

Nonequilibrium carrier dynamics in ultrathin Si-on-glass films

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Abstract. We present a femtosecond pump–probe spectroscopy approach for characterization of amorphous and microcrystalline silicon films grown on glass substrates. Such films are presently being considered as absorbers in tandem-type, Si-based photovoltaic cells. Our experiments consisted of time-resolved, two-colour femtosecond optical measurements, performed in the transmission mode in a wide range of delay times. Depending on the sample growth process, collected normalized transmissivity change ($\Delta T/T$) waveforms exhibited a bi-exponential relaxation dynamics with the characteristic times varying from picoseconds to nanoseconds. Experimental data were interpreted using a three-rate-equation models, and the relaxation was identified as, depending on the Si film type, being dominated by either carrier trapping or electron–phonon cooling and followed by electron-hole recombination. An excellent fit between the model and the $\Delta T/T$ transients was obtained and a correlation between the Si film growth process, its hydrogen content, and the associated trap concentration was demonstrated.

1. Introduction

The relaxation of optically excited carriers in amorphous microcrystalline silicon [(a-Si) and (mc-Si)] thin films has been part of many investigations that involved time-resolved optical measurements [1–4], driven by a better understanding of the carrier dynamics. It is also essential for determining the material's properties, which in this case are strongly influenced by a given deposition technique.

In this work, we demonstrate that a time-resolved, optical pump–probe technique provides an effective means for determining the details of the nonequilibrium carrier dynamics in ultrathin Si-on-glass films. We have collected a large family of normalized reflectivity change ($\Delta T/T$) waveforms of various a-Si and mc-Si films deposited under different conditions and have performed numerical fittings based on a general trap-dominated carrier-relaxation model to determine the optimum Si-deposition parameter space.

2. Sample fabrication and femtosecond optical pump–probe measurements

Two general sets of Si-on-glass samples were grown for this study. The first set (“S” samples) was deposited using a plasma-enhanced chemical-vapour-deposition (CVD) method and the fabricated films were primarily *p*-type SiCH and *n*-type a-Si films. Of notable interest, the H032811S1 sample was deposited with aCH₄/SiH₄ ratio of 0.85 and a BF₃/SiH₄ ratio of 1. The “P” samples were also



deposited by the CVD method but with no dopants and with the increased hydrogen dilution, as compared to the growth of S-type samples, and were predominantly mc-Si films.

Femtosecond optical pump–probe spectroscopy is a unique investigation tool, extensively implemented to characterize nonequilibrium carrier dynamics in many condensed-matter systems, ranging from metals to various semiconducting materials [5]. In our case, for time-resolved characterization of carrier lifetime, we used a two-colour, pump–probe setup similar to that used earlier in our laboratory by Zhang *et al.* [6].

3. Experimental results and discussion

A very large family of $\Delta T/T$ waveforms was measured at room temperature. Each sample was tested at least three times at three different spots to average any film inhomogeneities. All collected transients had the same general shape and consisted of a pump-pulse–limited rising edge, followed by relaxation with a phenomenological, double-exponential decay. The initial fast relaxation time, varied in our samples from 2.4 ps (S-type) to ~80 ps (P-type) and could be ascribed to either direct trapping of hot, optically excited electrons or electron-optic–phonon cooling. The subsequent relatively slow relaxation could be interpreted as electron-hole recombination, and for the B032811P5 sample, the corresponding time was as long as ~1 ns. Although the above bi-exponential fitting analysis of the $\Delta T/T$ waveforms provides a direct indication of the desired growth conditions for maximizing the electron lifetime in Si photovoltaic absorbers, it does not give a physical insight into the actual carrier-relaxation dynamics.

Carrier-relaxation dynamics observed in our experiments are relatively simple to understand, keeping in mind that the 400-nm–wavelength (ultraviolet) pump excites electrons highly into the conduction band, creating a hot-electron population, while 800-nm–wavelength (infrared) probe photons, having an energy well below both the a-Si and mc-Si band gaps,¹ couple to photoexcited electrons through free-carrier absorption. For pump–probe measurements in the transmission mode, the experimental $\Delta T/T$ dependence in the thin-film limit can be expressed as:

$$\Delta T/T = -\Delta\alpha d, \quad (1)$$

where $\Delta\alpha$ is the photo induced absorption change and d is the film thickness. For the probe photons with energies below the band gap $\Delta\alpha$ does not depend on the details of the electronic excitation spectrum and is described by the Drude model, which relates it to the total free-carrier concentration N [7,8]:

$$\Delta\alpha = \frac{Ne^2}{\epsilon_0\epsilon_b m^* \omega^2 \tau c}, \quad (2)$$

where ϵ_b is the material dielectric constant, m^* is the effective carrier mass, ω is the angular optical frequency, and τ is the momentum relaxation time. Combining equations (1) and (2), we see that in our experimental case, $\Delta T/T(t)$ is simply proportional to $N(t)$.

Recently, Jepsen *et al.* [9] have implemented a dynamic model that involves shallow trap sites in the band gap to reproduce the transient photoresponse of carriers in optically excited and THz-probed mc-Si wafers. Conceptually, a very similar model was used earlier to analyse femtosecond optical pump–probe studies of the transient photoresponse dynamics in low-temperature–grown GaAs films [5,10] that are known for their very large concentration of traps related to a distorted lattice and As precipitates.

Mathematically, the above scenario corresponds to the set of linear rate equations for time evolutions of concentrations of photoexcited electrons $N_{\text{hot}}(t)$, electrons at the bottom of the conduction band $N_{\text{con}}(t)$, and trapped electrons $N_{\text{trap}}(t)$, listed below:

¹For our tested Si samples, the energy gap values varied from 1.65 to 1.82 eV.

$$\begin{aligned} \frac{dN_{\text{hot}}}{dt} &= I(t) - \frac{N_{\text{hot}} - N_{\text{con}}}{\tau_{\text{cool}}} - \frac{N_{\text{hot}}}{\tau_{\text{trap}}}, & \frac{dN_{\text{con}}}{dt} &= -\frac{N_{\text{con}} - N_{\text{hot}}}{\tau_{\text{cool}}} - \left(\frac{1}{\tau_{\text{rec}}} + \frac{1}{\tau_{\text{trap}}} \right) N_{\text{con}}, \\ \frac{dN_{\text{trap}}}{dt} &= -\frac{N_{\text{trap}} - N_{\text{trap,e}}}{\tau_{\text{rec}}} + \frac{N_{\text{con}} + N_{\text{hot}}}{\tau_{\text{trap}}}, & \text{and } \tau_{\text{trap}} &= \frac{\tau_{\text{trap,max}}}{1 - \frac{N_{\text{trap}}}{N_{\text{trap,max}}}}, \end{aligned} \quad (3)$$

where $I(t)$ is the optical pump-pulse intensity (which is assumed to have a Gaussian shape with the width of 100 fs) and $N_{\text{trap,e}}$ is the final concentration of electrons in the trap sites. We stress that τ_{trap} is, as in [9], a function of the number of available trap sites and their individual lifetimes, with the $N_{\text{trap,max}}$ and $\tau_{\text{trap,max}}$ representing the maximum concentration of trap sites in the sample and the longest trapping time, respectively.

We have solved equations (3) numerically and, as a result, obtained the total concentration of excited electrons in our system, given as

$$N(t) = N_{\text{hot}}(t) + N_{\text{con}}(t) - N_{\text{trap}}(t), \quad (4)$$

where the minus sign in front of N_{trap} reflects the fact that traps reduce concentration of free carriers.

Figure 1 [main panels] shows our experimental $\Delta T/T$ transients (red dots, left axis) and the corresponding simulated temporal evolutions of $N(t)$ (solid black line, right axis) and $N_{\text{trap}}(t)$ (solid red line, right axis) for **S**-type [figure 1(a)] and **P**-type [figure 1(b)] samples, representing the a-Si and mc-Si cases, respectively. In addition, we also present in figure 1 insets that show early stages of the time evolution of the components of $N(t)$, i.e., $N_{\text{hot}}(t)$ (solid blue line), $N_{\text{con}}(t)$ (solid green line), and $N_{\text{trap}}(t)$ (solid red line).

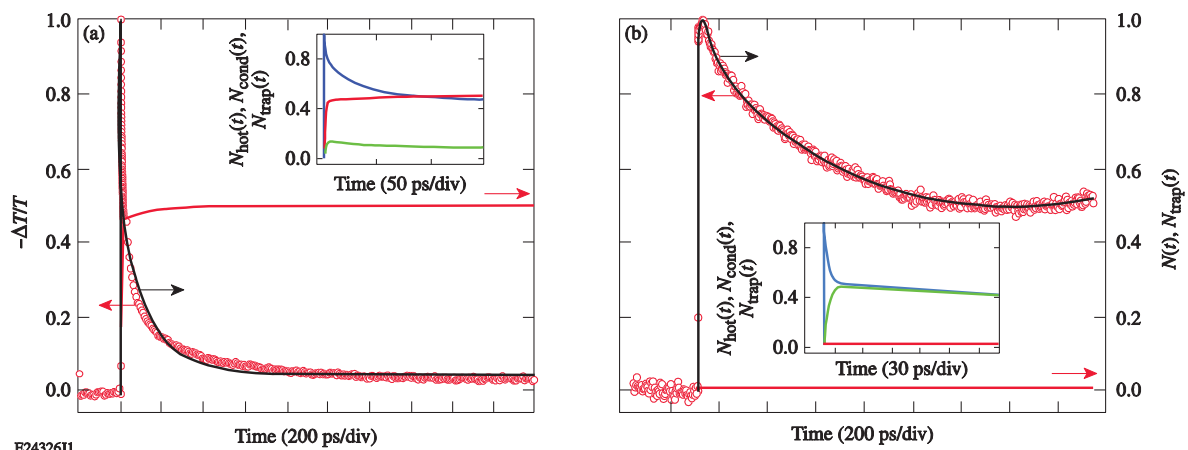


Figure 1. Experimental $\Delta T/T$ transients (red dots, left axis) of samples (a) H032811S1 and (b) B032811P5 and the corresponding $N(t)$ (solid black line, right axis) and $N_{\text{trap}}(t)$ (solid red line, right axis) simulation results. $N_{\text{trap}}(t)$ is normalized to $N(t)$. The insets present $N_{\text{hot}}(t)$ (solid blue line), $N_{\text{con}}(t)$ (solid green line), and $N_{\text{trap}}(t)$ (solid red line) components, corresponding in each case to the $N(t)$ presented in the main panel.

For an amorphous **S**-type sample [figure 1(a)], the concentration of trapped electrons is large and trapping at the very early stages of relaxation is very effective, resulting in rapid decay of the $\Delta T/T$

waveform or, equivalently, $N(t)$. The $N_{\text{trap}}(t)$ level reaches ~50% within the first 2 ps and remains approximately constant within our experimental window. Essentially a complete transfer of hot electrons to traps happens within ~60 ps [see inset in figure 1(a)] and the relaxation channel through the bottom of the conducting band represented by $N_{\text{con}}(t)$ is merely the background ($\tau_{\text{cool}} \gg \tau_{\text{trap}}$). Traps remain occupied (N_{trap} almost constant) at the end of our ~2-ns-wide observation window; therefore, trap lifetimes for these a-Si samples are very long and might even exceed the pulse repetition time of our laser (~13 ns). In fact, in our experiments, traps are likely to be emptied by the next incoming ultraviolet (400-nm) pump pulse, contributing to the hot-electron population.

In contrast to S-type samples, for the B032811P5 sample [figure 1(b)], which represents the best mc-Si case, the density of trapped electrons can be, actually, neglected. As seen in the inset in figure 1(b), the hot-carrier relaxation is now completely dominated by the electron-optic-phonon cooling and the initial transfer to the bottom of the conduction time. With $N_{\text{trap}}(t)$ negligible, the final relaxation step is through the electron-hole recombination process and, indeed, in this film we observe the longest value of the experimental recombination time ($\tau_{\text{trap}} \approx 200$ ps).

4. Conclusions

Our femtosecond spectroscopy pump-probe experimental studies and subsequent simulations based on a general carrier relaxation in a photoexcited semiconducting materials model have proved that shallow trap sites in the band-tail states play a very important role in the relaxation of excited carriers in Si-on-glass samples intended for solar-cell absorbers. The observed relaxation dynamics in samples grown under different conditions reflects the trap-site densities and trapping lifetime, providing much-needed feedback to the control of wafer growth conditions. The latter is a crucial element for designing and optimizing new generations of Si-absorber-based photovoltaic solar cells with higher efficiencies.

Acknowledgment

This work is supported in part by the Corning, Inc., grant to the University of Rochester and by the New York State NYSTAR grant to the University of Rochester Center for Emerging and Innovative Sciences. Additional support came from the ARO Grant No. W911NF-12-2-0076. J. S. acknowledges support from the Frank Horton Graduate Fellowship Program at the University of Rochester's Laboratory for Laser Energetics, funded by the U.S. Department of Energy Office of Inertial Confinement Fusion under Cooperative Agreement No. DE-NA0001944 and the New York State Energy Research and Development Authority. The support of NYSTAR, ARO, and DOE does not constitute their endorsement of the views expressed in this article.

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