STRUCTURAL DEFECTS IN AMORPHOUS SILICON PROBED BY SUB-PICOSECOND PHOTOCARRIER DYNAMICS

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ABSTRACT

The dynamics of a photogenerated electron-hole plasma in pure amorphous silicon (a-Si) in different stages of structural relaxation have been studied with sub-picosecond resolution using pump-probe reflectivity measurements. For high plasma densities ($> 10^{20}/cm^3$) the plasma evolution is dominated by Auger recombination. At lower plasma densities ($\approx 10^{18}/cm^3$) the plasma decays exponentially with a time constant τ, suggesting that carrier trapping dominates in this regime. The decay time τ increases with the temperature at which the a-Si has been annealed, ranging from τ=1 ps for as-implanted a-Si to τ=14 ps for a-Si annealed at 500 °C. This observation is consistent with a reduction in the number of defects in a-Si upon thermal annealing.

INTRODUCTION

Pure (non-hydrogenated) amorphous silicon (a-Si) is considered a model disordered system. The general consensus is that its structure is a continuous random network (CRN), in which each silicon atom is covalently bonded to four neighboring atoms [1]. Infrared [2] and Raman spectroscopy [3, 4] suggested that the network structure of a-Si is not well-defined but depends on the thermal history of the material. Confirmation of this effect, known as structural relaxation, was given by differential scanning calorimetry which showed that heating of as-implanted a-Si at low temperatures (100-500 °C) results in a one-time heat release [5]. Recent experiments have shown that the formation of defects by ion irradiation and defect annihilation by thermal annealing proceed similarly in a-Si and crystalline silicon (c-Si), suggesting that the structural relaxation of a-Si should be interpreted as the annihilation of point defects [6, 7]. This idea of point defects in a CRN has been corroborated by experiments probing the diffusion behavior of impurities in a-Si as function of structural relaxation [8, 9].

Structural defects are expected to affect the electronic properties of a-Si by introducing states for carrier trapping in the band gap [10]. In this paper pump and probe reflectivity measurements are described, which are used to study the dynamics of a photogenerated plasma in a-Si in different states of structural relaxation.

EXPERIMENT

350 nm thick a-Si layers were prepared by implanting 175 keV ^{28}Si ions to a dose of $4\times10^{15}/cm^2$ into Si(100) held at liquid nitrogen temperature. Thicker layers (1.2 μm) were made with multiple implants from 150 keV to 1 MeV at room temperature. The samples were annealed in vacuum (base pressure $< 10^{-7}$ Torr) at temperatures ranging from 100 °C to 500 °C to induce structural relaxation in the a-Si layers. Raman spectroscopy was performed to compare these samples with previous measurements of structural relaxation [4, 11]. Details of the Raman spectroscopy are described elsewhere [12]. Annealed samples were de-relaxed with 1 MeV Si implants at liquid nitrogen temperature [6, 7].

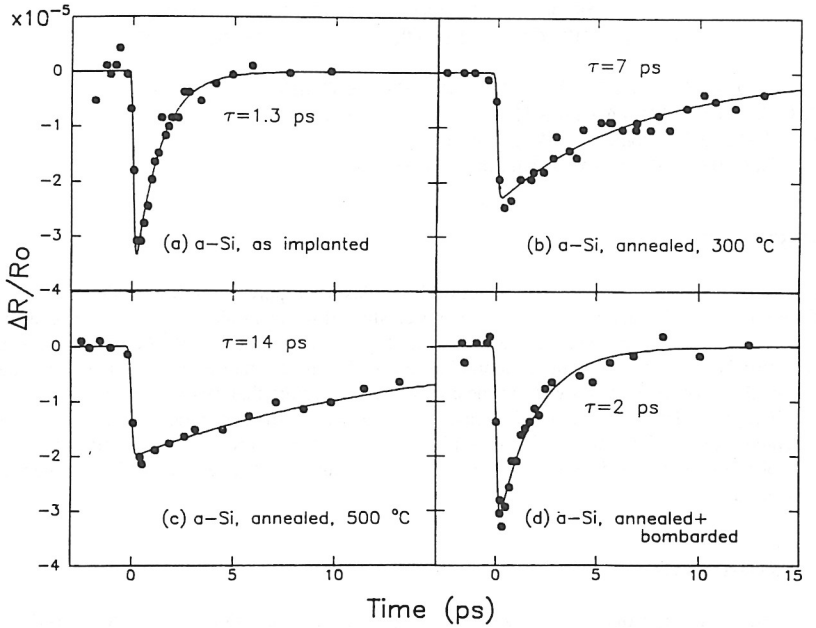

Figure 1. *Reflectivity (points) measured as a function of the time difference between pump and probe pulse, using a pump intensity of ≈ 4 μJ/cm². t=0 corresponds to the time at which pump and probe coincide on the sample. Solid lines are exponential decay curves convoluted with the instrumental resolution. (a) as-implanted a-Si, (b) a-Si annealed at 300 °C for 1 hr, (c) a-Si annealed at 500 °C for 1 hr, (d) a-Si annealed at 500 °C and subsequently implanted with 1MeV Si⁺ to 3×10⁻³ DPA.*

Electron-hole (e-h) plasmas in a-Si were generated and probed using pulses from a colliding pulse modelocked laser (CPM) [13]. The CPM produces 100 fs pulses with an intensity of 0.1 nJ at a repetition rate of 110 MHz. The average wavelength is 620 nm ($\hbar\omega$=2 eV). For low density plasmas ($<10^{19}/cm^3$) the output of the CPM was split in two beams. The first (pump) was chopped at 50 kHz in an acousto-optic modulator (AOM) and focussed to a 30 μm spot, yielding an energy density of ≈4 μJ/cm². The second (probe) was sent through a mechanical delay line and focussed to a 15 μm spot with an intensity ≈10 % of the pump. The probe and a sample of the pump were detected by photodiodes and amplified by a lock-in amplifier using the AOM as a reference. The observable relative reflectivity change is ≈ 3×10^{-6}. To obtain higher density plasmas the CPM output was amplified yielding 190 fs pulses with a peak intensity of 20 μJ at a repetition rate of 10 Hz. The pump beam was focussed to 300 μm with a maximum energy of 10 mJ/cm². The probe and a sample of the pump were detected using integrating photodiodes, yielding a measurable reflectivity change of ≈1×10^{-3}.

RESULTS

Figure 1 shows the measured reflectivity change as a function of the time delay between pump and probe for as-implanted a-Si, a-Si annealed at 300 °C, and a-Si annealed at 500 °C. Changes in reflectivity $\Delta R=R-R_0$ are shown normalized to the average reflectivity R_0 for t<0.

The peak plasma density is below $2\times10^{18}/cm^3$ for all measurements. All samples exhibit a sharp drop in the reflectivity near t=0, with the reflectivity change being larger for as-implanted a-Si than for annealed a-Si. The steepness of the initial dip indicates a time-resolution better than 200 fs. For as-implanted a-Si (Fig. 1a) the reflectivity returns to its original level (i.e. $\Delta R=0$) within several picoseconds. The reflectivity for annealed a-Si (Fig. 1b and 1c) recovers significantly slower. Only after 30 ps for 300 °C annealed a-Si, and after 60 ps for 500 °C annealed a-Si is the initial reflectivity finally reached (not shown). None of the samples exhibits a positive change in reflectivity.

After annealing at 500 °C a-Si was bombarded with 1 MeV Si ions. Monte Carlo simulations [14] were applied to estimate the amount of displacements per atom (DPA) in the a-Si layer probed by the laser. Fig. 1d shows the reflectivity of a sample irradiated with an ion dose corresponding to $\approx3\times10^{-3}$ DPA. The reflectivity is observed to recover much faster than for the annealed, not-irradiated sample (Fig. 1c).

DISCUSSION

Modeling

The pump pulse alters the reflectivity through the creation of an e-h plasma, and by heating the a-Si. According to a Drude model, the e-h plasma will reduce the reflectivity [15], which is indeed observed (Fig. 1). It has been shown that the relative change in reflectivity is linearly proportional to the plasma density [16, 17]. The reflectivity is known to increase with the temperature of the a-Si layer [17, 18]. The fact that for none of the samples a positive change in reflectivity is observed (see Fig. 1) indicates that there is no detectable heating by the low energy laser pulse on a ps-timescale. Hence, the observed reflectivity behavior is merely determined by the time evolution of the e-h plasma, which is given by:

$$\frac{dn}{dt} = \frac{\alpha(1-R)I(t)}{\hbar\omega} - \gamma n^2 - \frac{n}{\tau} \qquad (1),$$

where n is the plasma density. The first term on the right-hand side is the generation rate (α is the absorption coefficient, R is the reflectivity, and I(t) represents the laser intensity), the second term is the Auger recombination rate, and the final term is related to the trapping of carriers. The Auger recombination rate in evaporated a-Si and hydrogenated a-Si (a-Si:H) has been shown to have a n^2-dependence rather than the n^3 form observed for c-Si [17, 19]. The carrier trapping is assumed to occur with a single time constant τ to be determined from the reflectivity data.

The Auger rate coefficient γ was obtained from pump-probe measurements at high plasma densities ($>10^{20}/cm^3$) (not shown), yielding $\gamma\approx2\times10^{-9}$ cm^3/s for as-implanted a-Si and $\gamma\approx3\times10^{-9}$ cm^3/s for a-Si annealed at 450°C. This indicates that Auger recombination is not strongly dependent on the structural state of the a-Si. For all samples (Fig. 1) the plasma decay is observed to be much faster than the Auger recombination rate expected for plasma densities of $\approx 10^{18}/cm^3$, indicating that carrier trapping is dominant in this regime. Eqn. (1) shows that in the case of a trapping dominated decay, the plasma density n(t) decreases exponentially with a time constant τ. Since the relative change in reflectivity is linearly dependent on n(t), exponential fitting curves can be used to obtain the decay time τ for each sample from the reflectivity data.

Analysis

Exponential fits are shown with the data in Fig. 1 (solid lines). The value required for the decay time is τ=1.3 ps for as-implanted a-Si, τ=7 ps for a-Si annealed at 300 °C, and τ=14 ps for a-Si annealed at 500 °C. Figure 2a shows the decay time τ obtained over a wide range of annealing temperatures. The error in τ amounts to 20%. It is clear that above 100 °C, the decay

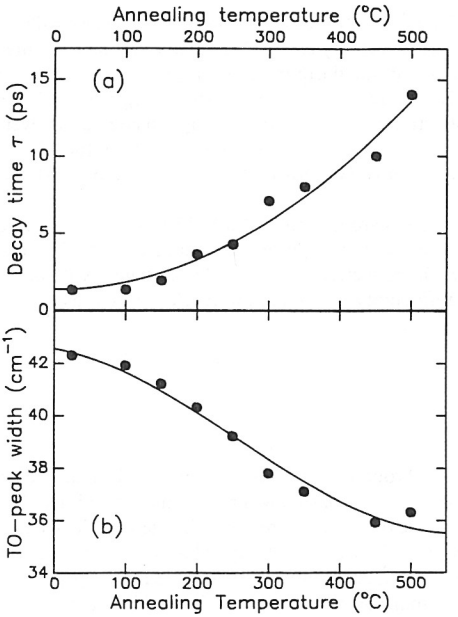

Figure 2. *(a) Decay time τ, and (b) Raman peak half-width as a function of the annealing temperature. Solid lines serve to guide the eye.*

time increases significantly with the annealing temperature. In addition, Fig. 2b shows the half-width of the transverse optical (TO) peak in the Raman spectrum for each sample. The error is about 0.5 cm^{-1}. Earlier work has shown that the TO-peak width is closely related to the state of structural relaxation in the a-Si [4, 7, 11]. From Fig. 2 it is therefore obvious that as structural relaxation in a-Si proceeds, the decay time τ becomes considerably longer.

The observed decay time τ reflects the average lifetime of photocarriers before they are trapped. Trapping can occur at different types of localized states, each with their characteristic cross section σ_i describing the efficiency in capturing free carriers. The capture probability per unit time for one type of trapping centers is given by $vN_i\sigma_i$, where v is the average carrier velocity and N_i represents the volume density of trapping centers of type i. The overall trapping rate $1/\tau$ can be calculated by summing the contributions of all types of trapping centers, leading to

$$\frac{1}{\tau} = v \sum_i N_i\sigma_i \qquad (2).$$

The average carrier (electron or hole) velocity v can be estimated using the thermal velocity $v_{th}=\sqrt{3kT/m^*_{e/h}}$, where $m^*_{e/h}$ is the effective electron or hole mass. This yields $v \approx 10^7$ cm/s for carriers in a-Si [20]. Since thermalization of hot carriers in a-Si is believed to occur on a short timescale (« 1 ps [21]), the initial kinetic energy of photocarriers can be neglected in calculating v. The average carrier velocity is not expected to be influenced by the structural relaxation. On the basis of eqn. (2), the observed increase in the photocarrier lifetime after annealing (Fig. 2) can therefore be attributed to a decrease in $\Sigma N_i\sigma_i$; $\Sigma N_i\sigma_i$ is reduced by a factor of 10 going from as-implanted to 500 °C annealed a-Si.

It has recently been suggested that structural relaxation is in fact annealing of point defects in the a-Si network [6-9]. The question arises how defect annihilation in a-Si relates to $\Sigma N_i\sigma_i$. It is known that in crystalline semiconductors, lattice defects give rise to deep gap levels and can act as trapping centers [22]. The structural defects in the a-Si are believed to be

vacancies and interstitials in the network, and clusters of these defects [6], probably leading to the formation of dangling and floating bonds as well as weak bonds. These are expected to introduce states within the gap, as has recently been shown by model calculations determining the electronic structure of a-Si [10]. The role that defects in a-Si play in carrier trapping is furthermore illustrated by the general use of hydrogen to passivate electrically active defects in a-Si, thereby increasing the lifetime. Hence, it is likely that the annihilation of defects in a-Si associated with structural relaxation will reduce the number of trapping centers, and thus $\Sigma N_i\sigma_i$. This implies that the carrier lifetime in a-Si should increase upon structural relaxation, which is indeed observed by present experiments.

For well-annealed a-Si with a defect density of 3×10^{-3} DPA the decay time is found to be τ=2 ps (see Fig. 1d). Using ion doses corresponding to 0.03 DPA and 0.3 DPA the decay time is further reduced to $\tau\approx1$ ps (not shown), indicating that the as-implanted level is reached. Raman spectroscopy reveals no large difference between the TO-peak width for the 500 °C annealed and the 3×10^{-3} DPA damaged a-Si ($\approx$ 0.5 cm^{-1}). Only for 0.03 DPA and higher doses does the peak broaden to the as-implanted width, which is consistent with earlier measurements [7]. This indicates that the number of defects needed to transform annealed a-Si 'electrically' to its as-implanted state (i.e. $\approx3\times10^{-3}$ DPA) is significantly lower than the de-relaxation threshold observed by Raman spectroscopy ($\approx3\times10^{-2}$ DPA). Apparently, the carrier lifetime is more sensitive to the changes in the a-Si resulting from a relatively small number of defects than is Raman spectroscopy, which probes the average bond angle distortion associated with defect-induced strain in the network.

When the density of dangling bonds in a-Si and a-Si:H as observed by electron spin resonance (ESR) decreases, the carrier lifetime is increased significantly [23, 24], suggesting that dangling bonds act as trapping centers. Since ESR may not resolve all gap states active in carrier trapping, this does not necessarily imply that the dangling bonds are the only type of trapping centers. Reported values for the trapping cross section of dangling bonds are inaccurate by at least one order of magnitude [24, 25]. This makes it difficult to estimate the density of dangling bonds or indeed of any kind of defect in the ion-implanted a-Si from the measured carrier lifetime.

CONCLUSIONS

The trapping and recombination of photo-generated carriers in pure a-Si prepared by ion implantation has been studied on a sub-picosecond timescale. For plasma densities of $10^{18}/cm^3$ carrier trapping is dominant, and the carrier lifetime is observed to increase from 1 ps for as-implanted a-Si to 14 ps for 500 °C annealed a-Si. This observation supports the assertion based on recent experiments [6-9] that structural relaxation in a-Si is controlled by the annihilation of structural defects. In addition, it was found that upon ion bombardment of well-annealed a-Si the lifetime returns to the as-implanted level for damage doses $\approx3\times10^{-3}$ DPA, which is significantly lower than the de-relaxation threshold observed by Raman spectroscopy [7]. This indicates that lifetime measurements are more sensitive in probing ion-beam induced changes in a-Si than is Raman spectroscopy. The exact nature of the defects involved in carrier trapping can not be unravelled by present experiments.

The authors would like to thank A.J.M. Berntsen, A.N. Buijserd, J.S. Custer, J.R. Liefting, L.D. Noordam, and P.C.M. Planken for their contribution to this work. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM) and was made possible by financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) and the Stichting der Technische Wetenschappen (STW).

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