Mat. Res. Soc. Symp. Proc. Vol. 609 © 2000 Materials Research Society

Self-interstitials have never been observed in crystalline Si. How about amorphous Si?

Sjoerd Roorda
Département de physique et Groupe de recherche en physique et technologie des couches mines,
Université de Montréal
CP 6128 succursale Centre-ville
Montréal, H3C 3J7
CANADA

Abstract

In the early days of point defect studies in electron irradiated crystalline silicon, it was surmised that the Si self-interstitial is highly mobile even at 4 K and escapes direct detection. The existence of self-interstitials has of course been confirmed through the diffusion behaviour of a range of impurities and the direct observation of larger interstitial-type clusters. Against this background, the direct observation of self-interstitials in *amorphous* Si would seem next to impossible. Yet just such an observation may have been made recently, through a comparison of the high-resolution radial distribution function of pure amorphous Si before and after thermal anneal and that of crystalline Si.

Introduction

The structure of pure amorphous silicon is believed to approach that of a perfect, fully connected, four-fold coordinated, continuous random network. This ideal cannot be obtained, much like that is the case for crystalline materials which are never as ideal as the perfect, defect-free crystal. Real amorphous silicon, therefore, would contain deviations from the ideal random network. These deviations can be defects that are typical for a random network, such as density variations, 5- or -7 member rings or defects much like those encountered in crystalline silicon, including vacancies and interstitials. It has been argued that removal of such defects, which requires atomic mobility just like defect annihilation in crystal silicon does, is in fact the origin of the phenomenon known as structural relaxation [1].

Considerable experimental evidence has been accumulated in support of the notion that *vacancy*-type defects do indeed exist in amorphous silicon. These include the solubility and diffusivity of metal impurities in amorphous silicon [2], the kinetics, energetics, and temperature dependence of structural relaxation [1], and the trapping and annihilation behaviour of positrons in amorphous silicon [3]. However, all of these measurements are in one form or other indirect and, moreover, none of these address the possible existence of *interstitial* type defects. In this paper, I will discuss recent experimental results [4, 5] and how they may give direct evidence for the existence of vacancies and interstitials in amorphous silicon and their role in structural relaxation.

Amorphous silicon by ion implantation: pure, void-free and non-compactable

The recent experimental data in question consists of high resolution x-ray diffraction data of pure amorphous silicon, prepared by ion implantation and, in some cases, thermal annealing. These

data have recently been published including a detailed description of the experimental conditions [5] and sample preparation [6] which will not be repeated here. Before discussing these data and because most other papers to be presented in this symposium concern hydrogenated amorphous silicon, a few words should be spend to explain the implications of "prepared by ion implantation". The starting material is high-purity undoped crystalline silicon, which is made amorphous by high-energy (0.5 - 27 MeV) Si ion implantation. Amorphous silicon thus prepared is the purest (all impurities measured to be well below 0.1 %) and densest (1.76 % less dense then crystalline silicon) [7] that can be made. It has been shown by small angle x-ray scattering to be free of voids and internal surfaces [8].

An important clue, at least in the context of this paper, is that according to surface profilometry, amorphous silicon prepared by ion implantation does not densify upon thermal annealing (it is "non-compactable"). In fact, wafer curvature measurements [9] have shown that annealing induces a slight expansion, but this is less than 0.1 vol. %. The absence of significant density changes during thermal annealing is an important ingredient in the following discussions because, if structural relaxation would be due to removal of vacancy-type defects only, then a densification of a few at. % would have to be observed. Since this is not the case, roughly equal numbers of vacancy and interstitial type defects are likely to be involved.

Radial distribution function and thermal annealing effects

In Figure 1 is reproduced the first few ångströms of the radial distribution function of pure amorphous silicon [5], as prepared by ion implantation (solid curve) and after thermal anneal at 600 °C (dotted line). To the eye, the effect of the thermal anneal is visible only in the second peak and beyond, but a quantitative analysis of the data reveals that the first neighbour peak is also affected. To be precise, the position of the first neighbour peak remains the same (2.351 and 2.532 +/- 0.001 Å; identical to within 0.05%) but the area (or coordination number) increases from 3.79 to 3.88 +/- 0.01 atom. As well, these same x-ray data have again confirmed that the density remains unchanged to within 0.1 %. Now, how can this be? Upon annealing, the coordination number increases and the average interatomic distance remains the same; together this would imply a densification by 2 % but no such densification is observed.

To understand this paradox, it should be understood that the coordination numbers quoted (3.79 and 3.88 atoms) are the result of Gaussian fits to the experimental data, and that only a small window has been used as input to the fit. Thus, any neighbours at distances (e.g. 1.9 Å) that are very different from a first (or second) neighbour distance would not contribute to the fit and would not be counted. Such neighbours would of course be qualified as "defects". An attempt was made to detect atoms at such uncommon distances as will be described in the next section.

In order to establish whether defects are present, on should integrate the radial distribution functions over a range between well-separated nearest neighbour peaks. This was done in the following way: first Gaussian fits were made to the first peak and to the first half of the second peak. Then the Gaussian fits were subtracted from the data, yielding curves that should be equal to zero if there would be no defects. (If the limits of the integration had been zero and the first neighbour distance, then only interstitials would contribute. Unfortunately, this is also the region where the density is determined, essentially by integrating and setting the integral to zero.) The

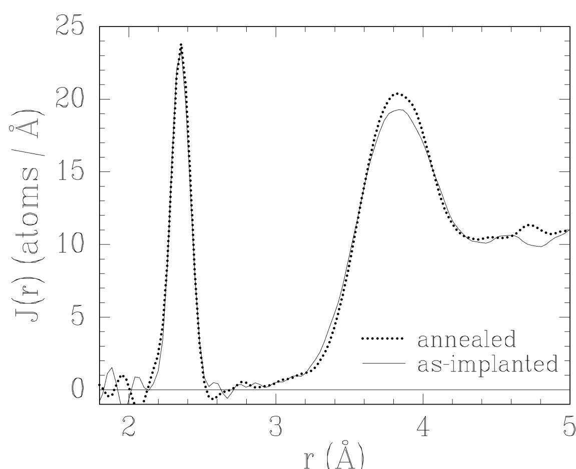

Figure 1. First two peaks of the radial distribution function of pure amorphous silicon, showing as implanted (solid line) and 600 ºC annealed amorphous silicon (dotted line). After [5].

results of this procedure are shown in Figure 2, for both as implanted material (left panel) and annealed material (right panel) [5]. A similar procedure was applied to the radial distribution function of crystalline silicon (not shown) which incidentally suffered from more prominent termination ripples. In Figure 2 it is seen that the residual data oscillates around zero, due to noise and termination ripple. Integrating these oscillating curves from the center position of the first peak to that of the second peak gave the values that are summarized in Table I.

Table I: Integrated radial distribution function between first and second neighbours

Material	*Coordination*	*In-between atoms*
Crystalline Si	4.02 ± 0.05	0.03
Annealed a-Si	3.88 ± 0.01	0.07
As implanted a-Si	3.79 ± 0.01	0.12

The first row in Table I gives the values for crystalline Si. Since the data were taken on a high-purity powder with an average particle diameter of 10 μm, the result of the "in between" integration should be zero. The actual value of 0.03 atoms is due to noise and termination ripples only and serves to give an estimate of the uncertainty of the procedure. (In fact, it can be regarded as an upper limit for the error margin since the data on amorphous silicon suffers from considerably less termination effects due to different experimental conditions.)

With the uncertainty thus established, it appears that the results of the "in between" integration in the amorphous silicon leads to values that are significantly different from zero. Moreover, there is a trend consistent with the scenario proposed for structural relaxation. In "as implanted" amorphous silicon, there are no less then 0.12 atoms with neighbour distances well separated from either the first or the second nearest neighbour distance, whereas after annealing this value has reduced to 0.07 atoms, significantly less then 0.12 but also significantly different from zero.

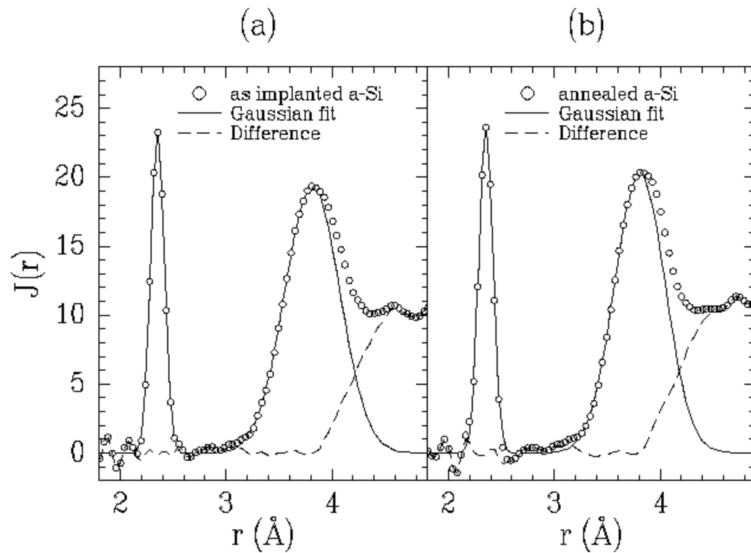

Figure 2. Radial distribution function (points), Gaussian fits to the first two peaks (solid lines) and residuals (dotted lines) for (a) as-implanted amorphous silicon and (b) amorphous silicon annealed at 600 ºC.

Really interstitials? Maybe not!

The integration procedure outlined and used in the preceding paragraphs, if valid, would indeed give an estimate of the number of defects. Making sure that these defects are indeed interstitials, however, is another matter. If the network around a defect would not relax (and "relax" in this context refers to local rearrangements only, similar to those around point defects in crystalline silicon), then there would be no contribution from vacancy type defects to the "in between" integration. In that case, the values quoted in Table I would be a direct measure of the concentration of interstitial type defects. As it stands, however, one may expect some local relaxation around defects to occur (it has been argued that these local rearrangements give rise to the large bond angle distortions measured in un-annealed amorphous silicon) and, consequently, the values shown in Table I contain contributions from both vacancies and interstitial type defects.

Maybe yes!

If we want to convince ourselves of having observed interstitials in amorphous silicon, it is not enough to look at the values in Table I only. These values have to be put in the context of all the other experimental data and how these change upon thermal annealing. In summary, the coordination increases but the interatomic distance remains the same, and a number of experimental techniques show a reduction in vacancies, but the density does not increase. Therefore, there must be mutual annihilation of vacancy and interstitial type defects. The

observation of a reduction of "in between" atoms with distances between the first and second nearest neighbour distance in concert with vacancy removal under constant density strongly suggests that at least a sizeable fraction of those atoms are, in fact, interstitials. Therefore, I am tempted to conclude that yes, there is experimental evidence for the existence of interstitials in amorphous silicon.

Acknowledgements

The experimental data to which this paper refers was the result of a group effort but I would like to thank in particular Khalid Laaziri for his dedication, patience and perseverance. This work is financially supported by the Natural Science and Engineering Research Council of Canada (NSERC) and the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (FCAR).

References

[1] S. Roorda, W. C. Sinke, J. M. Poate, D. C. Jacobson, S. Dierker, B. S Denis, D. J. Eaglesham, F. Spaepen, and P. Fuoss, Phys. Rev. B **44**, 3702 (1991).
[2] S. Coffa, J.M. Poate, D.C. Jacobson, and A. Polman, Appl. Phys. Lett. **58**, 2916 (1991).
[3] S. Roorda, R.A. Hakvoort, A. van Veen, P.A. Stolk, and F.W. Saris, J. Appl. Phys. **72**, 5145 (1992).
[4] K. Laaziri, S. Kycia, S. Roorda, M. Chicoine, J.L. Robertson, J. Wang, and S.C. Moss, Phys. Rev. Lett. **82**, 3460 (1999).
[5] K. Laaziri, S. Kycia, S. Roorda, M. Chicoine, J.L. Robertson, J. Wang, and S.C. Moss, Phys. Rev. **B 60**, 13520 (1999).
[6] S. Roorda, K. Laaziri, and S.C. Gujrathi, Nucl. Instr. and Meth. **B 148**, 360 (1999).
[7] J. S. Custer, M. O. Thomson, D. C. Jacobson, J. M. Poate, S. Roorda, W. C. Sinke and F. Spaepen, Appl. Phys. Lett. **64**, 437 (1994).
[8] D. L. Williamson, S. Roorda, M. Chicoine, R. Tabti, P. A. Stock, S. Acco and F. W. Saris, Appl. Phys. Lett. **67**, 226 (1995).
[9] C. A. Volkert, J. Appl. Phys. **74**, 7107 (1993).