PICOSECOND PHOTOCARRIER LIFETIMES IN ION-IRRADIATED AMORPHOUS AND CRYSTALLINE SILICON

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ABSTRACT

Crystalline silicon (c-Si) and structurally relaxed amorphous silicon (a-Si) were implanted with 1 MeV Si^+ at liquid nitrogen temperature. The photocarrier lifetime τ in the implanted samples was determined with sub-picosecond resolution through pump-probe reflectivity measurements. At low damage levels (i.e. $< 10^{14}$ ions/cm^2), τ decreases with increasing ion dose in both materials, indicating a build up of trapping and recombination centers. The dominant centers in c-Si appear to be related to simple defects. The generation rate of electrically active defects is found to be the same in relaxed a-Si and c-Si, which suggests that the structural defects formed in a-Si strongly resemble the simple defects in c-Si. For ion doses $> 10^{14}$/cm^2, τ saturates at a level of 0.8 ps for both materials. Strikingly, the saturation sets in far below the dose needed to amorphize ($>10^{15}$/cm^2). The defect density in a-Si at saturation is estimated to be $\approx$1.6 at.%.

INTRODUCTION

Recent experiments have indicated that a strong connection exists between defects in pure amorphous silicon (a-Si) and its thermodynamic and structural properties [1]. The changes in the structure of a-Si observed upon thermal annealing below the crystallization threshold, a process generally referred to as structural relaxation, have been attributed to annihilation of point defects in the a-Si network. Recently, we have shown that the photocarrier lifetime in a-Si increases from $\approx$1 ps to $\approx$11 ps during structural relaxation, which is consistent with the idea of annealing out electrically active defects [2, 3]. Conversely, introducing defects in relaxed a-Si by ion irradiation returns the material to the as-implanted state [1-3].

Differential scanning calorimetry (DSC) measurements on ion irradiated crystalline silicon (c-Si) and relaxed a-Si have suggested that the defect populations in both materials are similar [4]. In this paper, electrically active defects introduced by 1 MeV Si^+ irradiation of relaxed a-Si and c-Si are investigated by measuring the photocarrier lifetime with sub-picosecond resolution. This comparison gives further support for the notion that the structure of defects in c-Si and a-Si is similar.

EXPERIMENT

1.2 μm thick a-Si layers were prepared by implanting 0.5 and 1 MeV $^{28}Si^+$ into Si(100) held at liquid nitrogen temperature. The a-Si samples were structurally relaxed by annealing at 500 °C for 1 hr in vacuum (base pressure $< 10^{-7}$ mbar). These relaxed a-Si samples, as well as crystal Si(100) wafers (p-type, 5-15 Ωcm), were implanted with 1 MeV $^{28}Si^+$ at liquid nitrogen temperature to introduce damage. During the implants, samples were tilted 7° with respect to the ion beam to avoid channeling in the c-Si substrates. The implantation damage in the c-Si was investigated by performing channeling Rutherford backscattering spectrometry (RBS) using a 2 MeV He^+ beam and a scattering angle of 167°.

The dynamics of photogenerated carriers in the ion implanted c-Si and relaxed a-Si were investigated through pump and probe reflectivity measurements. This technique employs 100 fs pulses (λ=620 nm) from a colliding pulse mode-locked dye (CPM) laser and is described in detail elsewhere [2, 3]. Briefly, a CPM-pulse is focused on the sample generating an electron and hole

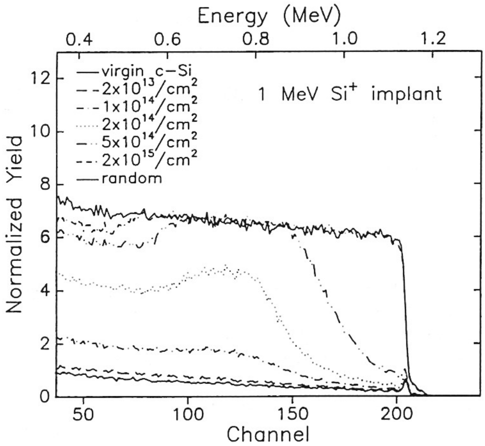

Figure 1. *Channeling RBS spectra of c-Si samples implanted with 1 MeV Si$^+$ at liquid nitrogen temperature. Implantation doses are indicated in the graph. A channeling spectrum of virgin c-Si and a random spectrum are shown as a reference.*

(e-h) plasma with a carrier density $<2\times10^{18}/\text{cm}^3$ [5]. A probe pulse, split off from the pump beam, is focused within the pump spot to measure the change in reflectivity induced by the e-h plasma. By varying the time delay between pump and probe, the evolution of the reflectivity is measured, and in this way the decay of the e-h plasma is probed with ≈0.2 ps resolution. Exponential fits were used to obtain the average carrier lifetime τ from the pump-probe reflectivity measurements [2, 6].

RESULTS

Figure 1 shows channeling RBS spectra for c-Si implanted with 1 MeV Si$^+$ at liquid nitrogen temperature. For ion doses $< 1\times10^{13}/\text{cm}^2$, no significant difference in the channeling yield is observed between implanted and virgin c-Si. For higher doses the backscattering yield increases above the level of unimplanted c-Si. At $5\times10^{14}/\text{cm}^2$, the random level is reached, indicating the formation of a buried, continuous a-Si layer. At $2\times10^{15}/\text{cm}^2$, the random area extends towards the surface channel which suggests that a 1.2 μm thick surface layer of a-Si is formed.

Figure 2 shows the measured reflectivity change (solid points) as a function of the time delay between pump and probe pulse for: (a) c-Si implanted with 1 MeV Si$^+$ to a dose of $5\times10^{12}/\text{cm}^2$, and (b) relaxed a-Si implanted with 1 MeV Si$^+$ to a dose of $6\times10^{12}/\text{cm}^2$. The reflectivity change is normalized to the average reflectivity R_0 for $t<0$. At $t=0$, the reflectivity instantaneously decreases in both samples, due to the generation of an e-h plasma by the pump pulse. For longer time delays, the reflectivity recovers to the initial level. The solid lines in Fig. 2 are exponential fits to the measured data points. The carrier lifetime is found to be $\tau\approx12$ ps for the implanted c-Si (Fig. 2a) [7] and $\tau\approx4$ ps for the implanted relaxed a-Si (Fig. 2b). It should be noted that the carrier lifetime in relaxed a-Si is ≈11 ps [3]. Exponential fits assuming a single decay time τ cannot fully account for the measured reflectivity decay in a-Si (as in Fig. 2b), which needs further investigation.

The behavior of the carrier lifetime in both materials was investigated over a wide range of 1 MeV Si$^+$ implantation doses. Figure 3 shows the carrier lifetime τ as a function of the ion dose implanted into c-Si (solid points) and relaxed a-Si (open circles) on a double-logarithmic scale. For each ion dose, τ was obtained by averaging the results of two or three independent pump-probe measurements, yielding an error of about 10%. In c-Si, τ is initially observed to decrease with increasing ion dose. At a dose of $\approx10^{14}/\text{cm}^2$, this decrease begins to level off and a saturation level of ≈0.8 ps is reached at higher ion doses. In relaxed a-Si, the carrier lifetime is

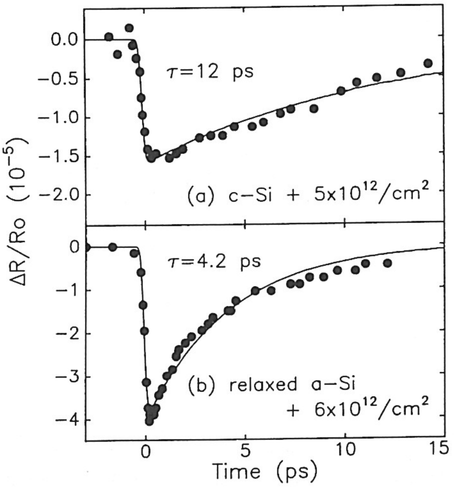

Figure 2. *Normalized changes in reflectivity as a function of the time delay between pump and probe pulse for (a) c-Si implanted with 1 MeV Si$^+$, 5x10^{12}/cm^2; (b) relaxed a-Si implanted with 1 MeV Si$^+$, 6x10^{12}/cm^2. Solid lines are exponential decay curves convoluted with the experimental resolution.*

reduced from $\tau \approx 11$ ps to $\tau \approx 8$ ps at a dose of $\approx 10^{12}$/cm^2. For higher ion doses, τ further decreases and follows nearly the same trend as that observed for c-Si. Above $\approx 10^{14}$ ions/cm^2 the lifetime saturates at 0.8 ps, which is the level characteristic of unrelaxed, as-implanted a-Si.

The RBS spectra in Fig. 1 reveal that the saturation in the carrier lifetime at 10^{14} ions/cm^2 occurs before the c-Si sample is fully amorphized. In addition, Raman spectroscopy [1, 8] indicates that the network strain in a-Si at the saturation dose of 10^{14}/cm^2 has not yet reached the level of unrelaxed a-Si, which shows that τ saturates below the dose needed for the full de-relaxation of the a-Si (i.e. $\approx 10^{15}$/cm^2) [3].

The carrier lifetimes in c-Si were also investigated for implants of 1 MeV B$^+$ at liquid nitrogen temperature and 2 MeV He$^+$ and 2 MeV Si^{++} at room temperature [9]. For all the implants, the carrier lifetime initially decreases with increasing ion dose until a saturation level in the range of $\approx$ 1 ps is reached. For these implants as well, channeling RBS shows that the displacement damage in c-Si at which saturation sets in is below the amorphization threshold. In earlier experiments on c-Si implanted with 100 and 200 keV O$^+$ [6], or 100 keV Ar$^+$ [10], τ was observed to reach comparable saturation levels.

DISCUSSION

I. Electrical defects in c-Si and a-Si

Lattice defects in crystalline semiconductors are known to be electrically active [11]. The efficiency of an electrical defect in capturing a free carrier is expressed in terms of its cross section σ. The carrier lifetime τ is related to the volume density N of trapping and recombination centers in a crystalline semiconductor according to:

$$\frac{1}{\tau} = v\,N\,\sigma \qquad (1),$$

where v is the carrier thermal velocity ($\approx 10^7$ cm/s). It is not clear whether the nature of free carrier capture at deep levels in amorphous semiconductors is ballistic (as Eq. (1)) or diffusive [12]. However, for diffusive capture also τ is expected to be inversely proportional to N [12]. Pump-probe measurements on hydrogenated a-Si have revealed a strong dependence of the free carrier lifetime on the defect density, but have not provided an unambiguous picture of the mechanism of free carrier trapping [13-15]. Figure 3 shows that the carrier lifetime τ in c-Si is reduced by 1 MeV Si$^+$ implantation up to ion doses of 10^{14}/cm^2. According to Eq. (1), this

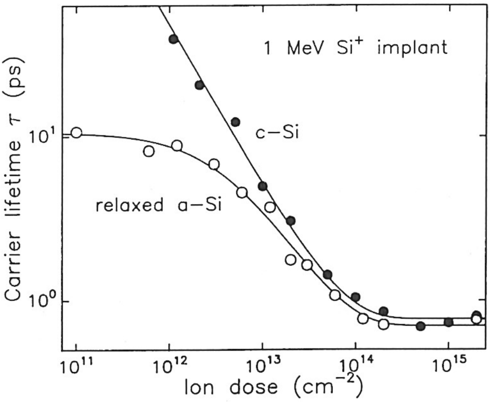

Figure 3. *Photocarrier lifetime τ as a function of the dose for c-Si (solid circles) and relaxed a-Si (open circles) implanted with 1 MeV Si$^+$. Solid lines are best fit curves which describe the trap density as a function of the ion dose (see text).*

indicates that the initial generation of implantation damage is accompanied by an increase in the volume density of traps. It is clear from Fig. 3 that in relaxed a-Si also the carrier lifetime is initially reduced by 1 MeV Si$^+$ implantation. This suggests that, analogous to c-Si, the density of trapping centers in relaxed a-Si increases by accumulating implantation damage in the a-Si network.

Using the approach described in ref. [16], the concentration of displaced atoms in c-Si implanted to a dose of 2×10^{13}/cm^2 is estimated from the RBS spectra (Fig. 1) to be 0.6 at.%. An estimate based on Monte Carlo simulations (TRIM89 [17]) at the given ion dose yields 0.9 at. %, which is in reasonable agreement. The carrier lifetime at this damage level is ≈3 ps, indicating that a relatively low level of structural damage in c-Si leads to a strong reduction in the lifetime. It is likely that a wide distribution of defects is generated by the 1 MeV Si$^+$ implant, varying from point defects to amorphous clusters. However, the carrier lifetime in c-Si is also strongly reduced by implanting 2 MeV He$^+$, in which case mainly simple defects (i.e. point defects and small defect clusters) are expected to be formed [4]. This suggests that for all the implants, the gap states responsible for the observed reduction in τ arise predominantly from simple defects. It is not clear, however, whether these states are related to dangling bonds or to weak, highly strained bonds formed upon bond reconstruction near defects.

The fact that τ in implanted a-Si and c-Si remains at 0.8 ps for ion doses $>10^{14}$/cm^2 suggests that the generation of traps in both materials is saturated. From channeling RBS (Fig.1), the damage level in c-Si implanted up to 10^{14}/cm^2 is estimated to be 2-4 at.% of displaced atoms. In a-Si only the upper ≈0.1 μm of the surface layer is probed, and an estimate for the damage rate in this region using the modified Kinchin-Pease model [18] gives 0.13 displacements per ion per Å [3]. From this number, the damage level in a-Si at a dose of 10^{14}/cm^2 is calculated to be 0.026 displacements per atom (dpa). The above estimates illustrate that the damage level needed to saturate the trap density is similar for c-Si and relaxed a-Si and lies significantly below the amorphization threshold (0.3-0.5 dpa).

II. Model for trap generation

A simple model which describes the dependence of the carrier lifetime on the ion dose is used to compare the generation of defects in c-Si and relaxed a-Si. In the model, each incident ion is assumed to influence the bulk density N of trapping centers in the implanted material. The increase in the trap density dN induced by an increment of the ion dose dϕ is taken as:

$$dN=g\times(1-N/N_{sat})\times d\phi \quad (2),$$

where g is the generation term describing the number of traps generated per ion per unit depth in trap-free material, and N_{sat} is the saturation trap density. The term $(1-N/N_{sat})$, which represents the effective volume fraction of undamaged material, is included to account for the observed

Table I. *Parameter values obtained from fitting Eq. (3) to the data for c-Si and relaxed a-Si in Fig. 3. τ_o and τ_{sat} are the carrier lifetimes in unimplanted and trap-saturated material, respectively, g is the trap generation term, and N_{sat} is the saturation trap density.*

material	τ_o (ps)	τ_{sat} (ps)	g/N_{sat} ($\times 10^{-14}$ cm^2)
c-Si	≥ 1000	0.77±0.06	1.6±0.2
relaxed a-Si	10.6±0.7	0.70±0.08	1.6±0.3

saturation in τ at high ion doses. Equation (2) was integrated to obtain an expression for the trap density $N(\phi)$. Irrespective of the actual trapping mechanism in a-Si and c-Si, an inverse relationship between τ and $N(\phi)$ can be assumed [12]. This gives:

$$\tau(\phi)=\frac{\tau_{sat}}{1+(\tau_{sat}/\tau_o-1)\times\exp(-g\phi/N_{sat})} \qquad (3),$$

where τ_o is the carrier lifetime in unimplanted material (i.e. for $\phi=0$), and τ_{sat} is the saturation lifetime for high ion doses.

Equation (3) was fitted to the measured data of τ vs. the ion dose for c-Si and relaxed a-Si separately. The values obtained for the free parameters τ_o, τ_{sat}, and g/N_{sat} are listed in Table I. The solid lines in Fig. 3 represent the fit results. The obtained fits reproduce the measured behavior of τ as a function of the implantation dose for both c-Si and relaxed a-Si. The fit to the data for c-Si does not depend on the value for the bulk lifetime τ_o in unimplanted c-Si as long as τ_o is larger than $\approx$1 ns, which is reasonable [19].

From the fitting, the parameter g/N_{sat} is found to be equal within the error for relaxed a-Si and c-Si. Since the final state reached for high dose implantation (2×10^{15}/cm^2) into both relaxed a-Si and c-Si is the same, i.e. unrelaxed a-Si, the saturation trap density N_{sat} is expected to be equal. The fitting results therefore imply that the parameter g, which describes the number of traps generated per ion per unit depth, is the same for c-Si and relaxed a-Si. Since in c-Si the dominant trapping centers are related to point defects and small defect clusters, this strongly suggests that similar types of structural defects are formed in a-Si. This finding is consistent with the results of DSC measurements on irradiated c-Si and relaxed a-Si [1, 4].

In order to obtain an estimate for the trap generation term g, it is assumed that every displaced atom is a single trapping center. In this view, g is simply equivalent to the calculated displacement rate in a-Si: $g\approx0.13$ traps per ion per Å [3]. Using g and the fit value for g/N_{sat} yields $N_{sat}\approx8\times10^{20}$/cm^3. This estimate for the maximum trap density in a-Si is equivalent to 1.6 at.% of displaced atoms, which is in reasonable agreement with estimates from other experiments [1, 20]. It should be noted that the density of dangling bonds in as-implanted a-Si, as measured by electron spin resonance, is significantly lower (i.e. 2×10^{19}/cm^3) [21], which could indicate that the trap states in a-Si are not necessarily related only to dangling bonds.

The experiments indicate that N_{sat} is reached in relaxed a-Si and c-Si at a dose of 2×10^{14}/cm^2. Implanting a-Si and c-Si to higher damage levels *does not* lead to a further reduction in τ, whereas it *does* induce further changes in the structural state, as measured by Raman spectroscopy and channeling RBS, respectively. A possible explanation is that above $\approx10^{14}$/cm^2, the generation of the most efficient trapping centers (i.e. those related to simple defects) levels off because they cluster into defect complexes. Another explanation might be that N_{sat} is related to the defect density at which carriers in extended, mobile states always have spatial overlap with one or more capture centers. In this regime, the decay rate is not influenced by a further increase in the defect density, because it may now be limited by a transition time required for carrier capture at one of the available centers.

CONCLUSIONS

Photocarrier lifetime measurements have been used to probe implantation damage in c-Si and relaxed a-Si. For 1 MeV Si$^+$ implants above a dose of 10^{12} ions/cm^2, the number of electrically active defects generated per incident ion per unit depth is found to be equal in relaxed a-Si and c-Si. This strongly suggests that structural defects are formed in a-Si which are of a similar nature to defects in c-Si, in accordance with earlier experiments [1, 4]. The carrier lifetime is observed to saturate at ≈0.8 ps when both materials are implanted at doses higher than 10^{14} ions/cm^2. The apparent saturation in the trap density in a-Si corresponds to a density of displaced atoms of ≈1.6 at.%. The striking observation is that the saturation occurs far below the damage level required to obtain fully unrelaxed a-Si, a fact which needs further investigation.

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