Defects in amorphous silicon probed by subpicosecond photocarrier dynamics

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The photocarrier dynamics in pure nonhydrogenated amorphous silicon (*a*-Si) have been studied with subpicosecond resolution using pump-probe reflectivity measurements. The photocarrier lifetime increases with the annealing temperature from 1 ps for as-implanted *a*-Si to 11 ps for *a*-Si annealed at 500 °C. The lifetime in annealed *a*-Si can be returned to the as-implanted level by ion irradiation. These observations indicate that *a*-Si can accommodate a variable number of defect-related trapping and recombination centers. The saturated defect density in as-implanted *a*-Si is estimated to be ≈ 1.6 at. %. Comparison with Raman spectroscopy suggests that various kinds of structural defects are present in *a*-Si.

The structure of pure, nonhydrogenated amorphous silicon (*a*-Si) is generally considered to be a continuous random network (CRN).[1] Raman spectroscopy indicated that strain in the *a*-Si network is reduced by thermal annealing.[2,3] Differential scanning calorimetry revealed a considerable decrease in the enthalpy of the *a*-Si during this process, known as structural relaxation.[4] Recent experiments have shown that structurally relaxed *a*-Si can be returned to the as-implanted state by high-energy ion implantation, suggesting that beam generated defects in *a*-Si derelax the network.[5] In addition, it has been suggested that structural relaxation is controlled by the annihilation of defects present in the CRN.[5] Experiments probing the diffusion behavior of impurities in *a*-Si confirm the dynamic behavior of defects in *a*-Si.[6,7]

The nature of structural defects in *a*-Si is believed to be similar to that of lattice defects in crystalline silicon (*c*-Si).[5] Crystal defects produce deep levels in the band gap and act as centers for carrier trapping and recombination. Similarly, structural defects in *a*-Si are expected to provide gap states as well, as indicated by recent model calculations.[8] In this letter, the lifetime of a photogenerated electron-hole (*e-h*) plasma in *a*-Si is determined with subpicosecond resolution. These measurements directly probe carrier trapping by electrically active defects in *a*-Si. Both the annealing characteristics and the defect generation by ion irradiation are investigated, giving evidence that defects are involved in structural relaxation of *a*-Si.

1.2-μm-thick *a*-Si layers were prepared by multiple implants of ^{28}Si ions with energies ranging from 150 keV to 1 MeV into Si(100) substrates held at liquid nitrogen temperature. The samples were annealed in vacuum (base pressure $\approx 10^{-7}$ Torr) at temperatures from 100 to 500 °C for 1 h. Samples annealed at 500 °C were reimplanted with 1 MeV ^{28}Si ions at doses between 6×10^{11} and 2×10^{15}/cm^2. Raman spectroscopy was performed on each sample using the $\lambda = 514.5$ nm line from an Ar ion laser. The Raman spectra of annealed samples show no features indicative of crystallization of the *a*-Si layers. Upon annealing at 600 °C for 1 h the *a*-Si is fully recrystallized, as is indeed expected for normal solid phase epitaxy of pure *a*-Si.[9]

A colliding pulse mode-locked dye laser (CPM)[10] was used to generate and probe electron-hole (*e-h*) plasmas in the samples. The CPM produces ≈ 100 fs pulses with a photon energy of 2 eV ($\lambda = 620$ nm). The CPM was split into two beams to form a pump-probe configuration. The pump beam was acousto-optically modulated at a fixed frequency between 10 and 100 kHz and focused to a 25 μm spot with an energy density adjustable to a maximum of ≈ 10 μJ/cm^2. The probe was mechanically delayed with respect to the pump and focused to a 15 μm spot with an intensity of $\approx 10\%$ of the pump. The reflected probe and an optically matched beam, split off before reflection, were detected by photodiodes. The difference of the two photocurrents was amplified by a lock-in amplifier referenced to the acousto-optical modulation frequency. The minimum observable fractional change in reflectivity was $\approx 2\times10^{-6}$.

The pump pulse is absorbed in the upper ≈ 100 nm of the *a*-Si,[9] generating an *e-h* plasma with a peak carrier density of $\approx 10^{18}$/cm^3. At this carrier density, the decay of the plasma is dominated by carrier trapping.[11] Trapping occurs at different defect states each with a characteristic cross section σ_i describing the capture efficiency. Assuming ballistic carrier capture,[12] the effective decay rate $1/\tau$ is obtained by summing the contribution of all types of defects:

$$1/\tau = v \sum_i N_i \sigma_i, \tag{1}$$

where τ is the average carrier lifetime, N_i is the volume density of defects of type i, and v is the average carrier velocity ($\approx 10^7$ cm/s). The plasma density is expected to decrease exponentially with the time constant τ. According to a Drude model, the *e-h* plasma induces a reduction in

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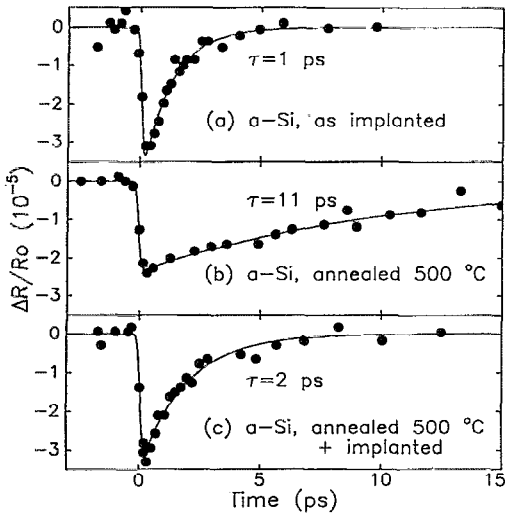

FIG. 1. Normalized reflectivity changes (points) as a function of the time difference between pump and probe for (a) as-implanted a-Si, (b) a-Si annealed at 500 °C for 1 h, (c) annealed a-Si reimplanted with $2\times10^{13}/\text{cm}^2$, 1 MeV Si^+. The pump intensity was ≈5 μJ/cm^2. Time 0 corresponds to overlap between pump and probe. Solid lines are exponential decay curves convoluted with the experimental resolution.

the reflectivity which scales linearly with the plasma density.[11,13,19] Hence, exponential fits were used to extract the average carrier lifetime τ for each sample.

Figure 1 shows the change in reflectivity as a function of the time delay between the pump and the probe pulse measured for: (a) as-implanted a-Si, (b) a-Si annealed at 500 °C, and (c) annealed a-Si reimplanted with $2\times10^{13}/\text{cm}^2$, 1 MeV Si^+. The change in reflectivity, $\Delta R = R - R_0$, is shown normalized to the average reflectivity level R_0 for $t<0$. At $t=0$, all samples show a sharp decrease in the reflectivity due to the generation of the e-h plasma by the pump. For both as-implanted and reimplanted a-Si [Figs. 1(a) and 1(c)] the reflectivity recovers to the initial level within less than 10 ps, whereas the a-Si annealed at 500 °C [Fig. 1(b)] exhibits a slower recovery. The solid lines in Fig. 1 represent the exponential fits for each sample. The obtained lifetimes are $\tau=1$ ps for as-implanted a-Si, $\tau=11$ ps for a-Si annealed at 500 °C, and $\tau=2$ ps for annealed and reimplanted a-Si. From Fig. 1 it is clear that the carrier lifetime in a-Si is variable: annealing increases τ, whereas ion irradiation reduces τ.

The effect of thermal annealing of a-Si on the carrier lifetime was investigated over a wide temperature range. Figure 2(a) shows τ for samples annealed for 1 h at temperatures from 100 to 500 °C. Above 150 °C τ increases significantly with annealing temperature, reaching a maximum of 11 ± 1 ps at 500 °C. Since structural relaxation is believed to be controlled by defect annihilation,[5] it is likely that this process results in a decrease in the trap density N_t. According to Eq. (1), a reduction in N_t leads to an increase in the carrier lifetime, which is indeed observed.

It has recently been shown that during vacuum annealing of a-Si at $T>500$ °C diffusion of hydrogen into the sample can occur and concentrations of $\approx10^{19}$ H/cm^3 (0.02 at.%) can be reached.[15] It could therefore be possible that the observed increase in τ [Fig. 2(a)] is an artifact of defect passivation by in-diffused H. However, in experiments in which the surface region of a-Si was implanted with H and subsequently annealed at 200 °C for 6 h to activate H diffusion, it was found that significant passivation requires H concentrations as high as $\approx10^{21}/\text{cm}^3$ (2 at.%). Comparatively, 5–10 at. % H is needed to obtain device-quality hydrogenated a-Si with reported carrier lifetimes ranging from ≈10 ps to ≈1 ns.[11,16,17]

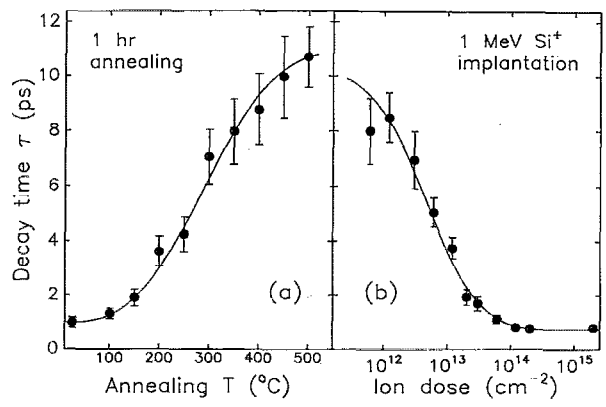

FIG. 2. (a) Carrier lifetime τ in a-Si as a function of the annealing temperature. The solid line serves to guide the eye. (b) Carrier lifetime τ in a-Si annealed at 500 °C as a function of the 1 MeV Si^+ reimplantation dose. Here, the solid line is the best-fit curve which describes the trap density as a function of ion dose.

The role defects play in carrier trapping in a-Si was further investigated by measuring the carrier dynamics in annealed a-Si reimplanted with 1 MeV Si^+ over a wide dose range. Figure 2(b) shows the decay time τ as a function of the implanted dose. At a dose of $\approx10^{12}/\text{cm}^2$, τ is reduced from 11 to 8 ps. For higher ion fluences, τ decreases further with the dose, demonstrating that the defects generated in relaxed a-Si by ion irradiation are active in carrier trapping. At a dose of $\approx10^{14}/\text{cm}^2$ τ reaches the level of as-implanted a-Si, indicating that the a-Si is electrically derelaxed. It should be noted that this derelaxation dose is well below the dose required for surface amorphization of c-Si under the same implantation conditions ($\approx2\times10^{15}/\text{cm}^2$). For doses in excess of $10^{14}/\text{cm}^2$, τ remains at 0.8 ps, suggesting that a saturated trap density N_{sat} has been reached. In earlier experiments measuring the carrier lifetime in ion irradiated and amorphized c-Si, similar saturation levels were observed.[13,14]

Using a simple approach to account for the saturation effect at high ion doses, the increase in the trap density dN induced by an increment $d\phi$ of ion dose is given by:

$$dN = g\left(1-\frac{N}{N_{\text{sat}}}\right)d\phi, \tag{2}$$

where g is the number of trapping centers generated per implanted ion per unit depth in trap-free material. Equation (2) was integrated to obtain the trap density $N(\phi)$ under the constraint that for $\phi=0$ the trap density equals that of the relaxed a-Si. In order to relate the calculated trap density to the carrier lifetime, an average trapping

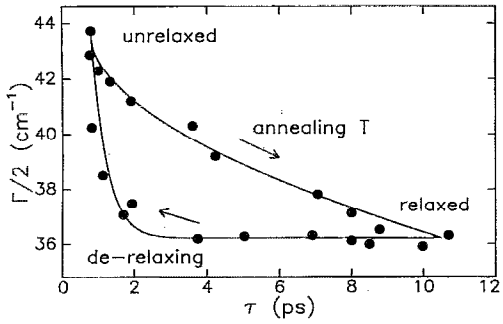

FIG. 3. The Raman peak half width $\Gamma/2$ vs the carrier lifetime τ displayed for a-Si annealed at increasing temperatures, and annealed a-Si derelaxed with increasing ion dose. The solid lines serve to guide the eye.

cross section σ_{av} is assumed for all traps. According to Eq. (1), the lifetime then becomes inversely proportional to $N(\phi)$. The result for τ as a function of the ion dose is:

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

where τ_{rel} and τ_{sat} are the carrier lifetimes in relaxed and trap-saturated (unrelaxed) a-Si, respectively. Fitting the data in Fig. 2(b) yields $g/N_{sat} = (1.6 \pm 0.3) \times 10^{-14}$ cm^2, $\tau_{rel} = 10.4 \pm 0.8$ ps, and $\tau_{sat} = 0.74 \pm 0.07$ ps. The fitted curve, shown in Fig. 2(b) (solid line), gives a good description of the experimental data.

To obtain an estimate for the trap generation, g, it is assumed that displacing an atom in defect-free material by atomic collisions effectively leads to the formation of one trapping center. Using the modified Kinchin–Pease model,[18] g can then be estimated from the average nuclear energy lost by recoil atoms in the first 100 nm of a-Si ($\approx$4.5 eV/Å for 1 MeV Si$^+$).[19] Assuming a threshold displacement energy of 15 eV yields $g \approx 0.13$ traps per Å per incident ion. For this g, the saturated trap density in a-Si is $N_{sat} \approx 8 \times 10^{20}$/cm^3 (1.6 at.%). The validity of this estimate for N_{sat} is limited because: (i) any recombination of displaced atoms is neglected, (ii) the displacement energy in a-Si may depend on the defect density, (iii) the assumed one-to-one relation between displacements and traps may not be valid, and (iv) the use of an average trapping cross section to obtain Eq. (3) may not be justified. Nevertheless, it is reassuring that the present estimate is in agreement with results obtained using other techniques.[5,7]

Raman spectroscopy was performed to investigate the relation between structural defects and electrical defects in a-Si. Figure 3 shows the measured half width of the Raman transverse-optical like peak, $\Gamma/2$, vs the carrier lifetime τ. $\Gamma/2$ scales with the average bond angle distortion in the a-Si and gives a measure of the strain in the a-Si network induced by the structural defects.[2,3,5] It is clear from Fig. 3 that upon relaxation, both $\Gamma/2$ and τ gradually change with increasing annealing temperature. For derelaxation a strikingly different behavior is observed. Up to a derelaxation dose of 10^{13}/cm^2, $\Gamma/2$ exhibits no significant change. The carrier lifetime, however, is considerably reduced (i.e., from 11 to 4 ps). Only at higher damage levels ($\tau < 2$ ps) does $\Gamma/2$ increase and finally reach the as-implanted level.

The data in Fig. 3 suggest the following scenario for derelaxation of a-Si. Low dose ion implantation ($< 2 \times 10^{13}$/cm^2) of relaxed a-Si generates a low level of point defects leading to an increase in the number of trapping centers with no measurable effect on the network strain. At higher damage levels, newly generated defects may cluster into complexes. This is accompanied by a saturation in the carrier trap density, while the network strain induced by the defects becomes observable. Finally, in the fully derelaxed a-Si a saturated distribution of point defects and defect clusters is reached with $\tau \approx 0.8$ ps and $\Gamma/2 \approx 43$ cm^{-1}.

In summary, we have investigated defects in a-Si by photocarrier lifetime measurements. The carrier lifetime in a-Si is increased from 1 to 11 ps by structural relaxation and is returned to the as-implanted level by ion irradiation. The derelaxation process can be described by a model in which the trap density in a-Si is assumed to saturate at $\approx$1.6 at.% for high ion doses. The observations indicate that structural relaxation and derelaxation of a-Si are controlled by the dynamic behavior of defects in the network, in accordance with earlier investigations.[5–7] The fact that neither carrier lifetime measurements nor Raman spectroscopy gives a unique fingerprint of the state of a-Si suggests that the structural nature of defects in a-Si is diverse.

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