Coherent Phonon Generation and Detection by Picosecond Light Pulses

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Using the picosecond pump and probe technique we have detected oscillations of photoinduced transmission and reflection in thin films of *a*-As_2Te_3 and *cis*-polyacetylene. These oscillations are due to the generation and propagation of coherent acoustic phonons in the film. We discuss the generation and detection mechanism, and we use this effect to measure the sound velocity in a film of *a*-SiO_2.

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The pump and probe technique can be used to study photoinduced changes in transmission and reflectance which occur on time scales as short as a fraction of a picosecond. In this Letter we report on measurements in *a*-As_2Te_3 and *cis*-polyacetylene $(CH)_x$ using this technique. We have discovered a remarkable oscillatory change in transmission and reflectance. This effect can be understood in terms of the generation and propagation of coherent acoustic phonons. These observations provide the basis for a new method for the study of the velocity and attenuation of high-frequency phonons in materials where the phonons' mean free path is very short.

The pump pulse was generated by a passively mode-locked dye laser which produced 1-ps pulses with 2.0-eV photon energy, 0.5-MHz repetition rate, and 1-nJ pulse energy. The probe pulse was derived from the same laser, and passed through a variable optical delay line. The intensity of the probe pulse was typically a few percent of the pump pulse. Both pulses were focused onto a 50-μm diameter spot on the sample. The experiment consisted of a measurement of the transmission and reflectance of the probe pulse as a function of time delay relative to the pump.

The As_2Te_3 samples were amorphous films dc sputtered onto sapphire substrates. The films of thickness 470, 900, and 1200 Å were prepared at substrate temperature $\theta_S = 300$ K, and the 1600-Å film was prepared with $\theta_S = 77$ K. The samples deposited at 300 K had an absorption depth ζ for 2.0-eV light of 300 Å, and the 77-K sample was slightly less absorbing. The *cis*-$(CH)_x$ film was 1000 Å thick and was deposited on a quartz substrate. The pump and probe pulses were both incident on the film from the substrate side.

The photoinduced changes in transmission in *a*-As_2Te_3 are shown in Fig. 1. One can see that the response is the sum of two components: (1) a steplike decrease in transmission ($\Delta T/T \approx 10^{-3}$) at time zero followed by a monotonic increase, and (2) a damped oscillation. We have previously ob-

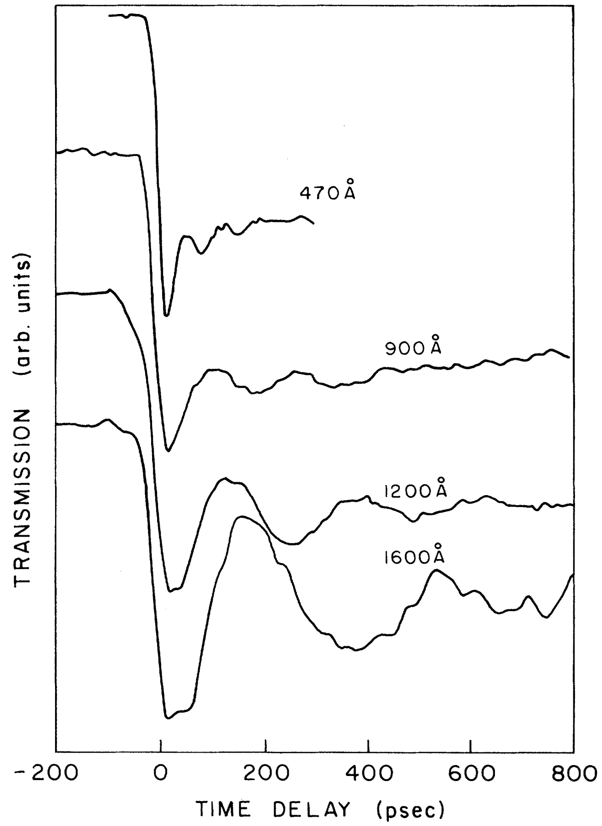

FIG. 1. Photoinduced transmission in *a*-As_2Te_3 for films of different thickness at room temperature.

served[1] response (1) in other chalcogenide glasses and in amorphous silicon, and attributed it to the excitation and trapping of carriers whose absorption cross sections decrease with decreasing energy of the trap.

Response (2) is a new observation. The order of magnitude of the amplitude of the oscillations is in the range 3×10^{-5} to 3×10^{-4}. This response is seen in photoinduced reflectance as well. In Fig. 2 the oscillation periods τ_0 are shown as a function of film thickness. We observed similar oscillations with the beam incident on the free surface of the film. The oscillations can also be observed at low temperature (10 and 80 K), and have the same period to within the experimental uncertainty. We have also observed it in *cis*-polyacetylene, but the oscillations were not found in the *trans* isomer.[2]

We propose the following explanation of these oscillations. The laser pulse generates a plane stress wave (or longitudinal acoustic phonon) which bounces back and forth in the film. The strain induced by this stress wave changes the gap in the As_2Te_3, and in this way changes the absorption of the time-delayed probe pulse. The period of oscillation is

$$\tau_0 = 4d/v, \qquad (1)$$

where d is the film thickness and v is the sound velocity. This formula holds because one surface of the film is free (zero-stress boundary condition), and the other is in contact with the hard sapphire substrate, which gives an approximately zero-displacement boundary condition. The measured periods[3] in Fig. 2 imply a sound velocity of 1.6×10^5 cm sec^{-1}. We have been unable to find a measurement in the literature to compare with this value. However, the result is consistent with the measured transverse sound velocity[4] of 10^5 cm sec^{-1} in crystalline As_2Te_3, and the velocity of 2.5×10^5 cm sec^{-1} for longitudinal sound[5] in amorphous As_2S_3.

Assuming that the shape of the absorption edge does not change significantly, we can write the change of the absorption coefficient α produced by strain as

$$\Delta\alpha = (d\alpha/dE_g)(dE_g/d\eta)\eta, \qquad (2)$$

where η is the strain (= fractional increase in volume $\Delta V/V$) and E_g is the optical energy gap. $dE_g/d\eta$ is the difference in the deformation potentials of the conduction band ($dE_c/d\eta$) and valence bands ($dE_v/d\eta$). The fractional change of transmission is

$$\frac{\Delta T}{T} = \exp\left(-\int_0^d \Delta\alpha\, dz\right) - 1 \simeq \frac{d\alpha}{dE_g}\frac{dE_g}{d\eta}\langle\eta\rangle d, \qquad (3)$$

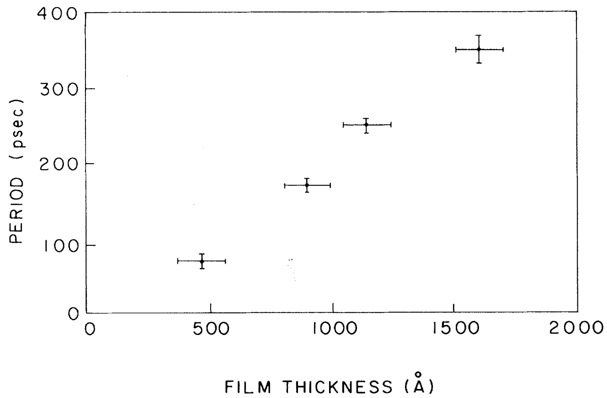

FIG. 2. Oscillation period τ_0 as a function of film thickness in a-As_2Te_3.

where $\langle\eta\rangle$ is the average strain in the sample and d is the equilibrium thickness.

Consider now the way in which the stress wave is generated. An obvious possibility is thermal expansion. The energy gap of a-As_3Te_3 is 0.8 eV and we excite with 2.0-eV photons. Excited electrons and holes relax quickly (within a few picoseconds) to the band edges, losing an excess energy of 1.2 eV per absorbed photon through phonon emission. The average temperature rise in the region of absorption as a result of this thermalization process is

$$\Delta\theta = (E_x/\zeta AC)(1-R)(1-T), \qquad (4)$$

where E_x is the excess energy in each pulse, A is the area of the beam, C is the specific heat per unit volume of the film, and R and T are the intensity reflection and transmission coefficients for light. The interference effects can be neglected because of the high absorption coefficient.

If the film temperature rises by this $\Delta\theta$ instantaneously, an isotropic stress $3B\beta\Delta\theta$ is set up in the film (B = bulk modulus, β = linear thermal expansion coefficient), and the film will then start to expand[6] normal to its plane so as to relieve this stress. This motion develops into an oscillation in which the average strain $\langle\eta\rangle$ oscillates with amplitude

$$[(1+\nu)/(1-\nu)]\beta\Delta\theta\zeta/d, \qquad (5)$$

where ν is Poisson's ratio. Taking the values $E_x = 0.5$ nJ, $A = 2\times10^{-5}$ cm^2, $C = 1.5$ J K^{-1} cm^{-3}, $R = 0.3$, and $T \ll 1$, we find that for $\zeta = 300$ Å, $\Delta\theta$ is 4 K. Then for[7] $\beta = 1.9\times10^{-5}$ K^{-1}, and assuming a Poisson's ratio of 0.3, we find the initial amplitude of the $\langle\eta\rangle$ oscillations to be 0.9×10^{-4} for the 470-Å sample. We can estimate $\Delta T/T$ using Eq. (3). Measuring the absorption edge of a-As_2Te_3 we found $d\alpha/dE_g \simeq -3.5\times10^5$ cm^{-1} eV^{-1}. For the deformation potential $dE_g/d\eta$ we took the value determined by Besson, Cernogora, and Zallen[8] in a a-As_3S_3 (2.3 eV). The calculated value of $\Delta T/T \simeq 3\times10^{-4}$ is in agreement with the magnitude of the observed oscillations.

We note that, in agreement with experiment, Eqs. (4) and (5) predict that $\Delta T/T$ does not change dramatically with temperature. The temperature dependence appears only through the factor β/C, which is a constant if Grüneisen's law holds.

Although this picture based on thermal expansion appears consistent with the experimental observations, we think that the real situation is more complicated. Suppose that the light changes the distribution functions of electrons and phonons by δf_i and δn_j, respectively (i, j label electron and phonon states of energy E_i and $\hbar\omega_j$). Then the induced stress σ is

$$\sigma = \sum_i \delta f_i \frac{\partial E_i}{\partial \eta} + \sum_j \delta n_j \hbar \frac{\partial \omega j}{\partial \eta}$$

$$= \sum_i \delta f_i E_i \gamma_i^{\mathrm{el}} + \sum_j \delta n_j \hbar\omega_j \gamma_j^{\mathrm{ph}}, \qquad (6)$$

where γ_i^{el} and γ_j^{ph} are "Grüneisen" factors for electrons and phonons, e.g., $\gamma_i^{\mathrm{el}} = E_i^{-1}(\partial E_i/\partial\eta)$.[9,10] Since in a-As_2Te_3, E_g (=0.8 eV) is close to the excess energy transferred to the phonons (1.2 eV), the total energies of the electrons and phonons are approximately equal. Thus, provided the electron and phonon Grüneisen factors are of the same order of magnitude, the electron and phonon contributions to the stress will be comparable. In fact, the average phonon γ estimated from the thermal-expansion coefficient[7] has the unusually small value of ~ 0.4. Thus, the electron contribution may well be dominant. An additional complication is that many of the phonon modes in As_2S_3, and therefore presumably in As_2Te_3, have intramolecular character,[8] and such modes often have long relaxation times.[11] Thus, the phonon system may not reach equilibrium until after the stress wave has been generated.

The oscillations in Fig. 1 are damped by transmission into the sapphire substrate, and possibly also by attenuation in the film. For a-As_3Te_3 on a fused quartz substrate the transmission into the substrate is so good (because the acoustic impedances are similar) that oscillations are not seen.

The fact that the oscillations can only be seen in one of the two polyacetylene isomers is understood by looking at their absorption coefficients as functions of photon energy. At 2 eV, α increases rapidly with photon energy in *cis*-polyacetylene, while in the *trans* isomer it has a broad flat maximum, which makes it much less sensitive to any modulation process.

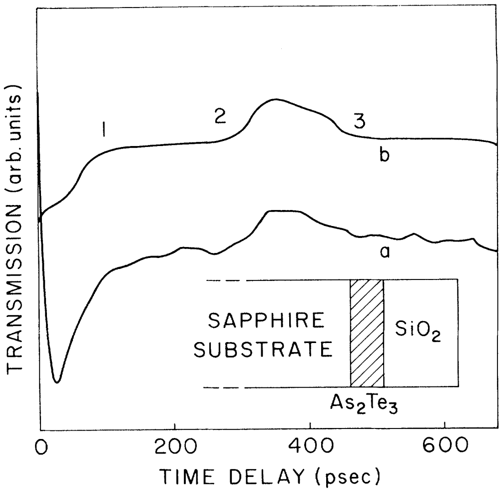

FIG. 3. Experiment to measure the sound velocity in an amorphous SiO_2 film. Curve a shows data for $\Delta T/T$. Curve b is a computer fit.

This generation and detection method has many possible applications in phonon physics. The frequency of the oscillations generated by our thinnest film is 14 GHz. This can be increased to ~ 100 GHz, if a thinner film (~ 100 Å) with a higher sound velocity ($\sim 4\times10^5$ cm sec^{-1}) is used. The generation and detection technique can be used at room temperature, where other methods such as tunnel junctions cannot be used. The excellent time resoltuion allows one to study the velocity and attenuation of phonons in very highly attenuating materials, such as glasses. There is also the exciting possibility of measurements of the attenuation of phonons under nonequilibrium conditions, for example when a material contains a nonequilibrium electron distribution.

As a demonstration of the technique, we have measured the longitudinal sound velocity in a 6000-Å film of a-SiO_2. This was deposited on top of a 900-Å film of a-As_2Te_3 as shown in the inset of Fig. 3. We have developed a computer model to calculate the $\Delta T/T$. This model includes the effect of the finite absorption length ζ, and the acoustic transmission and reflection coefficients at the interfaces. We have treated the velocity in the SiO_2 as an adjustable parameter. The experimental data and the best computer-generated fit are shown in Fig. 3, and it can be seen that the agreement is remarkably good. Because of the good impedance match to SiO_2 almost the entire stress wave leaves the As_2Te_3 film and the oscillatory part of ΔT goes to zero (points 1–2). Upon reflection at the free surface of SiO_2 the wave returns into As_2Te_3 with inverted sign (2–3) and leaves it again. In this way we have determined a velocity of $(4.8 \pm 0.3) \times 10^5$ cm $\sec^{-1}$ which is in reasonable agreement with the sound velocity measured by Rothenfusser, Dietsche, and Kinder.[12] We plan to use this technique to study the sound velocity in amorphous materials which can only be prepared as thin films.

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[6] The film cannot expand in its plane because of the rigid sapphire substrate.

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[9] If the electron and phonon distribution are equilibrium distributions corresponding to a temperature rise, the stress (6) is just what would be calculated from thermal expansion. In this case, the thermal energy of electrons and holes is negligible compared to that of phonons, and the electronic contribution to thermal expansion can be ignored.

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