full 3D information. Usual theoretical techniques require interatomic potentials for building the 3D structure. Such a general potential may provide different structure from the actual materials.

Reverse Monte Carlo (RMC) simulation is one of the experimental analysis techniques which provides a 3D model of the individual sample without any hypothesis of the interatomic potential. This method is very convenient for dense solids and liquids. RMC analysis has been applied to H free a-Si to study the microscopic structures by Kugler *et al* [18]. They also compared neutron data to conventional theoretical models [19]. In the amorphous case, there seems to be a little ambiguity and different constraints for the simulation are required [18]. For H free a-Si, unusual atomic arrangements are revealed by RMC simulation [20, 21].

In this work, a-Si:H films containing low H concentrations deposited by cat-CVD were analysed by RMC simulation. We discuss the need for coordination number constraints to fit the small hump at the larger Q side of the first peak in the measured structure factor $S(Q)$. The obtained distribution of the coordination number was compared to the FTIR intensity of Si–H and Si–H₂ and then the coordination number constraint was reconstructed. Finally, we calculated $g(r)$ and discussed the long range order of cat-CVD deposited a-Si:H films.

2. Experiments and analysis

The a-Si:H films were deposited by cat-CVD on a (100) Si wafer, where the flow rate of H was 10 standard cubic centimetres/minute (sccm) and that of SiH₄ was 50 sccm. The distance between the catalyser and the substrate was set to 50 mm and the catalyser temperature was 1750 °C. The substrate temperature was 270 °C. The gas pressure in the chamber was 1.1 Pa. These deposition conditions were the same as for device quality a-Si:H films using the cat-CVD device fabrication proposed by Sakai *et al* [9]. The H content was estimated from the Si–H wagging mode of the Fourier transform infrared (FTIR) spectra taken by a Shimadzu FT-IR 8300 FTIR spectrometer. The estimated H content was as low as 3.3 at.% which is suitable for practical use [22]. To obtain sufficient x-ray diffraction intensity, we used thick films of a-Si:H. The sample thickness was 1 μm.

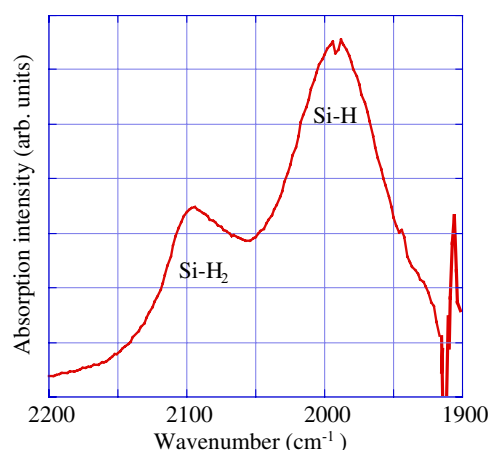


Figure 1. FTIR spectra for cat-CVD deposited a-Si:H. H content is 3.3%. Two absorption peaks for Si-H and Si-H₂ are shown.

The FTIR spectra are shown in figure 1. The wagging vibration mode of the spectra of Si-H was used for the H content estimation and the stretching modes of Si-H and Si-H₂ were used to estimate the ratio of Si atoms with smaller coordination number. The measured range of the spectra was between 1900 and 2200 cm⁻¹ so as to observe the Si-H stretching mode of 2000 cm⁻¹ and Si-H₂ stretching mode of 2090 cm⁻¹. The x-ray diffraction (XRD) spectra were measured using a Philips X'pert diffractometer with Cu K α radiation for the low wavenumber region. The wavenumber Q is defined as $Q = (4\pi/\lambda) \sin \theta$, where λ is the wavelength of the incident x-rays. A crystal graphite monochromator was used. The scanned range of angle 2θ was from 8° to 150° with a step of 0.005°, which corresponded to a wavenumber range of 0.64–7.86 Å⁻¹. For the high Q region, the XRD spectra were taken using a Rigaku Rint-2100 diffractometer with the Mo K α line, where the scanned range of angle 2θ was from 4° to 150° with a step of 0.1° that corresponded to a wavenumber range of 0.61–17.1 Å⁻¹. The constant low angle 0.4° incident beam was used for $S(Q)$ above 7.86. A density measurement is very important to extract meaningful information from the measured data. The density of a-Si:H films was estimated to be 2.28 g cm⁻³ from the Rutherford back scattering (RBS) spectra measured by using a NISSIN NH-1700H accelerator. The ratio between films and substrates in the RBS spectra was analysed by simulation, where the measured energy had different dependence on the Si sites. We estimated a density of the sample from the results of the number density.

RMC is a well established simulation method for building three-dimensional atomic structures [23, 24]. Here we used a cubic box with 4096 Si atoms (16 × 16 × 16 atoms), whose length was 43.6 Å in real space. Since the structure of a-Si is thought to be similar to that of c-Si, we start with the crystal structure of c-Si as the initial configuration. The minimum interatomic distance between Si atoms was set as 2.095 Å estimated by the Lennard-Jones interaction [25], where the chi-square χ^2 of the RMC calculation becomes minimum. As one of the advantages of the RMC simulation, we can introduce coordination number constraints. The differences between the coordination number of the calculated structure and the desired one are added as additional terms in χ^2 for convergence.

3. Results and discussion

For samples deposited on a glass substrate, there is no peak related to the Si crystal. But the first amorphous peak of a-Si:H deposited on a glass substrate was not so clear because

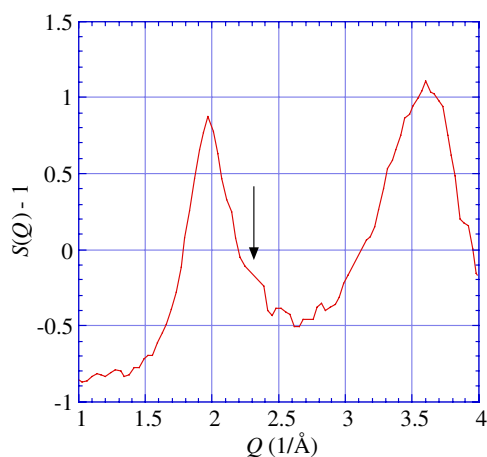


Figure 2. Experimental structure factor $S(Q)$ of cat-CVD deposited a-Si:H. H content is 3.3%. The small hump is pointed out by an arrow.

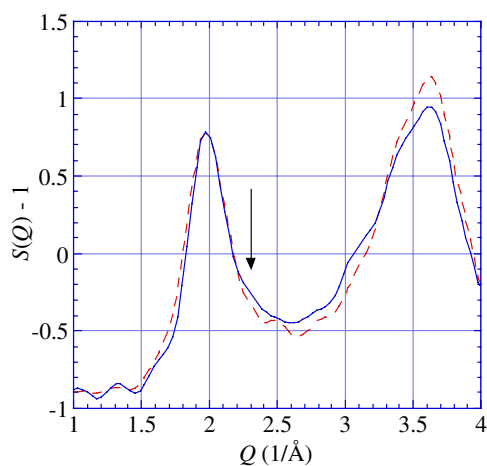


Figure 3. Structure factor $S(Q)$ obtained by RMC simulation. The dotted curves are for the simulation without constraints and the solid curves are for that with a coordination constraint where 97% of Si takes a coordination number of 4. Detailed constraint conditions are shown in the text.

of the superposition with amorphous broad peaks of the glass substrate. Therefore we used XRD spectra of a-Si:H deposited on c-Si substrate. We subtracted the Si substrate peaks from the XRD spectra data after correction for polarization, absorption and geometric factors. The $S(Q)$ of a-Si:H with 3.3 at.% H obtained in this way is shown in figure 2. Since the samples were deposited on a c-Si substrate and the $\theta-2\theta$ mode for the low Q measurement was used, large Si crystal peaks were also observed in the region from 4.1 to 5 \AA^{-1} in the raw data.

The first and second peaks in $S(Q)$ have moderately large values and the second peak was larger than the first peak. The small hump on the larger Q side in the first peak was observed as pointed out by the arrow.

Figure 3 shows $S(Q)$ calculated by RMC with and without the coordination number constraint. The constraint condition is that the coordination number of 97% Si atoms is set to 4.

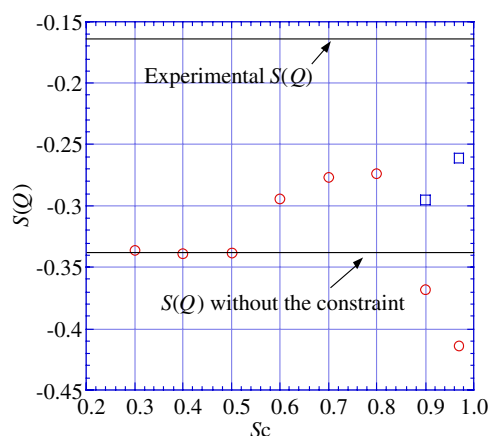


Figure 4. Coordination number fraction dependence of the shoulder at the first peak of $S(Q)$ calculated by RMC analysis. The $S(Q)$ values at $Q = 2.3 \text{ \AA}^{-1}$ are plotted. The circles are for the simulation with a constraint only for a coordination number of 4, and squares for that with extra constraints for the coordination number 2 and 3.

In the constrained case, some small discrepancies only appear at low Q below about 1.5 \AA^{-1} . The calculated $S(Q)$ without the constraint was in better agreement with the measured $S(Q)$ from the point of view of smaller χ^2 which indicates the efficient parameter of the difference between the measured and calculated $S(Q)$ s. But the small hump on the larger Q side of the first peak of measured $S(Q)$ (as pointed out by the arrow in figure 2) cannot be observed in the unconstrained case.

Although the low Q region of $S(Q)$ in the unconstrained case seems to have a good fit between experimental data and simulation, the first peak region is more important to obtain the local configuration such as the coordination number distribution. The proportion of Si atoms with a coordination number of 4 in the unconstrained case was 36.6%. This value is too small for the a-Si:H structure [21].

We checked the dependence of $S(Q)$ in this region on the constraint conditions. We started RMC simulations under the condition of a coordination number 4 at $S_c = 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$ and 0.97 , where S_c indicates the fraction of the constraint coordination number. Figure 4 shows the changes of $S(Q)$ at $Q = 2.3 \text{ \AA}^{-1}$ pointed out by the arrows in figures 2 and 3. The value of $S(Q)$ in this region increases with S_c up to $S_c = 0.8$ and the results of the fitting become better with the increase of S_c . Above $S_c = 0.9$, the $S(Q)$ value becomes small and the fitting of the $S(Q)$ is not so good. These structures had large coordination numbers such as 5, 6 and 7. This discrepancy at large S_c can be improved by the introduction of additional coordination number constraints. Therefore, we estimated the likely coordination number distribution from FTIR spectra.

From the ratio of the area of the two peaks in the FTIR spectra corresponding to Si-H (2000 cm^{-1}) and Si-H₂ (2090 cm^{-1}) shown in figure 1, the ratio of the bond numbers of Si-H and SiH₂ was estimated as 1:0.41 after correction of the atomic dependence [26]. The concentration of hydrogen related to the bonds was estimated as 2.3% and 1.0%, respectively, as the total H content is 3.3%. Therefore, the ratio of the Si atoms bonding to the hydrogen can be estimated as 1:0.205. Thus, we determined S_c for coordination numbers 3 and 2 for the RMC constraints to be 0.023 and 0.005, respectively. These values are not inconsistent with the fact that the dangling bond density is very small in comparison with the bonded Si atoms

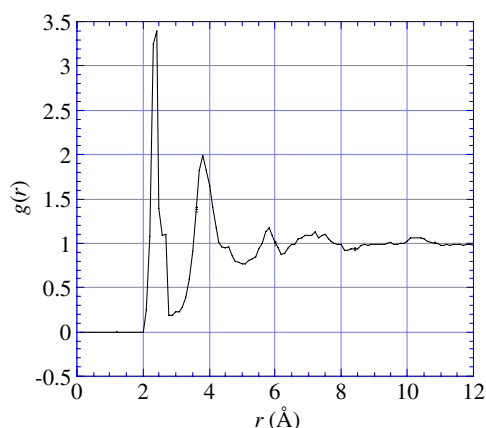


Figure 5. Calculated pair distribution function $g(r)$ for the a-Si:H films simulated with the constraint.

and are supported by the results of the dangling bond density estimated from the electron spin resonance to be about 10^{17} cm^{-3} for the same specimen.

The small hump at the first peak of $S(Q)$ might reach the measured value as the constraint fraction of four-coordinated Si is increased. Finally, under the condition that 97% Si atoms is assumed to be constrained to four coordination, 2.3% to three and 0.5% to two, we reduced the number of larger Si coordinations ($n > 4$) within the configuration. By using these fine constraint conditions for such small coordination numbers, the convergence and the fit became better, as shown by the square symbols in figure 4.

In figure 5, the $g(r)$ in the above constrained case is plotted. We observed an oscillation at larger r over 7.5 Å. This suggests that there is some long range order in the a-Si:H films. The $g(r)$ of H free a-Si films has small oscillating features at larger r [18].

Now, we refer to the structural analysis of liquid Si as an analogy. In liquid Si, the clear hump on the right shoulder of the first peak of $S(Q)$ and oscillations of the corresponding $g(r)$ at large r are observed [27]. Omote *et al* emphasize that these features are specific to the liquid phase of Si and the liquid is in an ordered state. The structure of a-Si:H deposited by cat-CVD might have some features similar to that of liquid Si. In other words, cat-CVD deposited a-Si:H seems to have some long range order; this means that the structure is not fully random. We think this feature is related to the stability of a-Si:H films and the hydrogenated a-Si has long range order.

The coordination number distribution has 97% of the coordination number of 4, and a small amount of coordination numbers 2, 3 and 5 as plotted in figure 6. Many unconstrained atoms in the RMC simulation take a coordination number of 5. A snap shot of the 3D configuration under the above coordination constraints is shown in figure 7. In this case, the bond angle distribution is mainly concentrated around 107° as shown in figure 8. We think this angle distribution comes from the modification by the internal strain. This is the same as that of H free a-Si [20], where small numbers of small bond angles were observed.

4. Conclusion

The structure of a-Si:H deposited by the cat-CVD technique was analysed by RMC simulations. A 3D structure for amorphous Si was constructed by applying a coordination constraint

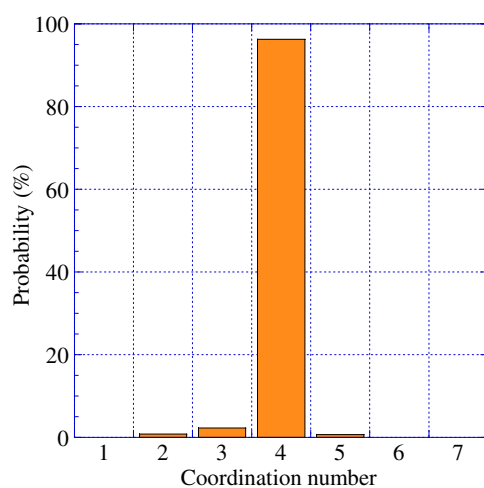


Figure 6. Calculated coordination number distribution for the a-Si:H films.

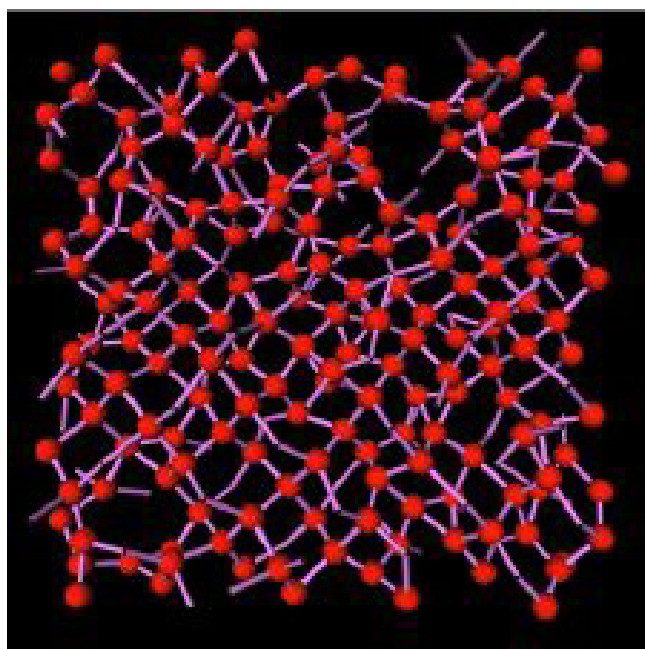


Figure 7. Representative 3D pictures for the a-Si:H films in the RMC simulation.

determined from the FTIR spectra. The small shoulder on the first peak of $S(Q)$ was in good agreement with the measured data. In the unconstrained case, although the total fit seems to be better, the structures have unlikely high coordination numbers. The constraint conditions for coordination numbers 2 and 3 can help the convergence of the RMC simulation. The obtained $g(r)$ has small oscillations at large r , which suggests some long range order related to the stability of these samples.

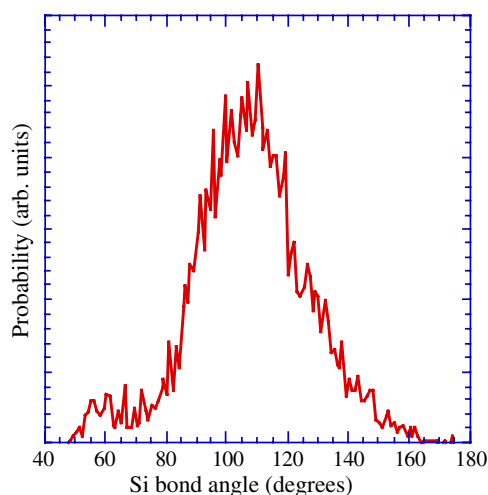


Figure 8. Calculated Si bond angle distribution for the a-Si:H films simulated with the constraint.

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