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L Pusztai[1] and S Kugler[2]

[1] Research Institute for Solid State Physics and Optics, PO Box 49, H-1525 Budapest, Hungary
[2] Department of Theoretical Physics, Budapest University of Technology and Economics,
H-1521 Budapest, Hungary

Abstract
The experimental structure factors of evaporated and ion-implanted amorphous silicon have been modelled by reverse Monte Carlo modelling. A detailed comparison, in terms of the pair correlation function and the distribution (of the cosines) of bond angles, is reported here for the two materials. It is found that for an acceptable reproduction of the measured structure factors the evaporated models must contain *more* 'small' bond angles, of the order of 75°, than their necessary abundance in the implanted models.

1. Introduction

A large number of diffraction measurements [1–5] and computer simulation studies [6–19] have been carried out on (and conjectures based on 'data mining' [20] have been made concerning) amorphous silicon (a-Si) during the past two decades, in order to understand (minute) details of the atomic scale arrangement. There is a general agreement concerning the basic structural features: all experimental and simulation studies found that the material is formed by a covalent network of (mostly) fourfold coordinated Si atoms. The mean bond angle is found to be close to the tetrahedral angle (which is 109.5°); usually it is found to be somewhat smaller (see, e.g. [1, 5, 21]).

There is a disagreement concerning the exact coordination number of atoms: experiments on evaporated samples [1, 2, 4] derived values of slightly less than 4, whereas the most recent experiment on ion-implanted samples [5] suggested a value of very nearly 4. Simulation studies using classical potentials (e.g. [6, 9]) most frequently construct the potential so that a coordination number of exactly 4 is preferred; quantum simulations (e.g. [10]) not rarely come up with Si atoms that are fivefold coordinated. It was pointed out [22] that this slight disagreement may have been caused by the different ways of 'preparing' a-Si samples: computer simulations—with the exception of [17]—usually apply rapid cooling from the liquid state, whereas most real samples have been prepared from the vapour phase.

Fairly recently, it was possible to prepare an amorphous sample via ion implantation [5]. This technique is very different from 'conventional' precipitation: during ion implantation, the

crystalline structure is being distorted, whereas in the other case, the origin is the *gaseous* phase. For this substantial difference (and considering that the amorphous phase is not an equilibrium phase but a metastable one) it seemed possible that the inconsistencies between simulations and experiment mentioned above would be reflected in the structure factors obtained from the two (evaporated and ion-implanted) samples. Recent computer simulation studies also consider the possible variety of amorphous silicon samples [18] (although the experimental methods realized are different from the cases to be discussed here).

The main objective of the present study was to reveal these structural differences (if there are any), by building structural models that are consistent with the results of the corresponding diffraction measurements [4, 5]. The method chosen for generating these models was the so-called reverse Monte Carlo (RMC) simulation [23]. This technique has proved to be extremely successful for evaporated a-Si samples [4, 24, 25]; however, results from ion-implanted samples have hardly been considered (for the only exception, see [26]).

In the following sections, some calculation details will be given; these are followed by a description of the results and their discussion. Finally, conclusions will be drawn.

2. Reverse Monte Carlo calculations

Potential independent reverse Monte Carlo modelling [23] has already been shown to be a powerful tool for interpreting amorphous structures, notably, of a-Si [4, 24]. For the present case, rather specific series of RMC calculations, similar to those reported in [25], have been carried out, with the aim of producing structural models closest to a—hypothetical—regular structure. The well known WWW model [6] was chosen to play the role of this 'ideal' regular structure, since in this model, only small deviations (of the order of about 10°) of the bond angles are found from the tetrahedral angle.

RMC calculations were started from 512 and 4096 atom WWW models and only very small moves (of the order of 0.002 Å) were allowed. The number density of the systems was kept at 0.0505 Å^{-3}. Coordination constraints, as in [25], have been applied for keeping the (exactly) fourfold coordination around each Si atom, within a spherical shell of radius 2.6 Å. According to previous experience, such constraints do not deteriorate the quality of agreement with experimental data [4, 24], indicating that fourfold coordination is a natural feature of the covalent network of amorphous Si.

Structural properties, such as the static structure factor, $S(Q)$, the pair correlation function, $g(r)$ and the cosine distribution of bond angles, $B(\cos\theta)$, have been monitored regularly, after about each 50 000 accepted moves. The results displayed here represent the 'best' fits, which have not changed significantly when calculations were run further, to the two structure factors.

3. Results and discussion

Figure 1 compares experimental structure factors for the evaporated [4] and ion-implanted [5] samples. (The scattering vector ranges for the two sets of data are practically the same, so no effects can be explained by the different Q-ranges.) At first sight, the differences between the two functions seem significant, particularly around the first and second maxima (between about 2 and 4 Å^{-1}). Before attributing any physical significance to these variations, it is worthwhile considering how reliable these experimental results are.

It has been demonstrated several times (see, e.g., [24, 27, 28]) that reverse Monte Carlo modelling can provide sensible estimates of possible experimental errors. In figures 2 and 3, the structure factors from RMC modelling are compared to the corresponding experimental ones
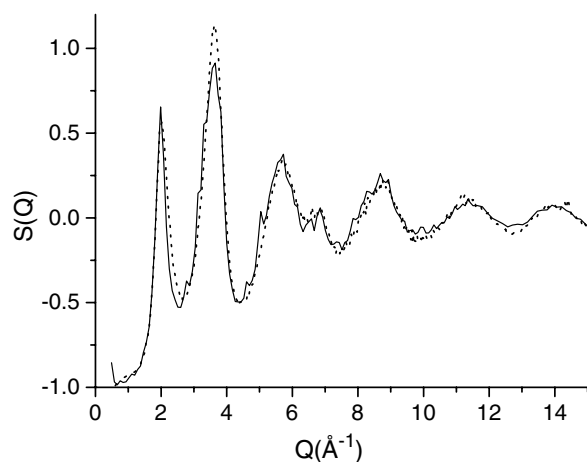
Figure 1. Experimental structure factors of evaporated (solid curve: neutron diffraction, [4]) and ion-implanted (dashes: x-ray diffraction, [5]) amorphous Si samples.
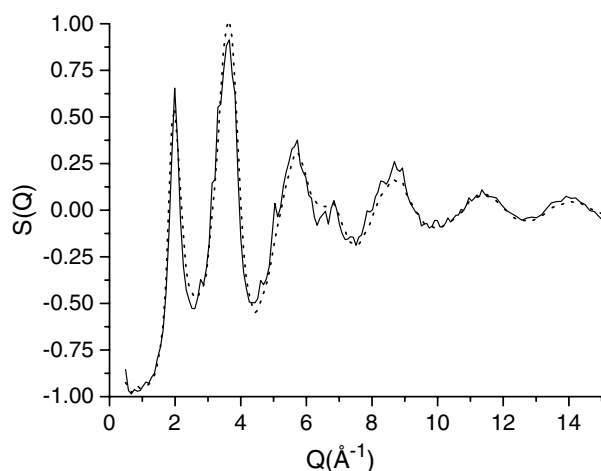

Figure 2. RMC fitted (dots) and experimental (solid curve) structure factors of evaporated (neutron diffraction, [4]) amorphous Si.

for the evaporated and ion-implanted samples, respectively. The overall agreement is quite good in both cases, although there are visible discrepancies. These, somewhat problematic, parts are concentrated in the region where the disagreement between the two sets of data is most significant (between 2 and 4 Å^{-1}). It is hard to tell which data can be approached the better; by looking at sheer numbers (at the χ^2 values) that reflect the 'goodness-of-fit' for the two calculations, the structure factor of the ion-implanted sample seems very slightly more reliable. However, since important details of the two data sets are not comparable (like Q-range and Q-spacing), the difference in terms of the χ^2 values cannot be judged as decisive. That is, the 'RMC-test' suggests that the two sets of data (from [4] and [5]) are roughly equally reliable.

We note, in passing, that the study of Biswas *et al* [26] reports an agreement with the data of Laaziri *et al* [5] (see *their* figure 2) which is visibly worse than the one in figure 3.
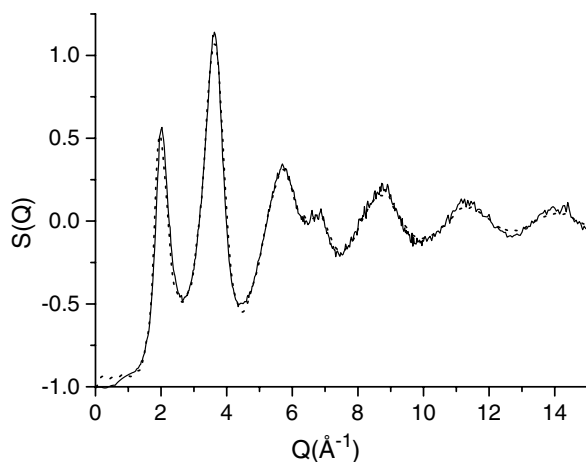
Figure 3. RMC fitted (dots) and experimental (solid curve) structure factors of ion-implanted (x-ray diffraction, [5]) amorphous Si.
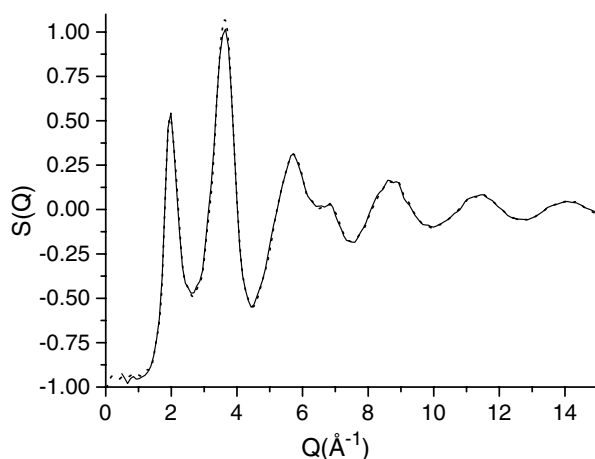

Figure 4. Structure factors, as obtained from RMC modelling, of the evaporated (solid curve) and ion-implanted (dots) amorphous Si samples.

The reason for this may lie in the difference in terms of system sizes, and also in that the constraints applied in [26] did not allow the system to reach a somewhat more favourable state. The difference between [26] and the present work in terms of the 'goodness-of-fit' is, however, minute.

Figure 4 compares the structure factors for the two samples as obtained by RMC modelling of the corresponding experimental data. It is now evident that the two different sets of data, taken on a-Si samples prepared via radically different methods, may correspond to extremely similar (indeed, nearly identical) structural models. This finding indicates that although in principle the evaporated sample, due to the way it has been prepared, may possess significantly more 'open' local structure (with more defects), there is only one generic amorphous silicon structure.

The level of statistical uncertainties of the RMC structure factors may be approximated by the level of noise (fluctuations from one data point to another) found in the individual curves.
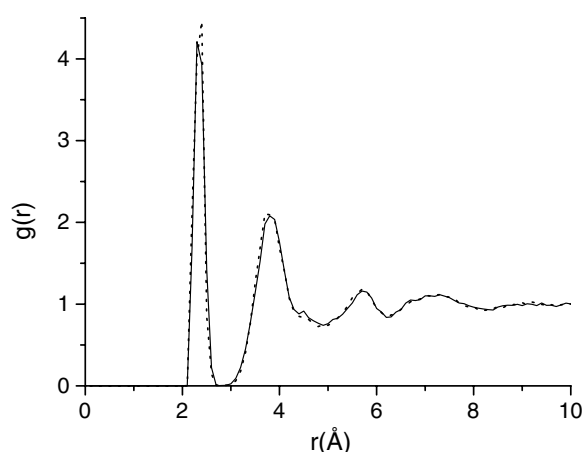
Figure 5. Pair correlation functions, as obtained from RMC modelling, of the evaporated (solid curve) and ion-implanted (dots) amorphous Si samples.

As can be seen in figure 4, there is only one small region, that of the main (second) maximum around 3.5 Å^{-1}, where differences that are outside the noise level can be detected. In the following, the effects of this small but visible alteration are going to be scrutinized.

Figure 5 compares the pair correlation functions, $g(r)$, for evaporated and ion-implanted samples, as calculated directly from the RMC configurations. (Note that the curves correspond to the same configurations whose $S(Q)$ are given in figure 4, that is, after the best fit was reached for both calculations.) Interestingly, the differences between the two curves seem greater than they were for the structure factors; note, however, that the level of statistical noise is also greater here for the individual functions. It is hard to pick up any feature which would clearly differ beyond noise level. A possibly significant one is the more pronounced presence of a (small) shoulder on the high-r side of the second maximum for the evaporated sample; another one may be that the first maximum for the ion-implanted sample appears somewhat narrower. This latter can point towards a (very slightly) better defined first coordination shell, in the case of the ion-implanted sample. (An explanation for the origin of the former difference, at nearly 5 Å, would be rather ambiguous since coordination spheres, other than the first one, are not defined unequivocally, and at these distances, correlations are practically impossible to trace individually.)

Now we turn to the characterization of the first coordination shell. Figure 6 displays the cosine distribution of bond angles, as calculated up to the upper boundary of the first coordination shell at 2.7 Å, for the two samples (again, for the very same particle configurations whose $S(Q)$ are given in figure 4). Although the overall shape and the intensities are very similar, there is a clear difference here: the distribution characteristic to the ion-implanted sample is slightly but significantly sharper. Note that, particularly, the intensities for the 'tail' featuring smaller bond angles (at larger values of cosines) are higher for the evaporated sample. (The small cosine (larger angle) tails, on the other hand, are more similar.) These cosine distributions support the observation made concerning the first maximum of the pair correlation function: the first coordination sphere in the ion-implanted sample is better defined (i.e., more similar to a regular tetrahedral local arrangement) than it is in the evaporated form.

The above finding is consistent with the results of [25], that is, for a satisfactory reproduction of the measured structure factor, a small, but noticeable fraction of 'small' bond angles, of the order of about 74°, is necessary. It is also clear, however, that the ion-implanted
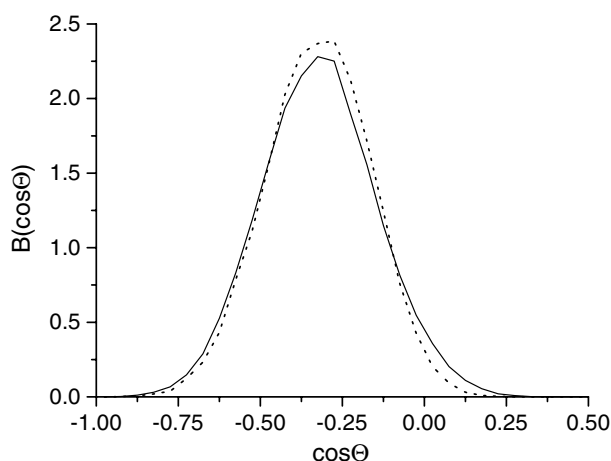
Figure 6. Cosine distribution of bond angles, as obtained from RMC modelling, for the evaporated (solid curve) and ion-implanted (dots) amorphous Si samples.
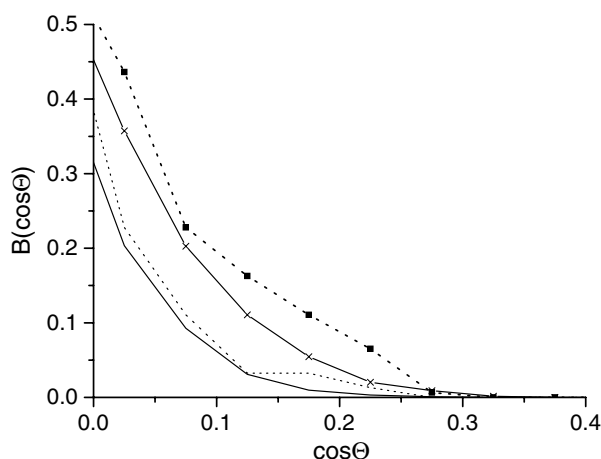

Figure 7. Cosine distribution of bond angles, as obtained from RMC modelling, for the ion-implanted (solid curve: 4096 atom model; dots: 512 atom model) and evaporated (solid curve with symbols: 4096 atom model; dots with symbols: 512 atom model) amorphous Si samples.

sample contains fewer of these small bond angles, and also that the smallest bond angle found in the ion-implanted structural model (at about 76°) is actually larger (closer to the tetrahedral) than the smallest one in the model of evaporated a-Si.

Figure 7 emphasizes the most important region of the bond angle distributions, for angles smaller than 90° (cosines larger than 0). For a more complete picture, the system-size dependence of the effect has also been investigated; in the figure, results for 512 atom systems are included for both samples. It is clear that, for both samples, smaller systems produce somewhat larger fractions of the smaller than usual bond angles. However, the effects resulting from the difference between samples are much larger than those from different system sizes; in particular, the 512 atom implanted model contains much fewer small bond angles than the 4096 atom evaporated model. We note that the RMC-based investigation of Biswas *et al*

[26], using 500 atom systems, also finds an appreciable proportion of small bond angles; based on figure 7, we suggest that the number of them would be decreased if the systems size were increased.

The appearance of these small bond angles has been shown to have a profound effect on the electronic density of states [25] of evaporated a-Si: the smaller the bond angle the more extra states appear in the gap. This finding forms a firm basis for the prediction that, for the ion-implanted form, fewer such extra states will be found, so the gap will be narrower than the gap of evaporated a-Si samples. This is the most important difference between the two samples considering the electronic properties.

4. Conclusion

The structure factors of amorphous silicon samples resulting from radically different methods of preparation (evaporation and ion implantation) have been modelled by means of the reverse Monte Carlo technique. It has been shown that there are no major differences in terms of the microscopic structure. For the successful reproduction of the experimental data (within errors) from both samples, the appearance of a small fraction of small bond angles, of the order of 75°, was necessary. As detailed comparison made it clear, the ion-implanted sample is somewhat more ordered, containing local environments that are more similar to the (ideal) regular tetrahedral one. This finding is consistent with the expectation based on simple considerations concerning the two methods of preparation: precipitation from the vapour phase was thought to result in a higher level of disorder (higher concentration of 'defects') than distorting the crystalline structure, as is done during ion bombardment.

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