

Dynamics of Si-H Vibrations in an Amorphous Environment

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We present results of the first vibrational photon-echo, transient-grating, and temperature dependent transient-bleaching experiments on *a*-Si:H. Using these techniques, and the infrared light of a free electron laser, the vibrational population decay and phase relaxation of the Si-H stretching mode were investigated. Careful analysis of the data indicates that the vibrational energy relaxes directly into Si-H bending modes and Si phonons, with a distribution of rates determined by the amorphous host. Conversely, the pure dephasing appears to be single exponential, and can be modeled by dephasing via two-phonon interactions.

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As early as 1911, Eucken [1] recognized that the thermal properties of noncrystalline solids are quite different from those of crystalline materials. Nowadays, it is well established that amorphous and glassy solids exhibit a set of universal thermodynamic characteristics not found in crystals [2]. Nevertheless, the physical picture explaining the “anomalous” phenomena is still not complete, as there is no consensus about the nature of the vibrational excitations in these systems. In particular, in the temperature region above the so-called “plateau” in the heat conductivity ($T \geq 10$ K), different theories assume the relevant vibrational modes to be localized [3], propagating [4], and diffusive modes [5]. Also, conclusions drawn from Raman [6], inelastic neutron [7], and inelastic x-ray scattering measurements [8] are not unanimous as to the nature of these modes.

Although experiments on nonequilibrium phonons in crystals have proven to give a wealth of information on elementary phonon scattering processes [9], the number of dynamical experiments investigating high-frequency ($\nu \gg 1$ THz) vibrations in noncrystalline solids is quite limited. Pulsed Raman spectroscopy has been used to examine phononlike modes in *a*-Si(:H) [10]. Results of those experiments suggest that high-frequency vibrations have a lifetime several orders of magnitude longer than in crystals, which disagrees with the outcome of the computer simulations by Fabian *et al.* [5] performed later. A difficulty in this comparison, though, is that in the experiments, charge carriers are used to generate vibrations over the full spectrum. In the simulations, however, decay rates are calculated for single-frequency vibrational excitations and electronic processes are ignored. As electronic excitations in amorphous environments may have very long lifetimes [11], they might affect the vibrational signals.

In a second class of experiments that examine nonequilibrium vibrations in glassy materials, the mentioned ambiguities are absent. With infrared light, vibrations are excited resonantly by direct conversion of infrared

photons into vibrational quanta, without excitation of charge carriers. A few infrared transient-bleaching experiments on molecular vibrations in amorphous hosts have been reported [12,13], and results of infrared vibrational photon-echo measurements on the CO stretching mode of $W(CO)_6$ in organic glasses have been published [14]. Yet the conclusions drawn from these studies mainly relate to the dynamics of molecular vibrations, and not to the vibrational properties of the amorphous host itself.

In this Letter, we present results of the first infrared vibrational photon-echo and transient-grating experiments on an inorganic glass. Using these techniques, and the infrared light of the free-electron laser FELIX (Rijnhuizen, The Netherlands), the vibrational population decay and phase relaxation of Si-H stretching vibrations in *a*-Si:H are investigated. *a*-Si(:H) is a technologically important material that has been extensively studied experimentally and theoretically [5,10,15]. The main goal of the experiments is to gain more insight into the dynamics of vibrations in amorphous systems, by taking full advantage of modern pulsed infrared techniques and of the intrinsic Si-H vibrations as a probe. Interestingly, all measured signals show a nonexponential decay, in contrast with the single-exponential decays observed in similar experiments on Si-H stretching vibrations of a *crystalline* hydrogen-terminated Si surface [16]. This illustrates the importance of the amorphous environment for the vibrational dynamics of the local Si-H stretching mode. In addition, the high quality of the data allows us to extract mean population relaxation and pure dephasing times vs temperature. From that, both the relaxation path and the mechanism responsible for the dephasing of the Si-H stretching mode are determined. The vibrational properties of the amorphous material turn out to be essential in the interpretation.

The samples studied consist of a $1.0 \mu\text{m}$ thick *a*-Si:H layer, grown by plasma enhanced chemical vapor deposition on a two-sided-polished *c*-Si substrate. The substrate is transparent for the infrared light used. The *a*-Si:H films

contain about 10 at. % H, giving rise to an infrared absorption line at 2000 cm^{-1} (100 cm^{-1} FWHM), corresponding to the stretching modes of isolated Si-H bonds. By tuning the wavelength of FELIX in resonance with that line, 12% of the infrared light is absorbed and directly converted into stretching vibrations. Because of the anharmonicity of the stretching modes [17], and the relatively narrow bandwidth of the laser, only excitation to the first vibrational level takes place. FELIX generates 0.5 ps micropulses at a repetition rate of 25 MHz. The micropulses form a macropulse with a duration of 2.5 μs . The macropulses are repeated at a rate of 5 Hz in the transient-bleaching measurements. The other experiments are carried out with a repetition rate of 10 Hz. To allow for temperature dependent measurements, all experiments are performed with the sample mounted in a cryostat. A LN₂-cooled HgCdTe detector is used for signal detection. Signals are averaged over 50 micropulses.

For the transient-bleaching and photon-echo experiments, standard pump-probe methods are used. The strong pump pulses excite a fraction of the Si-H bonds, creating a vibrational population. Transient-bleaching measurements give the population decay time T_1 [12]. The phase relaxation time, T_2 , is obtained from the photon-echo signals, which decay with $T_2/4$ [14].

An alternative way to examine T_1 is provided by the transient-grating technique [18]. By focusing two synchronous pump beams onto one spot in the sample, a vibrational population grating is formed. A delayed probe beam is Bragg diffracted off this grating, allowing for background-free signal detection. The diffracted probe intensity decays with $T_1/2$ [20]. Higher signal-to-noise ratios are obtained with this method than with the transient-bleaching technique. The latter, namely, requires the accurate detection of small changes ($\leq 3\%$) of the probe intensity. In any case, the transient-bleaching measurements are necessary to confirm that the grating signals are caused by a vibrational population grating, and not by spatial transport or thermal effects.

The graphs depicted in Fig. 1 are representative of the signals measured with the transient-bleaching, transient-grating, and photon-echo technique. As an example, results for two temperatures, 15 and 250 K, are shown. A remarkable characteristic of all curves is their nonexponential decay. As mentioned before, similar experiments on Si-H vibrations in a crystalline environment did not show any nonexponentiality [16]. We will demonstrate that this effect is caused by the amorphous surrounding.

To find an explanation for the nonexponential decay, the dependence of the temporal shape of the T_1 signals on temperature is of importance. We discovered that all normalized transient-grating signals can be merged to one universal curve [see the inset of Fig. 2(a)], just by rescaling the time axis of each curve $S_g(t)$ with the average time $\langle T_g \rangle = \int t S_g(t) dt / \int S_g(t) dt$ of that curve, proving that the shape of the T_1 signals is temperature independent.

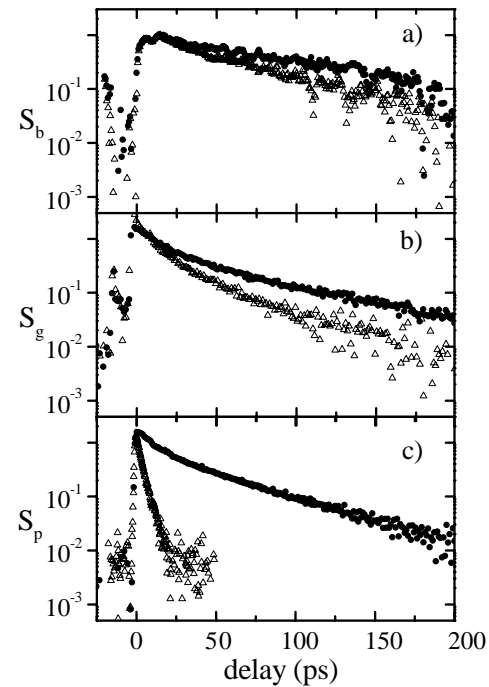


FIG. 1. (a) Transient-bleaching, (b) transient-grating, and (c) photon-echo signals (S_b , S_g , and S_p , respectively) for $T = 15\text{ K}$ (\bullet) and $T = 250\text{ K}$ (Δ), as a function of the delay between pump(s) and probe. S_b 's are obtained with micropulse energies of 3.5 and 0.1 μJ for pump and probe, respectively, S_g 's with two pump beams of 1.0 μJ pulses, and a probe of 0.35 μJ pulses, and S_p 's with a pump of 0.3 μJ and probe of 1.75 μJ . All beams are focused to a 150- μm -diam. spot in the sample.

From the ratios between the average times at different temperatures, the temperature dependence of the mean decay rate $1/\langle T_1 \rangle = 1/(2\langle T_g \rangle)$ is determined, as is shown in Fig. 2(a). A similar procedure was followed with the transient-bleaching data, leading to equivalent results (except for a larger error in $\langle T_1 \rangle$), and thus proving that the grating technique can be used to analyze the vibrational population decay.

Theoretical models exist that describe the relation between the decay rate $\gamma = 1/T_1$ and temperature T , depending on the frequency ω of the initially excited mode and the frequencies ω_i of the accepting modes, and obeying the energy conservation rule $\sum_i \hbar \omega_i = \hbar \omega$ [19],

$$\gamma(T) = \gamma(0) \frac{\exp(\hbar \omega / k_B T) - 1}{\prod_i [\exp(\hbar \omega_i / k_B T) - 1]}. \quad (1)$$

By fitting Eq. (1) to the data, we find that one stretching vibration decays into three Si-H bending vibrations ($623 \pm 2\text{ cm}^{-1}$) and one TA Si phonon ($133 \pm 6\text{ cm}^{-1}$); see Fig. 2(a). No other combination of accepting modes produces the measured T dependence of $1/\langle T_1 \rangle$ within the experimental error [20]. According to this fit, only modes within a narrow frequency range of the broad Si-H bending resonance [15] participate in the decay, indicating that the

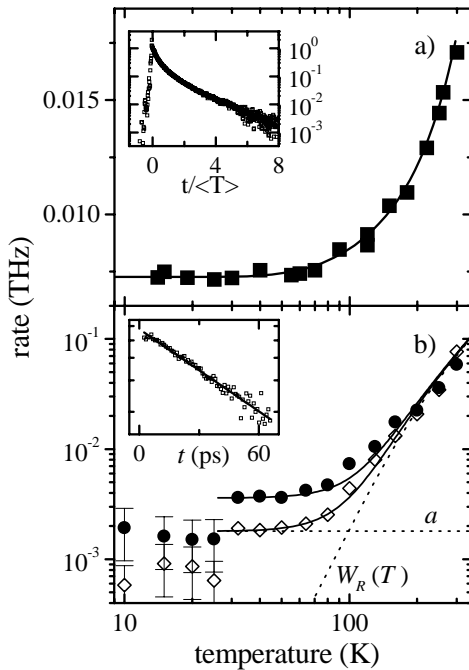


FIG. 2. (a) $1/\langle T_1 \rangle$ vs T . The solid line describes the decay of one Si-H stretching vibration into three bending vibrations (623 cm^{-1}) and a TA Si phonon (133 cm^{-1}), given by Eq. (1). No dependence of $1/\langle T_1 \rangle$ on power was observed. The inset shows the mean $S_g(t)$ obtained from averaging all scaled $S_g(t)$ curves. (b) $1/T_2'$ vs T , determined from the single-exponential S_p/S_g curves. In the inset, S_p/S_g vs delay Δt is shown for 100 K, yielding $T_2' = 230 \pm 20$ ps. Results are presented for $S_p(t)$ measured with normal (\diamond) and double (\bullet) excitation power. For $T > 30$ K, error bars are of the order of the symbol size. The lines are theoretical fits described in the text.

frequencies of the stretching and bending modes involved are correlated.

As mentioned above, we observe that the degree of non-exponentiality of the decay is temperature independent. This suggests that it cannot be explained by a sequence of processes that are assisted by vibrations or phonons of different energies, as proposed earlier [13]. These processes, namely, would have different temperature dependences. The conclusive argument, however, is the experimental fact that the echo and grating decay on the same time scale at low temperatures. In the case of successive decay via an intermediate state, $1/\langle T_1 \rangle$ is determined by the series of steps, whereas the echo decays with the rate of only the first transition. Therefore, we believe that stretching vibrations at different sites have different lifetimes, because of a variation in local environments. Hence, we search for temperature-independent factors that cause a variation of decay times over the ensemble of Si-H modes excited. Candidates are the local density of vibrational states to which the stretching vibrations decay, and the anharmonic coupling to those states. In particular, T_1 is expected to be sensitive to variations of these quantities, because of energy conservation. Since such restrictions are absent in

pure dephasing processes, we would expect the pure dephasing to be single exponential, as in crystals.

To examine the pure dephasing times, T_2' , the results of the transient-grating and photon-echo signals, $S_g(t)$ and $S_p(t)$, are combined. We write for the non-exponential decays $S_g(t) = \int g_1(\tau_1) e^{-2t/\tau_1} d\tau_1$ and $S_p(t) = \int g_2(\tau_2) e^{-4t/\tau_2} d\tau_2$, where $g_i(\tau_i)$ represents the distribution of τ_i 's leading to $\langle T_i \rangle$, and t is time. We assume that $g_2(\tau_2)$ can be separated into contributions from τ_1 's and τ_2 's, and write $g_2(\tau_2) d\tau_2 = g_1(\tau_1) d\tau_1 g_2'(\tau_2') d\tau_2'$. Then, replacing $1/\tau_2$ by $1/2\tau_1 + 1/\tau_2'$, analogous to what is accepted for the exponential case [14], we obtain

$$S_p(t) = \iint g_1(\tau_1) g_2'(\tau_2') e^{-2t/\tau_1} e^{-4t/\tau_2'} d\tau_1 d\tau_2'. \quad (2)$$

From this relation, it is clear that $S_p(t)/S_g(t)$ leads to an expression for the pure dephasing. The inset of Fig. 2(b) shows the outcome of dividing S_p by S_g for $T = 100$ K. In contrast to all results presented in Fig. 1, this curve is indeed single exponential, and according to Eq. (2) decays with $T_2'/4$. The same is true for all other $S_p(t)/S_g(t)$ obtained for $T \geq 30$ K. This fact justifies the assumption made in deriving Eq. (2), and is used to extract $1/T_2'$ as a function of temperature [see Fig. 2(b)]. We note that below 30 K, results of $S_p(t)/S_g(t)$ are noisy and seem slightly nonexponential. The $1/T_2'$ values found for those temperatures are ignored in the following.

In glasses, a T^2 dependence is generally observed for the optical linewidth in the temperature region of our experiments [21]. This behavior has been related to dephasing by “two-phonon Raman” processes. The rate, W_R , of such a process, in which a phonon (ω) is absorbed and emitted again (ω') into a random direction, is [22]

$$W_R \propto \iint \hbar^2 \omega \omega' n_\omega (n_{\omega'} + 1) \times \rho_\omega \rho_{\omega'} \delta(\omega - \omega') d\omega d\omega'. \quad (3)$$

Here, n_ω is the (Bose-Einstein) phonon occupation number and ρ_ω the vibrational density of states; the δ function ensures energy conservation. Several theories have been proposed to describe ρ_ω of the “phononlike” vibrations in glasses and to calculate W_R [21]. In the case of *a*-Si:H, however, ρ_ω can be determined from Raman measurements [23]. Using the ρ_ω obtained from the Raman spectrum of our sample, we find that the pure dephasing is well described by $1/T_2' = a + W_R(T)$ [which is not $\propto T^2$; see Fig. 2(b)], where a is a temperature-independent contribution. For the experiments performed with “normal” excitation power, we find $a = 1.8 \pm 0.1$ GHz and $W_R(40 \text{ K}) = (4.3 \pm 0.3) \times 10^{-2}$ GHz. In the case of double excitation power, a is twice as high, but $W_R(40 \text{ K})$ remains the same.

Apparently, two contributions add to the dephasing, one of which is temperature independent, but does depend on the number of Si-H vibrations excited. Such a contribution

is not observed in the experiments on electronic dephasing described in [21]. Different than in those studies, the excitations we examine are purely vibrational, and eventually decay into phononlike modes. Thus, it could be that the n_ω 's in Eq. (3) do not correspond to the Bose-Einstein occupation numbers at the indicated temperatures, but are higher, either because of heating effects or due to the presence of nonequilibrium "phonons."

To check if heating of the sample can cause the extra dephasing, we calculated the stepwise temperature rise resulting from the incident micropulse train. It turns out that we cannot account for the observed extra dephasing rates, even if we neglect thermal diffusion. Hence, heating alone cannot explain the results.

Next, we explore the effects of nonequilibrium phonons in the increase of the dephasing rate. We assume that the bending vibrations produced in the decay step described by Eq. (1) relax into two LA-like Si phonons with frequencies between 300 and 325 cm^{-1} . From Eq. (3) we compute that these modes should have occupations of ~ 0.23 and ~ 0.4 to produce dephasing rates a of 1.8 and 3.6 GHz, respectively. The corresponding amounts of energy in the excited sample volume (~ 0.18 and ~ 0.32 μJ) are remarkably close to the amount of energy absorbed by the sample during one micropulse. The measured constant dephasing rates suggest that the phonons survive the 40-ns delay between two micropulses, as the extra phonon population should not change during the dephasing period. The long lifetimes this implies agree with the lifetimes of LA phonons in a -Si:H found from Raman experiments [10]. We conclude that part of the energy of a micropulse remains in the excited volume until the next pulse arrives, and increases the dephasing rate of Si-H vibrations excited with the next pulse.

In summary, we present results of pulsed infrared experiments on the vibrational population decay and phase relaxation of the Si-H stretching mode in a -Si:H. Because of the amorphous environment, Si-H vibrations at different sites have a different lifetime, resulting in nonexponential decay. In contrast, the pure dephasing is single exponential. From the temperature dependence of the mean decay rate it is concluded that each stretching vibration decays into three Si-H bending vibrations and one TA Si phonon. The dephasing of the Si-H stretching mode appears to be induced by the presence of Si phonons, part of which stay excited for more than 40 ns.

We have shown that the experiments and analysis presented are a valuable tool to investigate the dynamics of vibrations in glasses, and can be exploited to shed light on the still elusive nature of vibrations in these systems.

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