Ultrafast Vibrational Dynamics and Stability of Deuterated Amorphous Silicon

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Infrared four-wave mixing experiments performed upon deuterated amorphous silicon layers (a-Si : D) reveal profound differences in the dynamics of Si-D stretch vibrations compared to those of analogous Si-H vibrational modes in hydrogenated amorphous silicon (a-Si : H). Remarkably, transient-grating measurements of the population decay rate of the Si-D vibrations show single-exponential decay directly into collective modes of the a-Si host, bypassing the local bending modes of the defect into which the Si-H vibrations decay. Photon-echo measurements of the vibrational dephasing suggest at low temperature contributions from TO nonequilibrium phonons and at elevated temperatures elastic phonon scattering of TA phonons.

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Hydrogen and its isotopes play a significant role in manipulating the properties of silicon-based materials for optoelectronic applications. Passivation of defect states reduces the concentration of charge-carrier trapping states and recombination centers, and increases the charge-carrier mobility and lifetime. This enhances, for example, performance in high-resolution displays and efficiency in solar cells. For terrestrial applications of devices such as solar cells, manufacturing costs can be prohibitive for large-scale use. The desire to reduce costs leads one to thin film materials, of which amorphous silicon thin films represent an attractive low-cost component [1].

The application of amorphous silicon in devices is unfortunately limited by the Staebler-Wronski effect [2] in which light-enhanced degradation occurs through the creation of defects. The diffusion of hydrogen is generally considered to be the mechanism that allows additionally created defects to be metastable and have a lasting detrimental effect on device performance. Recently a remarkable observation has been made: the hot-electron degradation for metal-oxide semiconductor (MOS) transistors and the light-induced degradation for amorphous silicon solar cells have been drastically reduced by simply replacing deuterium for hydrogen at the silicon/silicon dioxide interface and in the intrinsic region of the pin junction, respectively [3,4]. This so-called "isotope effect" has been attributed with inhibiting the deleterious effects which degrade silicon-based devices by factors of up to 50. Since the electronic properties of Si-H and Si-D are identical, one possibility for the microscopic origin of the isotope effect is that it is related to the principally different vibrational dynamics of the Si-D bond compared to that of the Si-H bond as noted in previous work [5,6].

In this Letter, we give the first report on the dynamics of deuterated amorphous silicon (a-Si : D) vibrations. We have utilized a free-electron laser (FELIX) to resonantly excite the Si-D stretching vibration of the C_{3v} symmetry Si-D defect at a wavelength close to 6.85 μm. Employing degenerate four-wave mixing techniques, in particular, transient-grating and vibrational echoes, we have measured both the longitudinal (population relaxation T_1) and transverse (phase relaxation T_2) decay times, and thus are able to assess the various relaxation channels available to the excited silicon-deuterium vibrational modes in a-Si : D. Previous time-resolved, nonlinear spectroscopy on the amorphous silicon system has concentrated on a-Si : H [7] stretch vibrations with the interesting result that the population decay occurred nonexponentially, with a distribution of rates apparently determined by the amorphous host. Remarkably, the results for a-Si : D are radically different and clarify the microscopic mechanisms for the "isotope effect" in amorphous silicon.

The a-Si samples consist of a 1.0-μm-thick a-Si : D layer, grown by plasma-enhanced chemical vapor deposition (PECVD) at a discharge frequency of 13.56 MHz from pure SiD_4 on a 250-μm-thick p-type c-Si wafer. The a-Si films contain around 10 at. % deuterium and no hydrogen. The optoelectronic properties of this intrinsic a-Si : D layer are of device quality, i.e., p-i-n thin film solar cells made with this material have a state-of-the-art energy conversion efficiency of 9%. In the transient-grating measurements, two nonlinear pump beams (with wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$) were spatially and temporally overlapped in the sample, creating a vibrational population grating. A weaker, spatially overlapped but time delayed probe beam (with wave vector $\mathbf{k}_3$) is then Bragg diffracted off this grating into a phase-matched signal direction ($\mathbf{k}_4 = \mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3$) with a signal intensity which decays as $T_1/2$ for variable delays between the fixed pump pulses and the probe. The photon echo measurement relies upon a two-pulse sequence which is applied to the sample, such that the first pulse (with wave vector $\mathbf{k}_1$) creates a coherent superposition of vibrational states. Immediately after the first pulse all of the microscopic dipoles of the vibrational ensemble oscillate in phase. Because of the distribution of frequencies within the inhomogeneous line shape, the

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initial phase relation is rapidly lost due to free induction decay. A time τ later a second pulse (with wave vector $\mathbf{k}_2$) causes an inversion of the macroscopic dipole moment which leads to a rephasing of these individual frequency components yielding, at an additional time τ, a phase-matched superradiant burst from the then rephased ensemble known as a photon echo. The time-integrated echo signal propagating along the $\mathbf{k}_{\rm echo} = |2\mathbf{k}_2 - \mathbf{k}_1|$ signal direction decays as a function of the delay between the incoming pulses with $T_2/4$.

Figure 1 shows the 4 K laser induced grating signal from a-Si : D. The apparent temporal resolution of > 3 ps is limited by residual multiple reflections coming from the wedged sample. The solid line displayed in the inset to Fig. 1 is a single-exponential fit to the data which yields a lifetime of 57 ps, a remarkable observation in light of recent results on a-Si : H stretch vibrations [7]. There the measured population decay was markedly multiexponential, a phenomenon attributed to a distribution of rates rising from modified Si-H bond strengths and from variations in the local density-of-phonon states in the amorphous environment. The low temperature Si-D lifetime is determined by its spontaneous breakup into lattice modes and/or internal modes of the Si-D bond such as the bending mode (at approximately 455 cm^{-1}). Such processes are possible thanks to coupling of the Si-D stretch mode to accepting modes through anharmonic terms in the vibrational potential. At higher temperatures, stimulated emission into the accepting modes may occur and it is this which gives rise to the temperature dependence of the decay rate $[T_1(T)]^{-1}$. The relatively weak dependence upon temperature observed in Fig. 2 suggests the involvement of only very high-frequency phonons in the decay processes. The temperature-dependent form for the energy decay rate is given by [8]

$$[\mathrm{T}_1(T)]^{-1} = [\mathrm{T}_1(0)]^{-1} \frac{\exp(\hbar\omega/k_B T) - 1}{\prod_i [\exp(\hbar\omega_i/k_B T) - 1]}, \qquad (1)$$

where $[\mathrm{T}_1(0)]^{-1}$ is the spontaneous decay rate (which we approximate by values at the lowest measured temperatures), $\hbar\omega$ is the Si-D vibrational energy (in cm^{-1}), $k_{\rm B}$ is Boltzmann's constant, and $\hbar\omega_i$ is the energy of the accepting modes into which the Si-D vibration decays via process of order i. Necessarily $\sum_i \hbar\omega_i = \hbar\omega$. Fitting Eq. (1), for three obvious possibilities is shown in Fig. 2. In all cases, $[\mathrm{T}_1(0)]^{-1}$ is taken to be 17.7 GHz, as determined from experiment. Three phonon decay processes with three accepting TO modes of equal energy (487 cm^{-1}) are shown as a solid line in Fig. 2 or with two accepting Si-D (455 cm^{-1}) bending vibrations plus one single 550 cm^{-1} lattice mode are shown as a dashed line in Fig. 2. However, decay into two bending modes and a 550 cm^{-1} lattice mode would not seem very likely by density-of-states arguments, since there is essentially no vibrational energy which can be transported by the lattice at that frequency. On the other hand, the TO mode frequency is the peak in the lattice density of states (DOS) [9] and would seem the most probable three-phonon decay route. Four-phonon decay processes, for example, decay into one LA (335 cm^{-1}), one TA (175 cm^{-1}), and two TO (485 cm^{-1}) phonons, are shown as a dotted line in Fig. 2. Apart from being of higher order and thus less efficient, four-phonon processes vastly overestimate the increase of the decay rate at high temperatures, because they activate extremely early due to the low-energy phonon involved in this process. We conclude that the accepting modes for the Si-D stretching mode are of a quite different nature from those of the hydrogen analog in that the deuterium vibrations are free to decay directly into delocalized lattice modes, while the Si-H vibrations have to decay into localized bending modes. It is tempting to consider the implications of this observation for the stability of the materials. Optoelectronic devices constructed from hydrogenated amorphous silicon materials show degradation due to dangling-bond creation under, for example, illumination and concomitant recombination processes at defect centers. In

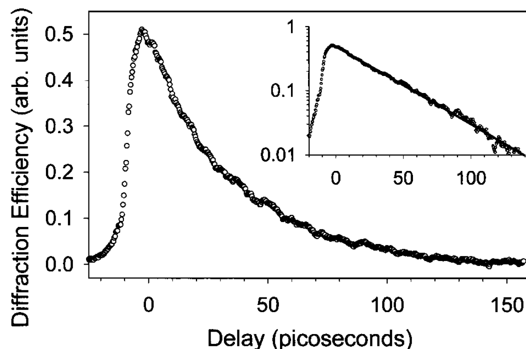

FIG. 1. 4 K transient-grating signals for resonant excitation of the a-Si:D stretching vibration at 6.85 μm. Inset: Semi-log plot with single-exponential fit.

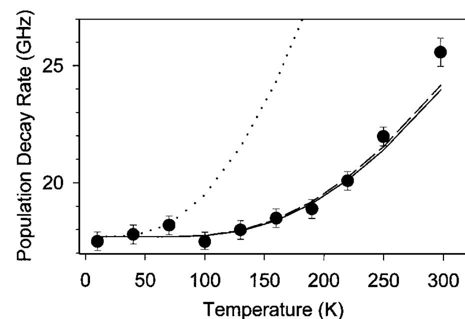

FIG. 2. Temperature-dependent population decay rates. • data points. The dotted line is a fit to four-phonon decay into one LA (335 cm^{-1}), 1 TA (175 cm^{-1}), and 2 TO (485 cm^{-1}) phonons. The dashed line is a fit to three-phonon decay into two Si-D bending modes (455 cm^{-1}) and a single 550 cm^{-1} phonon. The solid line is a fit to three-phonon decay into three TO phonons (487 cm^{-1}).

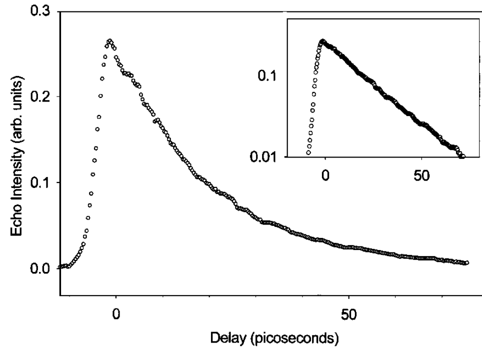

FIG. 3. 4 K photon echo signal for resonant excitation of the a-Si : D stretching vibration. Inset: Semilog plot.

case recombination takes place close to a Si-H bond, the electronic energy can be efficiently drained to the high-energy, Si-H stretching vibrations. However, since the stretching mode in a-Si:H decays to localized bending modes, the vibrational energy remains imprisoned on the Si-H site for a relatively long time and is likely to increase the probability of dissociation of the Si-H bond and the promotion of the liberated H ions or neutrals into transport states. On the other hand, in deuterated materials, energy conservation allows for a rapid release of vibrational energy from the Si-D bond to the Si-Si lattice, without the need of exciting the bending modes and provides a natural way to explain the stability of a-Si:D. We note that consistent with the early observations of enhanced stability of a-Si:D [4], we recently observed enhanced stability in p-i-n devices where we used the same deposition conditions for the Si-D layer in the cell as for the layers in the present study.

To obtain information on the homogeneous linewidth (T_2-dephasing) we must resort to the vibrational echo technique. The 4 K signal is shown in Fig.3 where again the decay is single exponential. Figure 4(a) shows the temperature dependence of the homogeneous linewidth inferred from the vibrational echo signal and the contribution to that linewidth from the population decay alone. The linewidth is not lifetime limited at 4 K, an effect we attribute to residual long-lived (i.e., exceeding the 40-ns repetition rate of the micropulses of the laser) nonequilibrium phonons created upon the decay of the stretch vibration itself. This effect is dependent upon the excitation power as shown in the inset to Fig. 4(a). The likely candidates are the TO modes into which Si-D stretch vibration decays. This assumption seems vindicated in light of time-resolved Raman measurements which suggests components of the TO population can live as long as 100 ns [9].

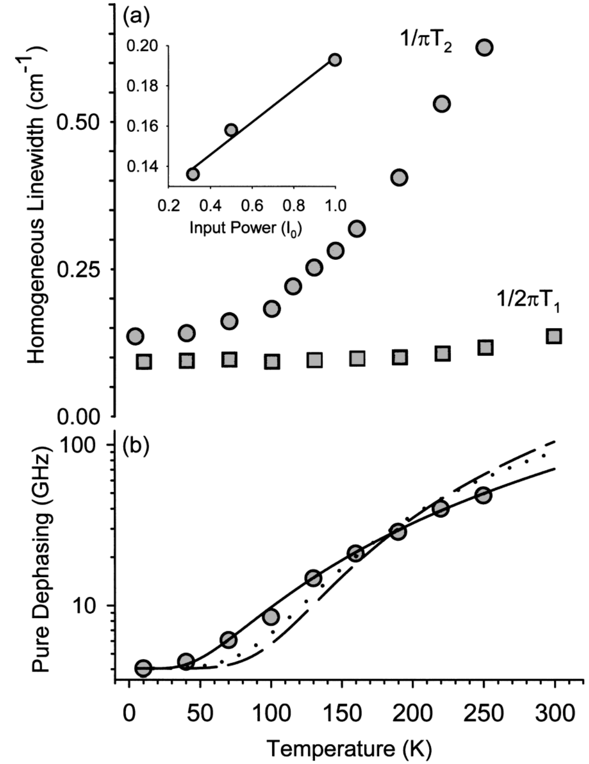

FIG. 4. (a) Temperature-dependent homogeneous linewidth inferred from photon echo signals shown as •, linewidth contribution from population decay shown as ■. Inset: excitation power dependent homogeneous linewidth. (b) Temperature-dependent pure dephasing. • data points. The dashed line is a fit to elastic phonon scattering assuming a Debye distribution for the a-Si phonon density of states. The dotted line uses the real phonon density of states obtained from Raman scattering. The solid line and best fit is obtained assuming dephasing via a single lattice mode at the TA peak (133 cm^{-1}). In all cases a temperature-independent contribution is included to account for dephasing via nonequilibrium phonons.

Pure dephasing ($1/\mathrm{T}_2^*$) is the adiabatic modulation of the vibrational energy levels through quantum phase fluctuations which we extract from the T_2 decay data by subtracting the appropriate temperature dependent population decay rate. The result is shown in Fig. 4(b). We believe the temperature dependent contribution to the pure dephasing in deuterated amorphous silicon can be related to dephasing by elastic phonon scattering events at the Si-D site. The rate $[\mathrm{T}_2^*(T)]^{-1}$, of such a process in which a phonon (ω) is absorbed and emitted again (ω') into a random direction has a temperature dependent form which follows from an integration over the entire phonon-field of a-Si as [10]

$$[\mathrm{T}_2^*(T)]^{-1} = a + A \iint \hbar^2 \omega\omega' n_\omega (n_{\omega'} + 1)\rho_\omega \rho_{\omega'} \delta(\omega - \omega') d\omega d\omega', \qquad (2)$$

where a is a constant which describes the residual dephasing induced by nonequilibrium phonons, A is a phonon coupling constant, n_ω is the Bose-Einstein phonon occupancy, and ρ_ω is the one-phonon DOS. The delta function ensures energy conservation in the elastic scattering. In the first approximation we assume a Debye distribution for the phonon density of

states of a-Si with a Debye temperature equal to 720 K. As shown in Fig. 4(b), this completely underestimated the activation temperature of the dephasing. It is worth noting that the Debye model can reproduce the data if an unrealistic value of T_D of 275 K is adopted, indicating the significance of scattering by low-energy phonons. This might be explained by the absence of the acoustic phonon peak around 150 cm^{-1} in the Debye model but, of course, present in the real a-Si one-phonon DOS [9]. A more physically acceptable model is to use a weighted sum over the real one phonon DOS obtained from Raman scattering [11], for example. Although the data are more closely reproduced, the agreement is hardly convincing, suggesting that the assumed frequency dependence of the coupling coefficient in Eq. (2) is not realistic enough. If, on the other hand, one considers dephasing through scattering of a single phonon mode, then Eq. (2) reduces to

$$[\mathrm{T}_2^*(T)]^{-1} = a + An_\omega(n_{\omega'} + 1). \tag{3}$$

The solid line in Fig. 4(b) shows the fit to this expression for dephasing via transverse acoustic phonons at 133 cm^{-1} with $A = 27$ GHz and using $a = 4.05$ GHz as with all other plots. The agreement between the calculation and the experimental data is excellent. This suggests that the TA modes dominate the dephasing of the Si-D vibrations.

At this point, we address the question of why in a-Si:H the amorphous surround leads to a multiexponential population decay of the stretching modes, while in a-Si:D we observe a single-exponential decay. One explanation for the multiexponential decay in a-Si:H is a local variation of the anharmonic coupling responsible for the decay. Since the accepting modes in the Si-H case are the bending modes, the process is very local and sensitive to the specific surroundings of the Si-H bond. In the case of the Si-D stretching vibration the accepting modes are all lattice modes and thus of an extended nature. Therefore the local surrounding and variations in it will play a minor role and, consequently, a single decay constant is expected. The other explanation for the multiexponential decay in a-Si:H is a local variation of the density of states of the energy conserving lattice phonon of 133 cm^{-1}. In the present case of the Si-D vibration we use three lattice phonons instead of one, which will give rise to a strong averaging out of the variations in the local density of states, if these are present at all. Therefore, the single-exponential character of the population decay of the Si-D stretching mode is directly related to the delocalized character of the accepting modes, unlike in the case of the Si-H stretching mode in a-Si.

In conclusion, the Si-D vibrational population decay has been shown to occur directly into a-Si phonon modes in a single-exponential decay process. This is the converse of a-Si:H stretch modes which show a markedly multiexponential population decay. We propose that this can be attributed to its decay into local Si-H bending vibrations, although it is clear that experiments performed directly exciting the bending vibrations themselves would be valuable. With the present new experimental evidence, the superior resistance of a-Si:D against light-induced dangling-bond creation as compared to that in a-Si:H can now be explained in light of the "H collision model" [12] as this model requires the initial release of H(D) from the Si-H(D) bond to form mobile H(D). The release of H is more likely than D because the excess recombination electronic energy dumped near Si-H configurations is more likely to become localized in bending modes. The temperature-dependent phase relaxation is attributed to two phonon elastic scattering of TA phonons which are accompanied by a small contribution from long-lived nonequilibrium a-Si phonons, probably TO modes created in the vibrational decay of the Si-D mode. In the case of hydrogenated amorphous silicon, a similar thing happens but in that case the decay products around 300 cm^{-1} of the bending modes are involved.

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