

# Scattering of terahertz phonons in amorphous silicon and germanium

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Propagation of terahertz phonons in thin amorphous *a*-Si:H and *a*-Ge films on crystalline *c*-Si substrates was investigated at  $T = 1.7$  K by means of optical detection of nonequilibrium phonons, utilizing the influence of the phonons on the exciton luminescence of *c*-Si. Efficient conversion of hf to lf phonons, due to inelastic scattering of phonons characterized by a probability which increased with the hydrogen content, was observed in *a*-Si:H films. Strong phonon scattering was manifested also by a time delay of phonon pulses in *a*-Ge and *a*-Si:H films. The nature of both elastic and inelastic scattering of terahertz phonons in *a*-Si:H and *a*-Ge was analyzed, and the possible role of two-level systems and soft potentials associated with the presence of impurity atoms (H in *a*-Si:H) was considered.

## 1. INTRODUCTION

Properties of vibrational excitations in disordered solids, such as amorphous materials and glasses, are currently attracting much attention. It is now clear that these properties differ considerably from those of vibrational excitations (phonons) in regular crystals characterized by translational symmetry. This difference applies to all the characteristics of vibrational excitations such as the spectral density of states, the fundamental nature of the vibrations associated with the spatial localization (or delocalization) of excitations, and dynamic properties (scattering) of phonons. The scattering and transport of phonons in amorphous materials and glasses have been investigated mainly under "equilibrium" conditions by determination of the thermal conductivity. The experimentally observed universal temperature dependence of the thermal conductivity  $\kappa(T)$  is complicated and is evidence of the great variety of mechanisms and of the complicated frequency dependence of the scattering of phonons in disordered media.

The properties of phonons with frequencies in the terahertz range ( $10^{11}$ – $10^{12}$  Hz) are of special interest. These phonons dominate the equilibrium distribution at temperatures on the order of a few kelvin where a plateau is observed in the dependence  $\kappa(T)$  exhibited by glasses and amorphous materials; the phonon wavelengths corresponding to these frequencies in crystals are on the order of several tens of angstroms and represent an important spatial scale of the disordered structure.

Several papers have appeared recently<sup>1-4</sup> reporting the first application of the method of nonequilibrium phonons, developed earlier in a study of the phonon dynamics in crystals, to the scattering of terahertz vibrational excitations in amorphous materials. The experiments reported in Refs. 1–4 were carried out at liquid helium temperatures in very thin (from 0.01 to 10  $\mu\text{m}$ ) amorphous films of Si, Ge, SiO<sub>2</sub>, etc. deposited on crystalline substrates. Nonequilibrium phonons were injected into a film and reached the substrate across the film where they were detected by superconducting tunnel-junction devices or by bolometers.

We investigated the passage of terahertz phonons through amorphous films by applying for the first time the method of optical detection of phonons. Such detection was possible because of the strong influence of phonons on the

exciton luminescence of crystalline silicon (*c*-Si),<sup>5-7</sup> used as the substrate of amorphous semiconductor films *a*-Si:H and *a*-Ge.

## 2. EXPERIMENTAL METHOD

We used an experimental setup shown in Fig. 1. Our sample was a rectangular crystalline silicon substrate of  $10 \times 5 \times 2$  mm<sup>3</sup> dimensions cut along the (111) plane and carrying a deposited amorphous semiconductor film. The substrate was made of dislocation-free ultrapure silicon (impurity concentration  $\sim 10^{12}$  cm<sup>-3</sup>) with an electrical resistivity of  $\sim 10^4$   $\Omega \cdot \text{cm}$ . The substrate surface was subjected to chemical etching after preliminary polishing with a diamond paste.

The bulk of our results was obtained for samples with an amorphous film of hydrogenated silicon *a*-Si:H. These films were formed by decomposition of silane, SiH<sub>4</sub>, in an rf glow discharge (pressure 20 Pa, rate of flow of pure SiH<sub>4</sub> 10 cm<sup>3</sup>/min). The films of *a*-Si:H were deposited on *c*-Si substrates kept at three different temperatures (150 °C, 250 °C, and 350 °C) and the corresponding nitrogen concentrations ( $N_H$ ) in the amorphous films were 16%, 10%, and 6%, respectively. Some of the experiments were carried out in amorphous germanium (*a*-Ge) films deposited on *c*-Si by thermal evaporation in vacuum.

A sample was placed in a cryostat and immersed directly in pumped liquid helium ( $T = 1.7$  K). Nonequilibrium phonons were injected into the amorphous film in the form

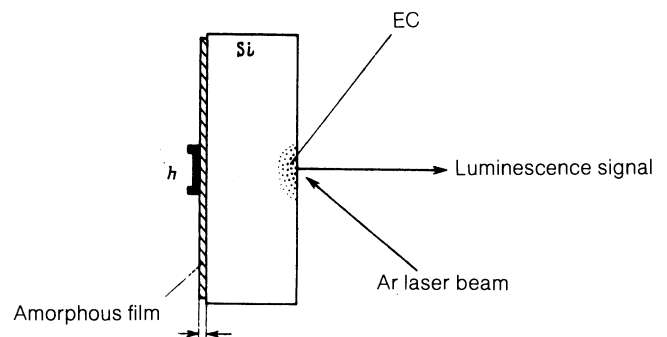


FIG. 1. Experimental setup.

of heat pulses of  $2 \times 10^{-7}$  s duration generated by electric-heating of a thin (100 Å) constantan film  $h$  of  $1 \times 1$  mm<sup>2</sup> area evaporated on the amorphous film. Heating of  $h$  injected phonons with a continuous spectrum. These phonons passed through the amorphous film (usually undergoing some scattering) and reached the  $c$ -Si substrate. In ultrapure  $c$ -Si these terahertz phonons propagated ballistically over distances of the order of several millimeters.<sup>5,8</sup> Therefore, the phonons entering the substrate from the amorphous film reached the opposite face of the substrate, where they were detected with a time resolution of 50 ns; this was accompanied by a rough analysis of the phonon frequency spectrum.

We used the phonon detection method based on the strong influence of terahertz phonons on the exciton photoluminescence of  $c$ -Si reported in Refs. 5–7. This exciton photoluminescence appeared when the surface of the sample opposite to that carrying the amorphous film (Fig. 1) was illuminated at an angle with a cw Ar laser beam ( $\lambda = 5145$  Å,  $P < 100$  mW, focused beam diameter 0.5–1 mm). This resulted in generation of free electrons (FE) in a surface layer of  $c$ -Si  $\sim 1$  μm thick; these excitons diffused into the substrate and created an exciton cloud near the surface. For  $T = 1.7$  K the spectrum of the steady-state luminescence emitted by this cloud included lines at 1.097 eV, 1.099 eV, and 1.144 eV, which were due to radiative annihilation of FE and creation of TO, LO, and TA phonons, as well as lines in the region of 1.093 eV due to annihilation (assisted by optical phonons) of excitons bound to impurities (BE). We observed the phonon-induced changes in the intensities of the FE and BE luminescence lines: we measured as a function of time the differential signal  $\Delta I(t) = I(t) - I_0$ , where  $I(t)$  is the luminescence intensity in the presence of a phonon pulse and  $I_0$  is the intensity of the steady-state luminescence at  $T = 1.7$  K in the absence of heat pulses.

According to Refs. 5–7 the influence of nonequilibrium acoustic phonons on the FE and BE luminescence in a surface exciton cloud is due to two main processes.

The first of these processes is the dissociation of bound excitons BE → FE under the influence of “hf” phonons of frequencies  $\Omega \geq 0.9$  THz (with the threshold corresponding to the binding energy of BE). The BE → FE dissociation process in the cloud depended on the occupation numbers  $\bar{n}_\Omega$  of phonons with frequencies  $\Omega \geq 0.9$  THz and resulted in a redistribution of the FE and BE concentrations in favor of FE and, consequently, enhanced the FE luminescence lines ( $\Delta I^F > 0$ ) and weakened the BE lines ( $\Delta I^B < 0$ ). The BE → FE processes increased<sup>5,7</sup> the real FE lifetime  $\tau$  which in the absence of phonons ( $\bar{n}_\Omega = 0$ ) was governed by trapping impurities, resulting in the formation of BE and was  $\tau_0 = 1.1$  μs (Ref. 9):

$$\tau = \tau_0(1 + w_{BF}/w_0), \quad (1)$$

where  $w_{BF} \propto \bar{n}_\Omega$  is the probability of the BE → FE dissociation and  $w_0$  is the probability of BE annihilation ( $w_0^{-1} = 0.6$ – $1.0$  μs is reported in Ref. 9).

The second process is entrainment of FE under the influence of a flux of “lf” acoustic phonons of frequency  $\omega < 0.4$  THz toward the surface of the sample, where FE are annihilated by fast surface recombination. This process reduces the FE concentration and, consequently, results in the quenching of the FE ( $\Delta I^F < 0$ ) and BE ( $\Delta I^B < 0$ ) lumines-

cence, because BE are formed from FE by the capture of the latter at impurities. The luminescence quenching efficiency depends on the drift velocity under the influence of the phonons<sup>10</sup>

$$v = s \Delta \bar{n}_\omega / \bar{n}_\omega, \quad (2)$$

where  $s$  is the velocity of sound and  $\bar{n}_\omega$  are the total occupancy numbers of “lf” phonons (including thermal phonons at  $T = 1.7$  K) and  $\Delta \bar{n}_\omega = \bar{n}_\omega^+ - \bar{n}_\omega^-$  is the anisotropy—characteristic of the phonon flux—of the occupation numbers of phonons with wave-vector projections directed toward the surface ( $\bar{n}_\omega^+$ ) and away from the surface ( $\bar{n}_\omega^-$ ).

The experimentally observed changes in the FE and BE luminescence intensities are determined by the combined influence of these two processes. Under the influence of both processes the BE luminescence always decreases ( $\Delta I^B < 0$ ). On the other hand, the phonon-induced change in the FE luminescence is governed by the relationship between the frequency-dependent contributions with opposite signs:  $\Delta I^F > 0$  (BE → FE dissociation under the influence of phonons of frequencies  $\Omega > 0.9$  THz) and  $\Delta I^F < 0$  (drag by FE phonons with frequencies  $\omega < 0.4$  THz). Therefore, in principle, the sign and magnitude of the FE luminescence signal represent the spectral composition of the phonon flux, namely the contributions of the hf ( $\Omega > 0.9$  THz) and lf ( $\omega < 0.4$  THz) phonons in a phonon pulse. This property of a luminescence-type phonon detector is important in studies of the transformation of the phonon spectrum due to the propagation of phonons across an amorphous film.

### 3. EXPERIMENTAL RESULTS

In our experimental setup (Fig. 1) the surface of  $c$ -Si, near which the exciton cloud was formed, carried an ultrathin layer of the oxide SiO<sub>2</sub> which grew as a result of exposure to air; this surface was immersed in superfluid liquid helium. Preliminary experiments established, in agreement with Refs. 5–7, that injection of heat pulses directly into  $c$ -Si (in the absence of an amorphous film) excited negative BE and FE luminescence pulses (i.e., reduced the luminescence intensity). The negative sign of the signal  $\Delta I^F$  was due to the dominant effect of the drag of FE by the flux of lf phonons  $\Delta \bar{n}_\omega$ , which appeared because of the ready escape of lf phonons across the oxide film into liquid helium (anomalous Kapitza transmission).

Investigation (Fig. 1) of  $c$ -Si samples carrying  $a$ -Si:H and  $a$ -Ge films deposited on the (111) face showed that the phonon-induced negative exciton luminescence pulses emitted by  $c$ -Si were quite different from the pulses observed when phonons were injected from the heater  $h$  directly into  $c$ -Si. The luminescence signals were very sensitive to the parameters of the amorphous film crossed by phonons on its way from the heater to the  $c$ -Si substrate.

#### a) Films of $a$ -Si:H

In the very first experiments we investigated the process of propagation of phonons across an amorphous film as a function of the film thickness (Fig. 2). We compared the relative intensities of the FE luminescence  $\Delta I^F(t)/I_0^F$  (Fig. 2a) and the BE luminescence  $\Delta I^B(t)/I_0^B$  (Fig. 2b) signals for two films with the same ( $a$ -Si:16% H) oxygen concentration, but with thicknesses differing by a factor of five

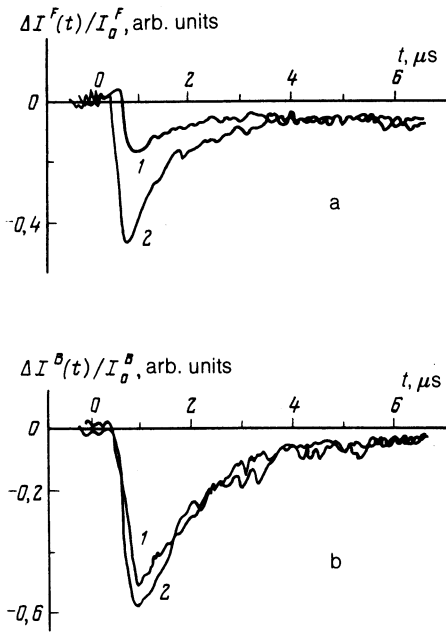


FIG. 2. Pulses of the FE (a) and BE (b) luminescence obtained from amorphous *a*-Si:16%*H* films of different thicknesses  $d$  ( $\mu\text{m}$ ): 1) 0.2; 2) 1.0.  $W = 1.1 \mu\text{J}/\text{mm}^2$ .

( $d_1 = 0.2 \mu\text{m}$ ,  $d_2 = 1 \mu\text{m}$ ). Special measures were taken to ensure that the film heaters deposited on the two films were identical, so that in the case of amorphous films of the same thickness they injected the same (moderate) energy of density  $W = 1 \mu\text{J}/\text{mm}^2$  per pulse. A comparison of the  $\Delta I^F(t)/I_0^F$  and  $\Delta I^B(t)/I_0^B$  pulses obtained for films of different thickness made it possible to reveal, in principle, the role of the phonon scattering processes in the bulk *a*-Si:H films and exclude the effects of the scattering at the *c*-Si/*a*-Si interface.

It is clear from Fig. 2 that the luminescence signal  $\Delta I^F(t)/I_0^F$  induced by the phonons transmitted by the amorphous film had a negative sign, which was also observed for the injection of phonons into *c*-Si directly from the heater  $h$  in the absence of the amorphous film, and when an exciton cloud was created on the opposite "ordinary" surface of *c*-Si which experienced natural oxidation.<sup>5,7</sup> It is clear from Fig. 2a that the amplitude of the negative signal  $\Delta I^F(t)/I_0^F$  increased considerably on increase in the amorphous film thickness from 0.2 to 1  $\mu\text{m}$ . On the other hand, the amplitude of the negative signal  $\Delta I^B(t)/I_0^B$  of the BE

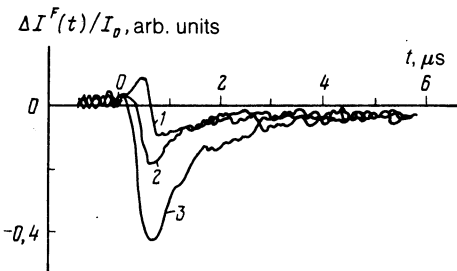


FIG. 3. Pulses of the FE luminescence emitted from *a*-Si:H films of  $d = 1 \mu\text{m}$  thickness with different hydrogen concentrations  $N_H$  (%): 1) 6; 2) 10; 3) 16.  $W = 1.1 \mu\text{J}/\text{mm}^2$ .

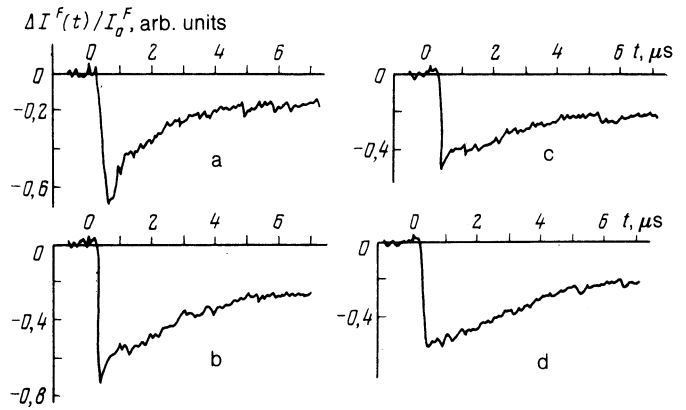


FIG. 4. Pulses of the FE luminescence obtained for heat pulses with high energy densities ( $W = 7 \mu\text{J}/\text{mm}^2$ ) in *a*-Si:H films,  $d = 0.2 \mu\text{m}$  thick, with different hydrogen concentrations  $N_H$  (%): a) 16; b) 10; c) 6, and in the absence of an amorphous film (d).

luminescence (Fig. 2b) changed only slightly as the film thickness increased.

It seemed important to investigate the dependence of the propagation of phonons across an amorphous film on the concentration  $N_H$  of hydrogen in a film of *a*-Si:H. Figure 3 shows the luminescence pulses  $\Delta I^F(t)/I_0^F$  determined for films of the same thickness  $d = 1 \mu\text{m}$ , but with different hydrogen concentrations  $N_H$  (6%, 10%, 16%) when the energy was injected from  $h$  at a constant intensity ( $W = 1.1 \mu\text{J}/\text{mm}^2$ ). Clearly, the amplitude of the pulses rose with  $N_H$ : when  $N_H$  was increased from 6% to 16%, the amplitude  $\Delta I^F(t)/I_0^F$  rose by a factor of four. In the case of some of the experiments on *a*-Si:H films of thickness 1  $\mu\text{m}$  and with  $N_H = 16\%$  the phonons injected into *c*-Si across the amorphous film reduced the FE luminescence more than twofold. Such strong quenching of the FE luminescence by heat pulses had not been observed in the absence of an amorphous film.<sup>5</sup>

Next we investigated the luminescence pulses when energy was injected from the heater at sufficiently high density to generate, in the *c*-Si substrate at the contact with  $h$ , a "phonon hot spot" representing a spatially small overheated region of the crystal from which phonons escape after a delay because of the phonon-phonon scattering.<sup>11,12</sup> Figure 4 shows the  $\Delta I^F(t)/I_0^F$  pulses for an amorphous film with the same thickness  $d = 0.2 \mu\text{m}$ , but with a different concentration  $N_H$  when the energy density was  $W = 7 \mu\text{J}/\text{mm}^2$ . This figure includes also a pulse  $\Delta I^F(t)/I_0^F$  obtained in the absence of an amorphous film (Fig. 4d), which is clearly much extended on the time scale, as expected in the presence of a phonon hot spot. In the case of films with a sufficiently high hydrogen concentration  $N_H > 10\%$  (Figs. 4a and 4b) it was found that during the initial stage of such an extended pulse  $\Delta I^F(t)$  there was a relatively short negative peak which was not observed in the case of amorphous films with  $N_H = 6\%$  (Fig. 4c) or in the absence of such films when phonons were injected directly from  $h$  into *c*-Si (Fig. 4d).

#### b) Films of *a*-Ge

We deposited *a*-Ge films on a part of the surface of a *c*-Si substrate by the method of thermal evaporation in Ge vacu-

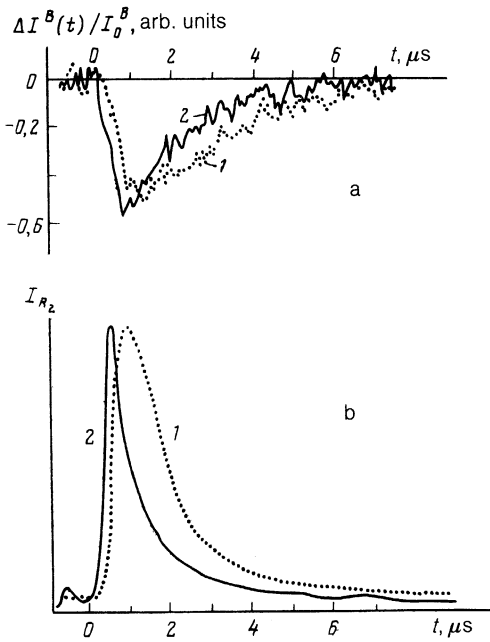


FIG. 5. Pulses of the BE (a) and  $R_2$  (b) luminescence induced by phonons which crossed an amorphous film of  $a$ -Ge of thickness  $d = 0.54 \mu\text{m}$  (1) or were injected into the substrate directly (in the absence of an amorphous film) from a heater (2). Here  $W = 4 \mu\text{J}/\text{mm}^2$ .

um at a pressure of  $10^{-3}$  Pa when the substrate temperature was  $T = 300$  K. Then two identical metal heater films were deposited on the amorphous  $a$ -Ge film and on the bare surface of the  $a$ -Si substrate.

Figure 5 shows the BE luminescence pulses  $\Delta I^B(t)/I_0^B$  recorded using the setup in Fig. 1 when phonons were injected into  $c$ -Si across an  $a$ -Ge film of thickness  $0.5 \mu\text{m}$  or when phonons were injected directly (in the absence of an amorphous film) into  $c$ -Si (the injected energy density was the same in both cases,  $W = 4 \mu\text{J}/\text{mm}^2$ ). In both cases we observed a negative peak characteristic of the BE luminescence. We also found a clearly manifested spreading of the leading edge of the  $\Delta I^B(t)$  pulse by an amount  $\Delta t = 300 \pm 100$  ns when the injected phonons also crossed the  $a$ -Ge film.

We also determined the delay of the phonon pulses in samples for a film of  $a$ -Ge with  $d = 0.5 \mu\text{m}$  deposited on a crystalline substrate made of ruby ( $\text{Al}_2\text{O}_3:0.05\% \text{Cr}^{3+}$ ). The  $R_2$  luminescence line (due to the  $2\bar{A}-4A_2$  transition in this crystal) made it possible to detect nonequilibrium "monochromatic" phonons of  $0.87$  THz ( $29 \text{ cm}^{-1}$ ) frequency, which induced  $\bar{E}-2\bar{A}$  resonant transitions between the sublevels of the metastable excited state of the  $\text{Cr}^{3+}$  ions in optically excited ruby.<sup>13</sup> Figure 5b shows positive  $R_2$  luminescence pulses induced either by phonons injected directly into the crystal or those that have crossed first the  $a$ -Ge film. Clearly, in the latter case there was a considerable delay of the leading edge of the pulse, similar to that observed in experiments on  $a$ -Ge films on  $c$ -Si (Fig. 5a).

#### 4. DISCUSSION OF RESULTS

##### a) Frequency conversion in the spectrum of nonequilibrium phonons in $a$ -Si:H films

An analysis of our results shows that the passage of nonequilibrium phonons across a film of  $a$ -Si:H is accompa-

nied by effective conversion of the hf part of the continuous phonon spectrum to lower frequencies. This conclusion follows unambiguously from the results of a qualitative investigation of the  $\Delta I^F(t)/I_0^F$  signals representing the FE luminescence emitted by samples carrying amorphous films of different thickness.

It is clear from the results reported in Sec. 3a (Fig. 2) that an increase in the amorphous film thickness from  $0.2$  to  $1 \mu\text{m}$  increases strongly the amplitude of the negative FE luminescence pulse  $\Delta I^F(t)$ . As pointed out in Sec. 2, the phonon-induced changes  $\Delta I^F(t)$  are governed by the sum of contributions with opposite signs: a negative one induced by phonons of frequency  $\omega < 0.4$  THz and a positive one induced by phonons of frequencies  $\Omega > 0.9$  THz. An increase in the flux  $\Delta \bar{n}_\omega$  of lf phonons ( $\omega < 0.4$  THz) due to conversion of hf to lf phonons increases the negative contribution, whereas a corresponding reduction in the concentration  $\bar{n}_\Omega$  of hf phonons ( $\Omega > 0.9$  THz) reduces the positive contribution. It therefore follows that the changes in the two contributions of each separately as a result of the conversion increases the amplitude of the net negative signal  $\Delta I^F(t)$ . Since such frequency conversion is due to inelastic phonon scattering in an amorphous film, the conversion efficiency rises with the number of scattering events experienced by phonons as they cross the amorphous film. This accounts qualitatively for the observed rise of the negative FE luminescence signal as in the amorphous film thickness increases.

In a quantitative analysis of the efficiency of the frequency conversion of phonons during their passage across a film of  $a$ -Si:H we shall use the expressions obtained in Ref. 5 for changes in the FE ( $I^F$ ) and BE ( $I^B$ ) luminescence intensities under the influence of phonons. The steady-state solution of the equations describing the drag of FE by lf ( $\omega < 0.4$  THz) phonons and the BE  $\rightarrow$  FE dissociation by hf ( $\Omega > 0.9$  THz) phonons under conditions of strong surface FE recombination gives

$$\frac{I^F}{I_0^F} = \frac{1}{\gamma + [\gamma^2 + (\sigma + 1)^{-1}]^{1/2}}, \quad (3)$$

$$\frac{I^B}{I_0^B} = \frac{1}{\sigma + 1} \frac{I^F}{I_0^F}, \quad (4)$$

where  $I_0^F$  and  $I_0^B$  are the initial steady-state intensities of the FE and BE luminescence ( $T = 1.7$  K), whereas  $I^F$  and  $I^B$  are the FE and BE luminescence intensities in the presence of terahertz phonons. The following parameters are used in Eqs. (3) and (4):

$$\gamma = \frac{1}{2} v \left( \frac{\tau_0}{D} \right)^{1/2}, \quad (5)$$

$$\sigma = \frac{\tau}{\tau_0} - 1, \quad (6)$$

which represent respectively the process of drag of FE by lf phonons [which affects the FE drift velocity  $v$  of Eq. (2)] and the process of the BE  $\rightarrow$  FE dissociation under the action of hf phonons [because of the relative change in the FE lifetime  $\tau$  in the exciton cloud given by Eq. (1)];  $D = 100 \text{ cm}^2/\text{s}$  is the FE diffusion coefficient in exciton cloud (Ref. 14).

The experimentally observed FE and BE luminescence pulses  $I^F(t)$  and  $I^B(t)$  (Fig. 2) were used to determine  $I^F/I_0^F$  and  $I^B/I_0^B$  (the values of  $I^F$  and  $I^B$  were taken at the maximum of the amplitude of a negative pulse). Combining

these data ( $I^F/I_0^F = 0.85$  and  $I^B/I_0^B = 0.50$  for a sample with  $d_1 = 0.2 \mu\text{m}$  and  $I^F/I_0^F = 0.55$  and  $I^B/I_0^B = 0.44$  for  $d_2 = 1 \mu\text{m}$ ) enabled us to find the values of the parameters  $\gamma$  and  $\sigma$  from Eqs. (3) and (4). Their values were as follows: for a film with  $d_1 = 0.2 \mu\text{m}$ , we obtained  $\gamma = 0.34$  and  $\sigma = 0.70$ , whereas for a film with  $d_2 = 1 \mu\text{m}$  we obtained  $\gamma = 0.70$  and  $\sigma = 0.25$ . According to Sec. 2 and Eqs. (5) and (6), the parameters  $\gamma$  and  $\sigma$  should be proportional to the occupation numbers  $\bar{n}_\omega$  and  $\bar{n}_\Omega$  of lf ( $\omega < 0.4 \text{ THz}$ ) and hf ( $\Omega > 0.9 \text{ THz}$ ) phonons, respectively. Hence, an increase in the thickness of the *a*-Si:H film by a factor of 5 doubled the lf phonon flux emerging from the film and reduced the hf phonon density more than twofold.

Our conclusion about the efficiency of frequency conversion of nonequilibrium terahertz phonons in *a*-Si:H was in agreement with the results of investigations of the propagation of phonons across amorphous SiO<sub>2</sub> (Refs. 1 and 4), Si (Refs. 2–4), and Ge (Ref. 4) films obtained by electrical phonon-detection methods, which revealed strong inelastic phonon scattering in amorphous films. Our experiments indicated a reduction in the concentration of hf phonons in the course of conversion of the phonon spectrum in *a*-Si:H as well as a considerable increase in the lf phonon flux in the distribution of the phonons emerging from the film.

Information on the nature of the inelastic scattering processes in *a*-Si:H, resulting in lowering of the scattered-phonon frequency, was obtained from the results of our investigation of the transmission of phonons across *a*-Si:H films with different hydrogen concentrations  $N_H$ . It is clear from Fig. 3 that an increase in  $N_H$  from 6% to 16% considerably increased the amplitude of the negative luminescence signal, indicating substantial enhancement in the process of frequency conversion in an amorphous film with increasing  $N_H$ . A quantitative analysis of the  $\Delta I^F(t)$  and  $\Delta I^B(t)$  curves in Fig. 3 in accordance with Eqs. (3) and (4) yielded the following phonon spectrum parameters: for a film with  $N_H = 6\%$ , we obtained  $\gamma = 0.35$  and  $\sigma = 1.1$ , whereas for a film with  $N_H = 16\%$ , we found  $\gamma = 0.7$  and  $\sigma = 0.25$ . According to Eqs. (1)–(4) this means that an increase in  $N_H$  in an amorphous film from 6% to 16% doubled the lf phonon flux  $\Delta \bar{n}_\omega$  in the spectrum of the phonons emerging from an amorphous film, while the concentration of hf phonons  $\bar{n}_\Omega$  was reduced by a factor of 4.

An increase in the probability of inelastic phonon scattering with increasing  $N_H$  was manifested not only by an increase in the amplitude of a negative pulse  $\Delta I^F(t)$  in going from  $N_H = 6\%$  to  $N_H = 16\%$ , but also by a change in the profile of the  $\Delta I^F(t)$  pulse. In fact, at a low concentration  $N_H = 6\%$  we found that the leading edge of a  $\Delta I^F(t)$  pulse had a short positive peak (Fig. 3, trace 1). According to Ref. 5, this peak was due to BE → FE dissociation under the influence of hf phonons in combination with the inertia of the drag of excitons by lf phonons, and it could be observed in the case of sufficiently low lf phonon fluxes (when the drag parameter  $\gamma$  was small). An increase in  $N_H$  to 16% suppressed the positive peak at the leading edge of  $\Delta I^F(t)$  (Fig. 3, trace 3). In this case the enhanced conversion made the lf phonon flux in the amorphous film sufficiently high for the drag of FE to the surface in the short time  $t < 1 \mu\text{s}$  and for compensation of the positive peak of  $\Delta I^F(t)$ , which was due to the BE → FE dissociation process.

The experimental results thus demonstrated a close relationship between the strength of the inelastic scattering of terahertz phonons in *a*-Si:H films and the hydrogen concentration in these films. It was natural to assume that, therefore, the scattering centers included H atoms known to compensate dangling Si bonds in *a*-Si:H. According to Ref. 15, the concentration  $N_H = 10\%$  is sufficient for complete saturation by hydrogen of single dangling bonds (when the concentration of the Si–H bonds was  $0.77 \times 10^{22} \text{ cm}^{-3}$ ), whereas the concentration of double compensated Si–H<sub>2</sub> bonds in a sample with  $N_H = 10\%$  was  $0.055 \times 10^{22} \text{ cm}^{-3}$  and it was found that the Si–H<sub>2</sub> bond concentration rose steeply when  $N_H$  increased above 10%. The fact that in our experiments the efficiency of phonon conversion rose and also when  $N_H$  rose above 10% (at least up to  $N_H = 16\%$ ) could indicate that the inelastic scattering centers were associated with the Si–H<sub>2</sub> bonds, although final conclusions could not be made without an analysis of the concentrations of the Si–H and Si–H<sub>2</sub> bonds in our films. It should be noted that the relationship between the strength of the inelastic scattering of phonons in *a*-Si:H films and the hydrogen concentration was pointed out already earlier.<sup>4</sup>

#### b) Time delay of phonon pulses in *a*-Ge and *a*-Si:H films

The time delay of phonons crossing an amorphous film was manifested clearly in *a*-Ge by a shift of the leading edge of a luminescence pulse induced in the crystalline substrate by phonons (Fig. 5). The delay of phonons with frequency  $\sim 1 \text{ THz}$  in *a*-Ge films  $0.5 \mu\text{m}$  thick amounted to  $\Delta t \approx 0.3 \mu\text{s}$  and was well reproduced by phonon detection in different substrates: *c*-Si (by measurement of the BE luminescence) and ruby (by measurement of the Cr ion luminescence).

In the case of *a*-Si:H films, where the influence of the film on the phonon-induced luminescence pulses generated in *c*-Si was strong and gave rise to the various major effects described above (Secs. 3a and 4a), the shift of the leading edges of the pulses  $\Delta I^F(t)$  and  $\Delta I^B(t)$  was not detected directly in our experiments. In view of the time resolution of our apparatus, we concluded that the shift of the leading edge of the  $\Delta I^F(t)$  and  $\Delta I^B(t)$  pulses in *a*-Si:H was less than 50 ns. An indirect confirmation of the delay of the terahertz phonons during their passage across *a*-Si:H films was provided by some features of the  $\Delta I^F(t)$  pulses observed on injection of a sufficiently high energy density from the heater. Under these conditions we found that the high concentration of hf phonons created a long-lived phonon hot spot in the *c*-Si substrate. It was manifested by a characteristic strong delay of the  $\Delta I^F(t)$  pulse which was observed for *a*-Si:H films of thickness  $d = 0.2 \mu\text{m}$  with different hydrogen concentrations ( $N_H = 6\%$ ,  $10\%$ , and  $16\%$ ), as demonstrated in Fig. 4. One of the properties of such a hot spot was strong scattering of lf phonons.<sup>16</sup>

In the case of *a*-Si:H films with a high hydrogen concentration  $N_H > 10\%$  there was an additional narrow negative peak at the leading edge of  $\Delta I^F(t)$  (Fig. 4). According to our hypothesis, this peak was due to a time delay of hf terahertz phonons in an *a*-Si:H film, which delayed the formation of a hot spot in the *c*-Si substrate. However, the lf phonons emitted by the heater during a current pulse crossed the amorphous film subject to a delay because of the strong fre-

quency dependence of the scattering in amorphous materials.<sup>1,4</sup> These phonons were injected into the substrate before the hot spot formed in *c*-Si; they were not scattered by hf phonons in the hot spot and they did not participate in the entrainment of FE, which was the reason for the short negative peak at the leading edge of the  $\Delta I^F(t)$  pulse (Fig. 4).

The delay of phonons in the amorphous film could clearly be due to any scattering processes, both elastic and inelastic. The time delay appeared in *a*-Si:H on increase in the  $N_H$  concentration which, as shown in Sec. 4a (and also in Ref. 4), increased the strength of the inelastic scattering process. It was natural to assume that the inelastic scattering centers associated with the presence of H (possibly Si-H<sub>2</sub> bonds) could act also as the inelastic phonon scattering centers. The ratio of the elastic and inelastic scattering cross sections determined how the observed shift of the phonon spectrum to the lf range took place (it could be due to multiple scattering of phonons accompanied by the excitation of small quanta or due to rare collisions resulting in the excitation of large quanta).

There were grounds for assuming that the time delay of phonons in *a*-Ge films was also due to the presence of foreign atoms in the amorphous material, namely the atoms of oxygen captured by an *a*-Ge film growing in fairly poor vacuum. In a recent paper<sup>4</sup> the inelastic scattering of phonons in *a*-Ge films was also attributed to the presence of oxygen. If we consider in a simplified manner the propagation of phonons in an *a*-Ge film as diffusion of nonequilibrium phonons, we can use the observed pulse delay  $\Delta t = 0.3 \mu\text{s}$  to estimate the effective mean free path  $\bar{l}$  of the detected phonons with frequency  $\sim 1$  THz. Substituting the thickness of the amorphous film  $d = 0.5 \mu\text{m}$  and the velocity of sound  $s = 4 \times 10^5$  cm/s into the appropriate expression, we obtain  $\bar{l} \sim 10^{-7}$  cm. This value is much less than the free path of  $\sim 1$  THz phonons in *a*-Ge, which is  $\bar{l} = 10^{-6}$  cm deduced from the temperature dependence of the thermal conductivity of *a*-Ge films<sup>17</sup> also using expressions describing the diffusion kinetics. The discrepancy may be due to the difference between the structure and the conditions during the growth of *a*-Ge films used in the present study and those employed in the investigation described in Ref. 17, because the latter films could possibly contain less oxygen.

The observed large (amounting to one order of magnitude) difference between the delay of the phonon pulses that crossed *a*-Ge and *a*-Si:H films was due to the difference between the dynamic properties of the original crystalline materials. It follows from general considerations based on the role of the density of the vibrational states that the phonon scattering cross section  $\sigma_{\text{ph}}$  depends very strongly on the spectral density of the vibrational states and, consequently, on the Debye frequency of a material. For example, the known expressions for the elastic Rayleigh scattering by static inhomogeneities of different origin give  $\tau_{\text{ph}} \propto (\omega/\omega_D)^4$ , whereas in the case of resonant elastic scattering by local two-level states we have  $\sigma_{\text{ph}} \propto \omega/\omega_D^3$  (Ref. 18). The Debye frequency (temperature) for *c*-Ge, amounting to  $\omega_D^{\text{Ge}} = 33$  meV, is 1.7 times less than for *c*-Si ( $\omega_D^{\text{Si}} = 56$  meV), which in principle may account for the large difference between the efficiencies of the scattering and the difference between the delay times of phonons traveling in *a*-Si:H and *a*-Ge.

## 5. CONCLUDING COMMENTS

We investigated the propagation of terahertz nonequilibrium phonons in amorphous *a*-Si:H and *a*-Ge films using for the first time a novel method for optical detection of phonons<sup>5-7</sup> based on the influence of phonons on the exciton luminescence of *c*-Si used as the substrate of the investigated amorphous films. The "spectroscopic" capabilities of the method established that the continuous phonon spectrum redistributed itself considerably in favor of lf phonons (frequency conversion), because of the strong inelastic scattering of phonons in *a*-Si:H. The pulsed nature of phonon injection in amorphous films (heat pulses) was of methodological importance, because it enabled us to investigate phonon dynamics and to detect directly the delay of terahertz phonons in an *a*-Ge film due to their multiple scattering in this film.

Our experiments established a direct relationship between the scattering of terahertz phonons in *a*-Si:H and the hydrogen concentration  $N_H$ : an increase in  $N_H$  increased the efficiency of frequency conversion (see Secs. 3 and 4 and also Ref. 4) and also increased the time delay of phonons during their passage through *a*-Si:H, which was manifested very clearly in experiments on high-power heat pulses (Sec. 3, Fig. 4). Judging by the experiments on electrical detection of phonons crossing amorphous films, which were reported in Ref. 4, we may conclude that the processes of inelastic scattering of terahertz phonons in *a*-Ge films are also associated with the presence of an impurity in the form of oxygen (O) atoms.

According to the current ideas, the stronger scattering of terahertz phonons in glasses and amorphous materials is responsible for the specific plateau in the temperature dependence of the thermal conductivity  $\kappa(T)$  in the range 3–10 K. Therefore, the very weak plateau in the dependence  $\kappa(T)$  exhibited by *a*-Ge films not deliberately doped with O, mentioned in Ref. 4, also confirms<sup>17</sup> the relationship between the strength of the scattering of terahertz phonons in *a*-Ge and the presence of oxygen. It is interesting to note (see Ref. 18 and the literature cited there) that the presence of O in *a*-Ge and of H in *a*-Si:H is regarded as the origin of the low-temperature (observed at  $T < 1$  K) "glass" anomalies associated with the scattering of lf (subterahertz) phonons on what are known as two-level systems in amorphous materials.

It therefore follows that the scattering of phonons in a wide range of frequencies in atomic amorphous materials *a*-Si:H and *a*-Ge depends strongly on the presence of foreign H or O atoms, which compensate the dangling bonds or form new bonds in the material. The presence of H (or O) is related both to the appearance of local scatterers responsible for the strong inelastic (and elastic) scattering of terahertz phonons, resulting in efficient frequency conversion of nonequilibrium phonons and the appearance of a plateau in the temperature dependence of the "equilibrium" thermal conductivity  $\kappa(T)$ ; the impurity is also responsible for the appearance of local low-energy two-level systems responsible for the scattering of subterahertz ( $\sim 1$  K) phonons as well as for different low-temperature anomalies of glasses.

It is of considerable interest to consider the possibility of a unified description of these phonon properties of *a*-Si:H and *a*-Ge containing H (and O) impurity atoms using the

framework of the recently proposed concept of local soft atomic potentials<sup>19</sup> (see also the review in Ref. 18), which extends the model of two-level systems to higher energies. In fact, the ensemble of soft potentials with a wide scatter of the parameters includes both low-energy two-level systems and excitations of higher ( $\sim 10$  K) energies. This ensures that a wide range of soft potentials can exist for different kinds of processes of resonant (and nonresonant) inelastic (and elastic) scattering of phonons in the terahertz and subterahertz ranges.

Finally, it should be mentioned that the mean free path of terahertz phonons in *a*-Ge, estimated (in Sec. 4) as  $\bar{l} \sim 10^{-7}$  cm from a kinetic diffusion expression, is less than the phonon wavelength ( $\lambda = 4 \times 10^{-7}$  cm at  $\Omega = 1$  THz for *c*-Ge). The ratio of  $\bar{l}$  and  $\lambda$  then approaches closely what is known as the Ioffe–Regel criterion  $2\pi\bar{l}/\lambda \lesssim 1$ , which applies to an electron and corresponds to its localization condition. It was pointed out in Ref. 20 that a similar phonon localization condition is satisfied by the mean free path  $\bar{l}$  of thermal phonons in a wide range of glasses and these phonons dominate the spectrum in the region of the plateau of the temperature dependence of the thermal conductivity. However, it is not correct to use the kinetic diffusion expressions in the limit  $\bar{l} \lesssim \lambda$ , and new approaches are needed in studies of the fundamental properties of excitations with energies of the order of 1 THz and their transport in glasses and in amorphous materials. The processes of passage of nonequilibrium phonons across amorphous films, studied experimentally using instruments with good spectral and time resolution, are a promising way of tackling this problem.

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