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Phonon dynamics in amorphous and nanocrystalline silicon

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Abstract

We present the results of experiments on the decay of nonequilibrium phonons created by pulsed laser excitation in an amorphous silicon film (a-Si : H) with and without a high volume fraction of 5 nm crystalline Si clusters (nc-Si). In one type of experiments, 29 cm^{-1} phonons are detected in the ruby substrate via phonon-induced luminescence and appear to decay on a much longer time scale ($\geqslant 100$ ns) in the film with nc-Si than in the film without nc-Si (~ 40 ns). In pump–probe Raman experiments, we observe a marked increase in the decay time for high-energy TA ($\sim 150\ cm^{-1}$) phonons in the film with nc-Si. We discuss the results in terms of a model in which phonons propagate in loosely coupled nanoscopic regions in the a-nc-Si material. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Nanocrystalline silicon; Nonequilibrium phonons

Dynamical properties of phonons such as transport and anharmonic decay in disordered, amorphous and nanostructured materials attract a lot of interest nowadays [1]. An effective experimental way of studying the phonon dynamics is to monitor the decay of population numbers of nonequilibrium phonons created by an optical pulse. There are several experimental observations where such type of materials show an anomalously long decay for high-energy phonons. In amorphous silicon (a-Si), a decay time $\tau_\omega \sim 70$ ns for nonequilibrium phonons with $\hbar\omega = 250$–$480\ cm^{-1}$ was measured [2,3]. In porous nanocrystalline corundum millisecond long lifetimes of size-quantized vibrations (Lamb modes) with $\hbar\omega = 20\ cm^{-1}$ were found [4,5]. Finally, in small-grain polycrystalline corundum anomalously long phonon decay $\tau_\omega > 1$ ms was discovered for phonons with $\hbar\omega = 29$–$80\ cm^{-1}$ [6]. Often the anomalies are explained by localization effects for phonons with $\hbar\omega > \hbar\omega_0$, where $\hbar\omega_0$ is the energy value separating extended and localized states and corresponds to phonons with wavelength $\lambda \sim d$, where d is a typical size of nanoscale inhomogeneity in the material. Sometimes $\hbar\omega_0$ is called the phonon mobility edge.

In the present contribution we study the dynamics of nonequilibrium THz phonons in a film of amorphous hydrogenated silicon (a-Si : H) containing a high volume fraction of nanocrystalline silicon clusters (nc-Si). To study the phonon dynamics we use inelastic light scattering and

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phonon-induced luminescence to monitor the time evolution of the phonon spectrum. We find that the dynamics of phonons in the film with nc-Si is very different from that in a pure a-Si : H film. This observation shows that in a film with nc-Si clusters phonons are imprisoned in and hop between weakly coupled nanoscale regions.

The samples we used were 500-nm thick a-Si : H films with and without nc-Si, grown by PECVD on ruby substrates (Al_2O_3 containing 20-at ppm of Cr^{3+} ions). From a careful analysis of the Raman spectrum of the a-nc-Si : H sample, an average nanocluster size of 5 nm and a 25% volume fraction of nc-Si were estimated [7]. Two types of experiments were carried out at 1.8 K. In both cases nonequilibrium phonons were generated in the film during the fast (< 1 ps) relaxation of photoexcited hot carriers created by a pulsed laser (penetration depth of the laser light into the film ~100 nm):

(a) *Ruby phonon spectrometer* (Fig. 1a): This scheme was used earlier to study the emission of 29 cm^{-1} nonequilibrium phonons from a pure a-Si : H film [8]. Here hot carriers are created by the 1 ns pulses from a mode-locked Ar-laser (514.5 nm) with average power on the sample up to 10 W/cm^2 and repetition rate 800 kHz or 4 MHz. Nonequilibrium phonons are emitted from the a-nc-Si : H (a-Si : H) film and detected in the ruby substrate by means of a luminescence technique which is sensitive to phonons with $\hbar\omega = 29\ cm^{-1}$, resonant to the $\bar{E}(^2E) - 2\bar{A}(^2E)$ electron–phonon transitions of Cr^{3+} ions (for details see Ref. [9]). The temporal evolution of the detected luminescence signal, $I_{29}(t)$, directly reflects the flux of 29 cm^{-1} phonons from the a-nc-Si : H (a-Si : H) film into the ruby substrate and can be measured with a time resolution of 10 ns [8]. We used two experimental configurations: (1) one in which phonons are generated on the open side of the film (configuration (1) in Fig. 1a) and thus have to travel a distance of ~400 nm from the phonon source to the detector; (2) one in which phonons are generated on the substrate side (configuration (2) in Fig. 1a) and thus typically travel only ~100 nm to the detector.

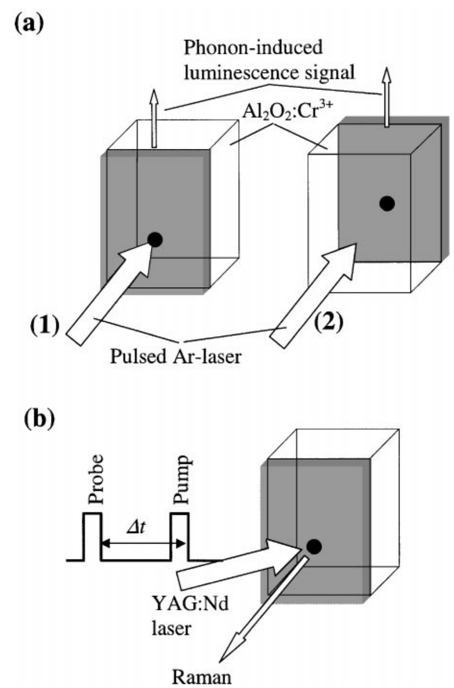

Fig. 1. Experimental setups for ruby (a) and Raman (b) experiments.

(b) *Pulses Raman experiments* (Fig. 1b). This technique was used to measure lifetimes of high-energy phonons ($\hbar\omega > 120\ cm^{-1}$) in a-Si [2,3]. We use the well-known fact that the anti-Stokes and Stokes Raman intensities directly relate to the average phonon occupation numbers in the film. A pump-probe configuration with two pulsed Nd : YAG lasers is used to study the temporal evolution of the phonon population in the film. Photoexcited carriers were created by the 10-ns pulses of a frequency doubled Nd : YAG laser (532 nm) with average intensity on the sample of 0.5 W/cm^2, and a repetition rate of 30 Hz. For the probe beam, a second (identical) Nd : YAG laser synchronized with the first one was used. Pulses of the second laser (probe) can be electronically delayed with respect to those of the first (pump). By measuring the anti-Stokes intensities as a function of the delay between pump and probe, Δt, the decay of nonequilibrium phonons, generated during the pump pulse, was examined in the range of 10 ns up to 15 ms. This technique enables to monitor the decay of phonons with energies $\hbar\omega$, corresponding to a Raman shift which lies in the range of 150–500 cm^{-1} for a-Si : H

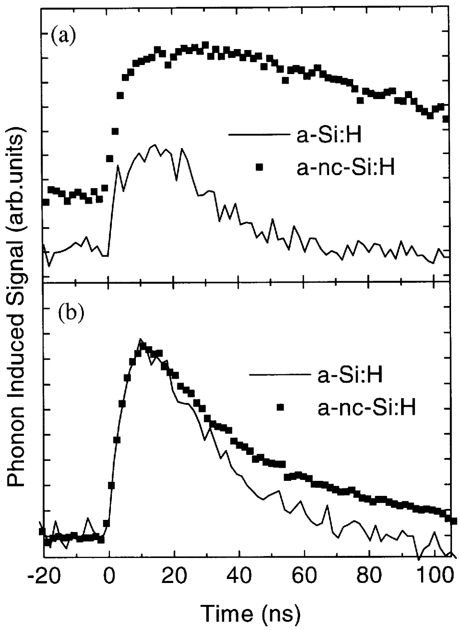

Fig. 2. Temporal evolution of the normalized detected signals in the ruby substrate induced by $29\ \mathrm{cm}^{-1}$ phonons which are generated in a-nc-Si : H or a-Si : H films: (a) configuration (1); (b) configuration (2). Different baselines in (a) are due to the incomplete recovery of the phonon signal in a-nc-Si : H at 4 MHz repetition rate.

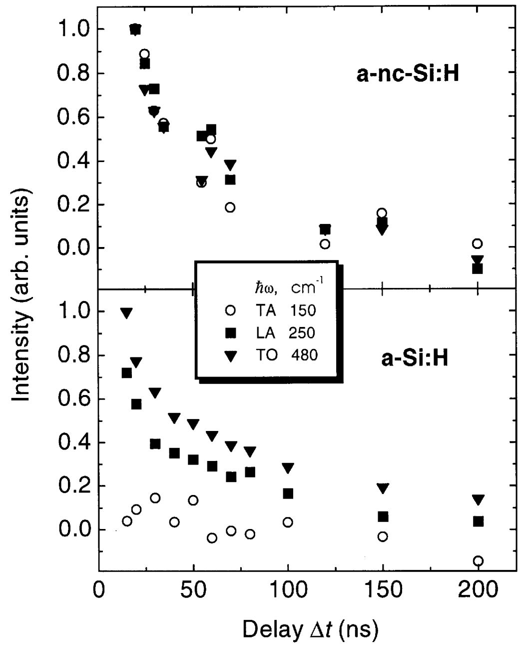

Fig. 3. Time-dependent anti-Stokes intensity measured in a-nc-Si : H and a-Si : H at three energies as a function of delay Δt. The background corresponding to the signals at $\Delta t = 15$ ms and a 30% background corresponding to electronic effects [11] are subtracted.

and 510–$530\ \mathrm{cm}^{-1}$ for the crystalline-like modes in nc-Si clusters.

Results of the ruby experiments are shown in Fig. 2. In Fig. 2a (corresponding to configuration (1)), the temporal evolution of the signal $I_{29}(t)$ is observed to be very different in a-nc-Si : H than for pure a-Si : H films. The trailing edge of $I_{29}(t)$ in the a-nc-Si : H film is much longer ($\geqslant 100$ ns) than the one of pure a-Si : H (≈ 40 ns). The duration of the leading edge of $I_{29}(t)$ has almost the same value (≈ 10 ns) as a-nc-Si : H and a-Si : H. In configuration (2) (Fig. 2b), the difference in the temporal shapes of $I_{29}(t)$ is not so large as in configuration (1). Both signals have sharp leading edges (≈ 10 ns) and relatively fast decay times (40–60 ns).

A difference in phonon dynamics is also clearly seen in Raman experiments where the temporal evolution of phonons with much higher $\hbar\omega$ is studied directly in the a-nc-Si : H and pure a-Si : H films. Fig. 3 shows the nonequilibrium phonon occupation numbers created by the pump as a function of pump-probe delay Δt for the phonon modes in a-Si : H. The decay time for $\hbar\omega = 250$–$480\ \mathrm{cm}^{-1}$ (LA and TO phonons in a-Si) has a value between $\tau_\omega \sim 50$ and 70 ns both in a-nc-Si : H and a-Si : H films.[1] However, the decay time for phonons around $150\ \mathrm{cm}^{-1}$ (TA phonons) is much shorter in pure a-Si : H ($\tau_\omega \leqslant 10$ ns) than in a-nc-Si : H film where the decay time has the same value as for TO phonons ($\tau_\omega \approx 50$ ns). The values of decay times in pure a-Si : H reproduce the earlier results [2,3].

We start the discussion with the analysis of the ruby experiments (setup in Fig. 1a, results in Fig. 2). The results of these experiments can be accounted

[1] The decay time of the signal at $\hbar\omega = 505$–$515\ \mathrm{cm}^{-1}$ in a-nc-Si : H which corresponds to vibrations in nc-Si clusters is shorter than in pure a-Si : H and decreases with the increase of $\hbar\omega$. For details see Ref. [10].

for when considering the feeding of 29 cm^{-1} phonons from decaying high-energy phonons characterized by $\hbar\omega'$. In both samples the diffusion coefficient, D_{29}, for $\hbar\omega = 29$ cm^{-1} is relatively high ($D_{29} \sim 1$ cm^2/s [8]) as judged from the sharp leading edges observed which are limited by the time resolution of our setup (10 ns). In order to explain the decay time of $I_{29}(t)$ in the a-Si : H film without nc-Si we need a long decay time $\tau_{\omega'} = 50$ ns for the high-energy phonons that down-convert to feed the 29 cm^{-1} modes [8]. Obviously, such a feeding source can be found because phonons in the range of $\hbar\omega' = 250$–480 cm^{-1} have anomalously long decay time ($\tau_\omega \approx 50$–70 ns, see Raman experiments of Fig. 3). In the case of a-nc-Si : H, however, we need in this approach to assume that the feeding from high-energy phonons ($\hbar\omega' \geqslant 60$ cm^{-1}) lasts for a very long time ($\tau_{\omega'} > 1$ μs), and that these phonons diffuse extremely slowly in the film ($D_{\omega'} \sim 10^{-2}$ cm^2/s). However, we do not observe such long decay times in Raman data for $\hbar\omega = 150$–480 cm^{-1} (see Fig. 3), signifying that the feeding of 29 cm^{-1} phonons must be produced by the down-conversion of phonons with $\hbar\omega' < 150$ cm^{-1}.

We associate the anomalously long decay times and the small diffusion coefficient of the high-energy phonons with local imprisonment in and hopping between loosely coupled regions on a nanometer scale formed by the nanocrystals itself and the surrounding amorphous tissue. We take for the typical nanoscopic scale the size d of the nanoparticles. The lowest phonon frequency supported in the nanoparticle can be estimated to be $\hbar\omega_0 \sim 2\hbar\pi v/d$, where v is the sound velocity. For $d = 5$ nm we obtain $\hbar\omega_0 = 35$–80 cm^{-1}, exactly in the region of phonon energies which can feed the 29 cm^{-1} modes by anharmonic break up. The typical hopping time (τ_h) between the nanometer scale regions can now be estimated from the measured diffusion coefficient $\tau_h \sim d^2/3D_\omega$, yielding $\tau_h \sim 10^{-11}$ s. Here we have identified the typical hopping distance with d. This hopping time implies that the phonons typically last for 20 oscillation periods in the nanometer scale regions, confirming that the coupling between the regions is indeed small. In that case we think that the anharmonic decay of the lowest frequency phonons is suppressed by roughly the same factor, simply because the strain exerted outside the nanometer scale region is reduced correspondingly. The anharmonic lifetime of 60 cm^{-1} phonons in crystalline Si is ~ 0.3 μs [12], yielding for our a-nc-Si sample, including a suppression of 20, a lifetime of 6 μs, long enough for the diffusion limited escape of the phonons from the film that we assumed earlier. The reason for the anomalously long TA decay time around 150 cm^{-1} observed in a-nc-Si (Fig. 3) is not totally clear. One can argue that in the decoupled nanometer size regions, anharmonic decay of these 150 cm^{-1} modes is suppressed because there are less-accepting modes available to decay than those that allow for energy conservation. This suppression must, however be quite large, say 10^3, in order to account for the observations. This value is possibly beyond the one that one expects to find in our sample. More likely is it, that the anharmonic decay time is shorter and that the TA phonon population is maintained by the slow decay in LA and TO modes (see upper panel Fig. 3). In any case the anharmonic lifetime of the TA modes in a-nc-Si must be significantly longer than that in pure a-Si : H to explain our Raman results.

Finally, we would like to point that the reason of the anomalously long decay times for the highest energy phonons ($\hbar\omega = 250$–480 cm^{-1}) in pure a-Si : H, which is not found in computer simulations [13], is not clear yet. May be it is reasonable to consider a-Si as a material consisting of loosely coupled regions with a typical scale $d \sim 1$ nm between the phonons hop.

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