Vacancy-type and electrical defects in amorphous silicon probed by positrons and electrons

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Amorphous Si has been investigated by variable-energy positron annihilation spectroscopy (PAS) and lifetime measurements of optically generated free carriers. The density of positron-trapping defects can be reduced by thermal annealing at 500 °C. Simultaneously, the density of bandgap states is reduced as indicated by an increased photocarrier lifetime. Hydrogen, implanted and annealed at 150 °C, leads to an increased photocarrier lifetime and reduced positron trapping. It appears that (some of) the electrical defects are associated with positron-trapping, and therefore possibly vacancy-type, structural defects. Finally, both methods have been used to detect small amounts of ion irradiation damage in amorphous Si.

I Introduction

The electrical and the structural properties of a-Si appear to be dominated by defects [1,2]. Structural relaxation, which is also known as short range ordering, is thought to be mainly controlled by atomic motion similar to that responsible for damage repair in heavily defected c-Si. Moreover, the structural defects may also dominate the electrical properties because the electrical defects are most likely dangling and strained bonds associated with the structural defects. Such a spatial correlation has been suggested from the hydrogen induced detrapping of metal impurities in a-Si [3].

For the work described in this paper, we have used positron annihilation spectroscopy (PAS) [4] to study structural relaxation, radiation damage, and defect passivation in a-Si; in addition, lifetime measurements of photogenerated carriers have been performed. The PAS results are consistent with the notion that a-Si contains a large variety of vacancy-like defect structures, some of which disappear upon thermal annealing, while the carrier lifetime measurements show that annealing leads to a reduction in the density of carrier trapping centres. The combined results seem to indicate that a spatial correlation exists between electrical and structural defects. A more detailed report including a quantitative analysis will be given in a forthcoming publication [5].

II Sample preparation and measurements

Amorphous layers of ≈ 1 μm thickness were formed on c-Si wafers by $^{28}Si^+$ ion implantation (0.5 and 1 MeV, 5×10^{15} cm^{-2} each). The ion beam was defocussed and rastered electrostatically over the sample surface. The temperature of the targets during the implantations was ≈ -100 °C. One piece was set aside ('as-implanted'). Most pieces were annealed in vacuum at 500 °C for 1 hour ('annealed'), some of which were subsequently re-implanted (at ambient temperature), with 0.5 MeV $^{28}Si^+$ ions, but this time to much lower doses ('damaged'). Some a-Si samples were implanted with H^+ ions and annealed at 150 °C. One implant (for PAS) was performed using an energy of 50 keV and a dose of 1×10^{17} ions/cm^2. This implant resulted in a hydrogen implantation profile which peaks at a depth of ≈ 0.5 μm, where it reaches a local H-concentration of ≈ 7 at. %. In addition, a sample (for carrier lifetime measurements) was implanted with 2, 4, and 15 keV moleculair hydrogen ions to a dose of 5×10^{15} cm^{-2}, resulting in a hydrogen profile which is distributed over 0.15 μm in the near-surface region. For the low energy implant, the peak hydrogen concentration is about 2.5 at. %.

All samples were irradiated with mono-energetic positrons and the Doppler shape parameter S was determined as a function of the positron energy (E) [6]. This parameter is dependent on the width of the gamma ray peak due to annihilation of positrons with electrons. S has certain characteristic values depending on where annihilation takes place: at the surface, in the perfect solid, or at a defect site in the solid. Annihilation in different kinds of defect sites

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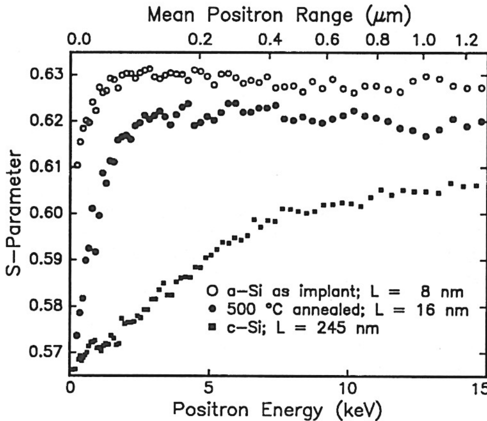


Fig. 1 S parameter as a function of positron energy for c-Si (squares), and for as-implanted (solid circles) and 500 °C annealed (open circles) pure a-Si. The depth scale (top) corresponds to the mean positron range.

can also give rise to different S values. The measured S parameter is a weighted average of the different contributions. See also Schultz [4] and van Veen [7]. The measured $S(E)$ curves can be described by theoretical fits to the positron diffusion-annihilation equation which allows the positron diffusion length to be extracted [4,7]. Such fits assume certain energy dependent positron implantation profiles. We have assumed a Makhovian profile with parameters n=1.6 and m=2. For homogeneous materials (that is without depth dependent defect profiles) the only free parameters in the fit are the S parameter at the surface and in the bulk and the positron diffusion length L.

Electron-hole plasmas in a-Si were generated and probed using pulses from a colliding pulse modelocked laser (CPM) [8]. The 100 fs duration pulses of 0.1 nJ each have an average wavelength of 620 nm. The output of the CPM was split into two beams, the first (pump) was chopped at 50 kHz and focussed to a 25 μm spot, yielding an energy density of $\approx$ 4 μJ/cm^2. The second (probe) was sent through a mechanical delay line and focussed to a 15 μm spot. The energy density in the probe spot was about one tenth of that in the pump. The probe and a sample of the pump were detected by photodiodes. Using a lock-in technique, the observable relative reflectivity change is $\approx 2\times10^{-6}$. The experimental set-up has been described in more detail elsewhere [9].

III Results

Ion implantation and thermal annealing -- In Fig.1, S is shown as a function of E (*i.e.* $S(E)$) for c-Si, as-implanted a-Si, and annealed a-Si. The top axis shows the mean depth z of the positrons, with z proportional to $E^{1.6}$. $S(E)$ for c-Si is similar to earlier measurements on the same system. For very low positron energies, a large fraction of the annihilation events takes place at the surface and this is accompanied by a low surface S value of 0.56. For high positron energies (> 15 keV, not shown), all annihilation takes place in the undamaged crystal and this gives the S value of defect-free c-Si of 0.6069. For intermediate energies, some positrons annihilate at the surface and some in the bulk, therefore S is a weighted average of surface and bulk values. The slope of $S(E)$ is related to the diffusion length L of the positrons in c-Si, which turns out to be 245 nm in this sample, in good agreement with literature [10,11]. This value is the result of fitting the data to the positron diffusion annihilation equation. Results are listed in Table I.

The $S(E)$ measurements for the a-Si samples differ in two ways from that for c-Si: (1) The bulk value S_b is considerably higher, and (2): the slope with which this value is approached is much steeper in a-Si than in c-Si. It is observed that annealing at 500 °C results in a slight decrease of S in the bulk (to 0.6225) and a substantial increase in L (to 16.2 nm). It should be noted that such a temperature is far below that necessary for noticeable crystal nucleation while solid phase epitaxial crystallization at the c-Si/a-Si interface is limited to a few Ångströms [12]. Annealing of as-implanted a-Si at a temperature of 150 °C only led to small changes in $S(E)$.

Table I: Results of PAS fitting (S(bulk), L) and carrier lifetime measurements (τ)

sample description	2nd implant	anneal Temp. (°C)	S	L (nm)	τ (ps)
c-Si	-	-	0.6069	245	
as-implanted	-	-	0.6299	7.9	1
low T annealed	-	150	-	-	1.6
high T annealed	-	500	0.6225	16.2	11
deep hydrogen	50 keV H^+	150			
shallow hydrogen	low energy H^+	150	-	-	1.6 & 13

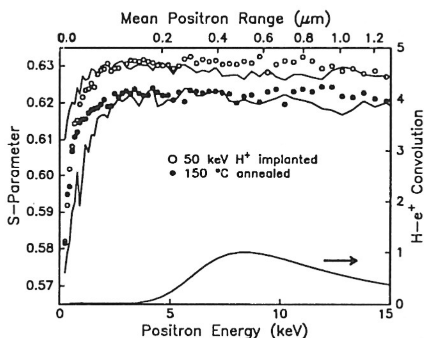
It is believed that a-Si contains a wide variety of structural imperfections, including vacancy-type defects [2,3]. These defects are expected to act as traps for positrons, thus reducing the diffusion length and increasing S. This is indeed observed, and therfore the present results confirm that defects play an important role in structural relaxation of a-Si.

Hydrogen implantation and annealing -- Fig. 2 shows the $S(E)$ curves taken on a-Si which had been co-implanted with 50 keV, 5×10^{16} cm^{-2} H^+. In addition, the depth profile of the implanted hydrogen, according to calculation and convoluted with the positron implantation profile, is shown as a solid line. It can be seen that merely implanting hydrogen does not change the interaction of positrons with the a-Si to a measurable extent. However, the anneal behaviour of this material differs from that of pure a-Si. This is evident from the change in S which reaches a value equal to that in 500 °C annealed pure a-Si after prolonged (25 h) annealing at 150 °C. It appears that the effect of high temperature annealing of pure a-Si on the PAS measurements (decreasing S) can be mimicked by hydrogen implantation and low temperature annealing. It is well known that hydrogen passivates electrical defects in a-Si; the present result therefore suggests a connection between the passivation of dangling as well as strained bonds by H and the high temperature anneal behaviour of pure a-Si.

Radiation damage in annealed a-Si -- In the previous two sub-sections, the effect of thermal annealing on the interaction between positrons and a-Si has been investigated. This section deals with data on the inverse effect: positrons have been used to detect the damage generated in *annealed* a-Si by ion bombardment. Three samples of a-Si were prepared by ion implantation as described in sect. II and annealed in vacuum at 500 °C. Following the anneal treatment, the specimens were bombarded with 500 keV Si^+ ions to a dose of 2.5×10^{11}, 2.5×10^{12}, and 2.5×10^{13} cm^{-2}, respectively. The amount of ion damage in the a-Si samples has been (indirectly) estimated by channeling measurements of 2 MeV He^+ ions backscattered from identically bombarded c-Si samples. A piece of c-Si bombarded with 2.5×10^{11} Si^+ ions/cm^2 could not be distinguished from unimplanted c-Si, indicating that the density of displaced atoms is well below an at. %. The other samples showed a measurable increase in the channeled yield consistent with 0.013 and > 0.10 DPA (displacements per atom) due to the 2.5×10^{12} and 2.5×10^{13} Si^+/cm^{-2} bombardments, respectively.

The $S(E)$ curves for the three ion damaged a-Si samples are shown in Fig. 3. The data for as-implanted and 500 °C annealed a-Si are reproduced from Fig. 1 for comparison (lines). It can be seen that $S(E)$ for a-Si bombarded with the lowest ion dose already differs from that of annealed a-Si. The ion channeling measurements on the c-Si samples suggest that the density of displaced target atoms is as low as 0.001 DPA. Yet the PAS measurements clearly distinguish between this slightly damaged annealed a-Si, and that which had not been re-implanted. It shows that PAS is a sensitive technique for detection of displacement damage in a-Si.

The $S(E)$ curve for annealed a-Si, bombarded with 2.5×10^{13} Si^+ ions/cm^2 already closely resembles the curve for a-Si in the as-implanted state. Apparently the damage generated by ion bombardment begins to saturate when the density of displaced target atoms is several at. %. Such saturation has also been observed by Raman spectroscopy measurements and calorimetry [2] of ion damage in a-Si. It suggests that the defect density in a-Si cannot exceed a few at. %.



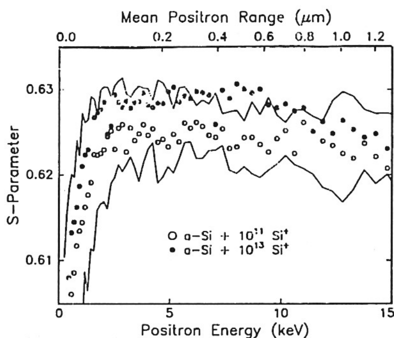


Fig. 2 *S(E)* for a-Si co-implanted with H^+ (open circles), and after prolonged annealing at 150 °C (solid circles). The data for pure a-Si (as-implanted and 500 °C annealed) shown in Fig. 1 are reproduced as thin lines. The depth scale (top) corresponds to the mean positron range. The overlap of the positron implantation profile with the H implantation profile is shown (bottom curve).

Fig. 3 *S* parameter as a function of positron energy for a-Si annealed at 500 °C and then implanted with 500 keV Si^+ ions to a dose of 2.5×10^{11} cm^{-2} (open circles) and 2.5×10^{13} cm^{-2} (squares). The data for pure a-Si (as-implanted and 500 °C annealed) shown in Fig. 1 are reproduced as thin lines.

Carrier lifetime measurements -- Free carriers (electrons and holes) have been generated and detected optically in samples similar to those previously investigated with positrons. Measurements of the reflectivity as a function of time, following generation of a plasma of free carriers by a 100 fs light pulse, are shown in Fig. 4. For as-implanted a-Si (Fig. 4a), the reflectivity returns to its original level within several ps. The reflectivity for 500 °C annealed a-Si recovers significantly slower, and only after 60 ps the initial reflectivity is reached (not shown). A positive change in reflectivity, which would be indicative of sample heating, has not been observed at the low laser intensities employed here. Higher irradiation conditions would also lead to a situation where Auger recombination processes become important. The decay time τ, deduced from the single exponential decay curves, is 1 ps in as-implanted a-Si and 11 ps in a-Si which had been annealed at 500 °C.

The a-Si sample which had been co-implanted with low energy H^+ and annealed at 150 °C shows a reflectivity recovery, shown in Fig. 4c, intermediate between those of the previous two samples. The decay cannot be described by a single exponential but appears to be characterized by an initial fast decay (τ = 1.6 ps), followed by a slower process (τ = 13 ps). In our opinion, this is caused by the light probing two distinct regions. Around the hydrogen peak in the profile electrical defects have been passivated but deeper (and shallower) layers which are also probed have not changed at all, except for a small thermal effect resulting from the 150 °C anneal (τ = 1.6 ps). The line through the datapoints represents the sum of two single-exponential decay curves with τ = 1.6 and 13 ps and relative contributions of 70 and 30 %, respectively.

A 500 °C annealed a-Si sample was re-implanted with 1 MeV Si^+ ions to a dose of 2×10^{13} cm^{-2} has also been measured and the results are shown in Fig. 4d. The density of displaced target atoms in the near surface layer of this sample has been estimated to amount to 0.3 at. %. The reflectivity is observed to return quickly to its original value. Similar to the reflectivity decay curves of as-implanted and 500 °C annealed a-Si, it can be characterized by a single exponential decay time but with a value of τ = 2 ps. It appears that photocarrier lifetime measurements, like PAS, can be used as a sensitive probe of collisional damage in annealed a-Si. A full report of lifetime measurements in a-Si and c-Si, including ion dose and projectile mass dependence will be given elsewhere [13].

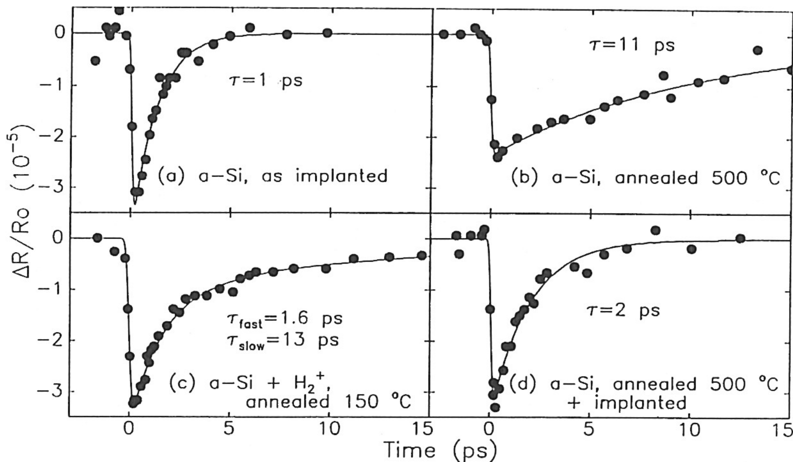


Fig. 4. Normalized reflectivity changes (points) as a function of time difference between pump and probe for (a) as-implanted a-Si, (b) a-Si annealed in vacuum at 500 °C, (c) a-Si co-implanted with low-energy H^+ and annealed at 150 °C, and (d) a-Si annealed at 500 °C and re-implanted with 1 MeV Si^+ ions to a dose of 3×10^{-3} DPA. Time 0 corresponds to overlap of pump and probe. Solid lines are exponential decay curves convoluted with the experimental resolution.

IV Discussion

The most obvious explanation of the present data is in terms of structural defects acting as traps for positrons *and* electrons. Starting from a (hypothetical) defect-free continuous random network (CRN), real a-Si can be represented as a CRN with defects. These defects can be unique to the network (*e.g.* single dangling or floating bonds) or may be similar to point defects and small point defect clusters in c-Si (*e.g.* divacancies). In principle, both vacancy and interstitial-type defects can exist in a-Si, but positron *trapping* is most likely to occur only at vacancy-type defects (by comparing with the behaviour of positrons in other solids [4]). Defects are expected to be accompanied by a strain field, similar to that surrounding point defects in c-Si. Differences in the defect population in the a-Si network are then thought to give rise to the variable short range order or structural relaxation phenomena. In addition, it is reasonable to expect that structural defects have dangling or highly strained bonds (or both) associated with them. These would give rise to bandgap states that are not necessarily unique for the CRN but similar to defect states in c-Si.

Structural defects can be removed by thermal annealing, they can be generated by ion irradiation, and the electrical activity can be passivated by hydrogen. Such treatments are expected to modify the interaction of positrons with a-Si because vacancy type defects are known to act as traps for positrons. A high concentration of defects therefore reduces the positron diffusion length. Annealing or passivation is expected to lead to larger, and ion irradiation to smaller diffusion lengths. This is exactly what we have observed.

Other interpretations of the PAS data are possible, some of which cannot be completely excluded. For example, the slope in $S(E)$ may not be due solely to positron diffusion but to positron drift in an electric field (band bending) that might be present near the surface. Although in a-Si such a field is not expected to penetrate far into the material (because of the high density of states in the gap) it may play a role in the case of c-Si. This would make it hard to quantify the present results.

Although it is fully expected that the formation and removal of vacancy-type defects leads to the appearance and disappearance dangling bonds, it is not easily shown experimentally. A spatial relation between 'defective' bonds and radiation damage sites in ion bombarded a-Si has previously been suggested to exist by Heidemann *et al.* [14], who used ellipsometry of bevelled a-Si samples. Moreover, Coffa and Poate observed that hydrogen

implanted in a-Si leads to de-trapping of metal impurities which had previously been gettered in a defected a-Si layer. This strongly suggests that the electrical defects are located at the same site as the structural defects which can trap metal atoms [3]. It is concluded that the present data and the explanation presented in this paper are consistent with these results, and can therefore be taken as additional evidence for the spatial correlation between structural and electrical defects in a-Si.

V Conclusions

In summary, we have studied structural and electrical defects in amorphous Si by positron annihilation spectroscopy employing slow, variable energy positrons, and by lifetime measurements of optically generated free carriers. The PAS data indicate that a-Si contains a number of vacancy-like defects, some of which can be annealed out by heating to 500 °C. However, other explanations of the data are possible and cannot be completely excluded.

Concurrent with the apparent removal of vacancy-type defects from a-Si by the annealing, a tenfold increase in the lifetime of an optically generated free carrier plasma is observed, suggesting a significant reduction in the number of bandgap states. A large increase in the free carrier lifetime has also been obtained by a low temperature (150 °C) anneal, but with hydrogen co-implanted in the a-Si. Such a low temperature anneal (with co-implanted hydrogen) also leads to a reduction of the *S*-parameter for positron annihilation similar to that obtained by a high-temperature anneal without hydrogen. This suggests that the bandgap states acting as recombination centres for free carriers are associated with the vacancy-type defects.

Finally, it has been found that both positron spectroscopy and carrier lifetime measurements can be a sensitive probe of ion radiation damage in 500 °C annealed a-Si. When the estimated density of displaced atoms due to nuclear collisions approaches 10^{-3}, both methods clearly detect a change. This suggests that the defect density in a-Si annealed at 500 °C is less than 0.1 at. %.

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