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Surface generation and detection of phonons by picosecond light pulses

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We report experiments in which picosecond light pulses are used to generate and detect very short stress pulses (coherent longitudinal phonons). We present a theory of the generation process, and describe how the spatial shape of the stress pulse is related to the optical, electronic, and acoustical properties of the material. The stress pulses are detected through a measurement of the changes they induce in the optical reflectivity of the sample surface. We describe the theory of this effect. We present experimental results we have obtained for *a*-As_2Te_3, *a*-Ge, *a*-As_2Se_3, and Ni.

I. INTRODUCTION

In a recent paper[1] we have reported pump and probe measurements of photoinduced changes in optical transmission in thin films of *a*-As_2Te_3 and *cis*-polyacetylene. In these measurements an ultrashort pump light pulse was absorbed at the surface of a thin film of the material to be studied (Fig. 1). The optical transmission of the film was then measured with a probe pulse delayed by a time t relative to the pump. The probe thus sensed changes in optical transmission induced by the pump pulse. We found that these photoinduced changes were oscillatory in time, and we proposed the following explanation. When the pump pulse is absorbed in the sample an elastic stress is set up. This generates an acoustic pulse which bounces back and forth inside the film. The acoustic pulse causes a periodic modulation of the optical properties of the film. We were able to show that the period of the experimentally observed oscillations varied linearly with film thickness as expected, and that the amplitude of the oscillations was consistent with the model.

In this paper we describe more quantitatively the way in which the acoustic pulses are generated, and we calculate the spatial form of the generated pulse. We describe how the pulses can be detected through a measurement of a reflectivity,[2] rather than transmission. We describe the theory of this detection process, and derive an expression for the time dependence of the reflectivity changes that are caused by the acoustic pulse. The theoretical predictions are then compared with experimental measurements we have made on several materials. Finally, we describe measurements we have made of the velocity and attenuation of the acoustic pulses in *a*-As_2Te_3.

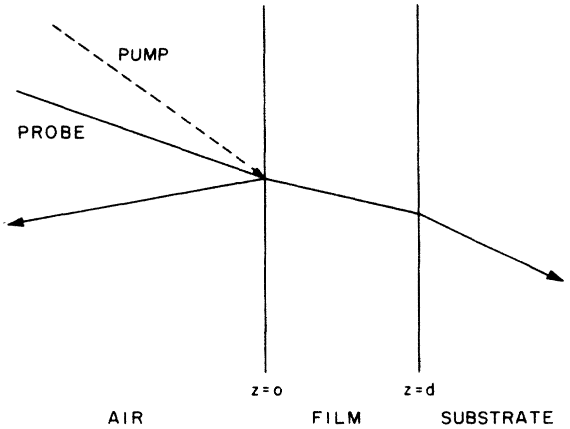

FIG. 1. Schematic diagram of the experiment.

II. THEORY

A. Strain generation

We consider[3] the experimental situation shown schematically in Fig. 1. A short light pulse (duration $\tau_0 < 1$ psec) of energy Q is incident on the free surface of a film of thickness d. We assume that the absorption length ζ of the light is much smaller than the film thickness d. The linear dimensions of the area A illuminated by the light pulse are assumed to be large compared to d and ζ. The total energy deposited per unit volume at a distance z into the film is

$$W(z)=(1-R)\frac{Q}{A\zeta}e^{-z/\zeta}\ , \tag{1}$$

where R is the reflectivity. This heating gives a temperature rise

$$\Delta T(z)=W(z)/C\ , \tag{2}$$

where C is the specific heat per unit volume. This sets up an isotropic thermal stress given by

$$-3B\beta\Delta T(z)\ , \tag{3}$$

where B is the bulk modulus and β is the linear expansion coefficient. We have assumed that the film is elastically isotropic. Since the stress only depends upon z, the only motion is parallel to z, and the only nonzero component of the elastic strain tensor is η_{33}. Hence, we have to solve the equations of elasticity in the form:

$$\sigma_{33}=3\frac{1-\nu}{1+\nu}B\eta_{33}-3B\beta\Delta T(z)\ , \tag{4}$$

$$\rho\frac{\partial^2 u_3}{\partial t^2}=\frac{\partial\sigma_{33}}{\partial z}\ , \tag{5}$$

$$\eta_{33}=\frac{\partial u_{33}}{\partial z}\ , \tag{6}$$

where ν is Poisson's ratio, u_3 is the displacement in the z direction, and ρ is the density. These equations have to be solved with the initial condition of zero strain everywhere. In addition, the stress σ_{33} must always be zero at the free surface $z=0$. The solution is

$$\eta_{33}(z,t)=(1-R)\frac{Q\beta}{A\zeta C}\frac{1+\nu}{1-\nu}\left[e^{-z/\zeta}\left(1-\tfrac{1}{2}e^{-vt/\zeta}\right)-\tfrac{1}{2}e^{-|z-vt|/\zeta}\operatorname{sgn}(z-vt)\right]\ , \tag{7}$$

where v is the longitudinal sound velocity given by

$$v^2=3\frac{1-\nu}{1+\nu}\frac{B}{\rho}\ . \tag{8}$$

The strain given by Eq. (7) is shown in Fig. 2. One can see that for large times the strain can be divided into two parts. The region near $z=0$ has a time-independent strain due to thermal expansion. The stress is zero in this region. The second part of the strain is a pulse which propagates away from the free surface at the speed of longitudinal sound. This comes from the second term in Eq. (7). The width of this pulse is of the order of twice the absorption length ζ. After propagating across the film the pulse will be reflected at the boundary with the substrate. This effect is not included in Fig. 2, i.e., we assume either perfect acoustic matching of the film to the substrate, or that the time is much less than the transit time $2d/v$.

There are several assumptions in this result. The area heated by the light pulse is assumed to be very large relative to the film thickness, so that ΔT, σ, and η only depend on the distance from the surface. For a large propagation distance, the shape of the strain pulse will change because the pulse will leave the "near-field" region of the source. Since the pulse has an effective wavelength of $\sim 2\zeta$, the near-field region where (7) is valid extends to a distance Z of order of magnitude[4]

$$Z\sim\frac{w^2}{\zeta}\ , \tag{9}$$

where w is of of the order of the linear dimensions of the heated region. In our experiments, w is 10 to 30 μm, whereas ζ is typically less than 0.1 μm. Since the propagation distance is at most a few microns we are certainly in the near-field regime.

We have also assumed that the temperature rise occurs instantaneously and that after this rise the temperature remains constant. Consider first the effect of the finite duration τ_0 of the light pulse. During this time the strain pulse moves a distance $v\tau_0$. If $v\tau_0$ is very small compared to the spatial length of the strain pulse, then the effect of the finite duration will be unimportant. Thus, we have the condition

$$v\tau_0 \ll \zeta\ . \tag{10}$$

The shortest absorption distances are in metals for which ζ can be ~ 100 Å. A typical velocity is 4×10^5 cm sec^{-1}, or equivalently 40 Å psec^{-1}. Thus, condition (10) becomes $\tau_0 \ll 2.5$ psec, which is well satisfied[5] in the experiments we will describe. Our pulse length is typically 0.2 psec.

Consider now the effect of heat flow after the light pulse is absorbed. If the thermal diffusivity is D (equal to K/C, where K is the thermal conductivity) then the temperature rise at z at time t is changed from the time-independent result (2) to

$$\Delta T(z,t)=\frac{(1-R)Q}{A\zeta C}\Theta(z,t)\ , \tag{11}$$

where

$$\Theta(z,t)=\int_{-\infty}^{\infty}dz'(4\pi Dt)^{-1/2}e^{-(z-z')^2/4Dt}e^{-|z'|/\zeta}\ . \tag{12}$$

This can be derived from Fourier's law using the initial temperature distribution given by Eqs. (1) and (2). One can then consider how this changing temperature distribution generates a stress pulse. A change in temperature at any space-time point (z,t) gives rise to two strain pulses which propagate towards positive and negative z. The negative-going pulse is reflected from the free surface. When the sum of these contributions is considered we find that the strain pulse propagating away from the surface is given by

$$\eta_{33}(z,t)=(1-R)\frac{Q\beta}{A\zeta C}\frac{1+\nu}{1-\nu}F(z-vt)\ , \tag{13}$$

where

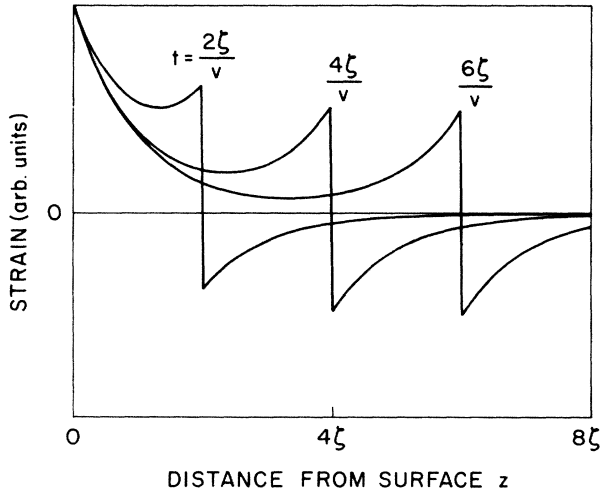

FIG. 2. The spatial dependence of the elastic strain at different times after the pump pulse has been absorbed [Eq. (7)]. At $t=0$ the elastic strain is zero.

$$F(z-vt)=-\tfrac{1}{2}e^{-(z-vt)/\zeta}-\tfrac{1}{2}\int_{0+}^{\infty}dt'\int_{0}^{\infty}dz'\frac{\partial\Theta(z',t')}{\partial t'}\delta(z'-z+v(t-t')) \tag{14}$$

or

$$F(z-vt)=\tfrac{1}{2}e^{(z-vt)/\zeta}-\tfrac{1}{2}\int_{0+}^{\infty}dt'\int_{0}^{\infty}dz'\frac{\partial\Theta(z',t')}{\partial t'}[\delta(z'-z+v(t-t'))-\delta(z'+z-v(t-t'))]\ . \tag{15}$$

Equations (14) and (15) hold for $z > vt$ and $z < vt$, respectively. The function F which determines the spatial shape of the pulse is shown in Fig. 3. The shape is completely determined by the quantity $D/v\zeta$. For metals at room temperature this quantity is usually between 0.2 and 2, so heat conduction has a rather large effect on the shape of the generated pulse. For dielectric glasses $D/v\zeta$ is typically of the order 0.01 or smaller, and so one sees from Fig. 3 that heat conduction makes only a very small change in the pulse shape.

This treatment of the generation process in terms of heating is not necessarily valid. At a more general level we have to consider that the light pulse changes the electron and phonon distribution functions $n_e(\mathbf{k})$ and $n_p(\mathbf{k})$ by $\delta n_e(\mathbf{k})$ and $\delta n_p(\mathbf{k})$, respectively. These changes produce a stress which is[6]

$$\sigma_{ij}=\sum_{\mathbf{k}}\delta n_e(\mathbf{k})\frac{\partial E_{\mathbf{k}}}{\partial\eta_{ij}}+\sum_{\mathbf{k}}\delta n_p(\mathbf{k})\hbar\frac{\partial\omega_{\mathbf{k}}}{\partial\eta_{ij}}\ , \tag{16}$$

where $E_{\mathbf{k}}$ and $\omega_{\mathbf{k}}$ are the energy of an electron and the frequency of a phonon of wave vector $\mathbf{k}$, respectively. The first term in Eq. (16) is an electronic contribution to the strain associated with the deformation potential $\partial E_{\mathbf{k}}/\partial\eta_{ij}$. If the electrons and phonons are in local thermal equilibrium then (16) reduces to the earlier result (3).[6] This microscopic description of the origin of the stress introduces several new effects. Consider first what happens in metals. Immediately after the absorption of light the electron system will not be in a state of equilibrium with the lattice. The electrons transfer their excess energy to the lattice through electron-phonon collisions, but they may diffuse a significant distance before they lose all their energy. Thus, the distance over which the energy is distributed will be larger than the absorption length ζ, and hence the acoustic pulse generated by thermal expansion will be broadened. Energy transfer between electrons and a lattice has been investigated theoretically,[7,8] and has recently become of experimental interest[9,10] because of the availability of sub-picosecond light pulses which can be used to probe an electron system during the time it takes to come to equilibrium with the lattice. We have not tried to calculate the shape of the acoustic pulses generated when electron diffusion is important.

In semiconductors the light will produce electrons and holes. These electrons and holes will emit phonons and relax to the band edge in a short time (~1 psec). Recombination occurs on a much longer time scale[11] (1 nsec to 1 μsec, typically). From (16) the electron-hole contribution to the stress is

$$\begin{aligned}\sigma_{ij}^{e}&=\frac{\partial E_g}{\partial\eta_{ij}}\delta n_e\\&=-B\frac{dE_g}{dP}\delta_{ij}\,\delta n_e\ ,\end{aligned} \tag{17}$$

where δn_e is the total number of electrons (equal to the number of holes), E_g is the band gap, P denotes pressure, and the assumption has been made that the solid is elastically isotropic. The spatial dependence of δn_e, and hence of σ_{ij}^{e} can again be modified by diffusion. For each photon of energy E which is absorbed, thermal phonons of total energy $(E-E_g)$ are produced. If these phonons are

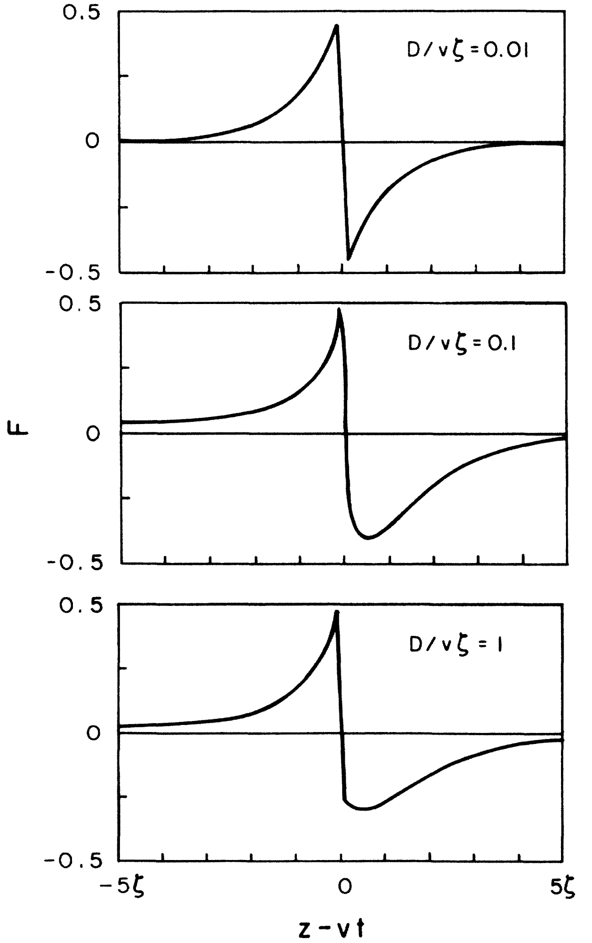

FIG. 3. The effect of thermal conduction on the shape of the acoustic pulse for different values of the thermal diffusivity.

well described by a thermal distribution, their contribution to the stress is

$$\sigma_{ij}^{p} = -\frac{3B\beta}{C}(E-E_g)\delta_{ij}\,\delta n_e \ . \tag{18}$$

The contributions (17) and (18) are generally of the same order of magnitude, but may have different signs. Usually β is positive so the phonons produce a negative stress. On the other hand, dE_g/dP may be positive or negative and so the electronic strain from (17) may add to or subtract from the phonon strain. For most chalcogenide glasses[12] dE_g/dP is negative, while in tetrahedrally bonded amorphous semiconductors[13] it is positive.

B. Strain detection

In our detection scheme we use a time-delayed probe pulse to measure the reflectivity of the surface of the film. This reflectivity undergoes a change ΔR when a strain pulse arrives close to the surface. This ΔR occurs because the optical constants of the film are changed by the propagating strain. We have

$$\Delta n(z,t) = \frac{\partial n}{\partial \eta_{33}}\eta_{33}(z,t) \ , \tag{19}$$

$$\Delta\kappa(z,t) = \frac{\partial \kappa}{\partial \eta_{33}}\eta_{33}(z,t) \ . \tag{20}$$

$\Delta n(z,t)$ and $\Delta\kappa(z,t)$ are the changes in the real and imaginary parts of the complex index of refraction, respectively, from their values n and κ in the absence of strain. The imaginary part κ is related to the absorption coefficient ($\alpha = 2\omega\kappa/c$). We are considering the case that η_{33} is the only nonvanishing component of the strain tensor.

When the strain is zero, a light wave at normal incidence with electric field

$$\mathcal{E}_x^{(i)} = \mathcal{E}_0 e^{i(k_0 z - \omega t)} \tag{21}$$

will generate reflected and transmitted waves:

$$\mathcal{E}_x^{(r)} = r_0 \mathcal{E}_0 e^{i(-k_0 z - \omega t)} \ , \tag{22}$$

$$\mathcal{E}_x^{(t)} = t_0 \mathcal{E}_0 e^{i(kz - \omega t)} \ , \tag{23}$$

where the reflection and transmission coefficients are

$$r_0 = \frac{k_0 - k}{k_0 + k} = \frac{1 - n - i\kappa}{1 + n + i\kappa} \ , \tag{24}$$

$$t_0 = \frac{2k_0}{k_0 + k} = \frac{2}{1 + n + i\kappa} \ , \tag{25}$$

and k_0 and k are the wave vectors in vacuum and the film, respectively. To calculate the change in reflectivity due to the strain we have to solve Maxwell's equations inside the film when the optical properties vary with position. We have

$$\frac{\partial^2 \mathcal{E}_x}{\partial z^2} = -\frac{\omega^2}{c^2}[\epsilon + \Delta\epsilon(z,t)]\mathcal{E}_x(z) \ , \tag{26}$$

where ϵ is the dielectric constant in the film in the absence of strain, and is related to n and κ through

$$\epsilon = (n + i\kappa)^2 \ . \tag{27}$$

$\Delta\epsilon(z,t)$ is the change in ϵ caused by the strain. Consider first what happens when the strain exists only at a distance z' from the interface, i.e., let

$$\Delta\epsilon = F\delta(z - z') \ . \tag{28}$$

The wave transmitted into the film will be partially reflected at this discontinuity. The reflection coefficient is found from (26) to be

$$r_1 = \frac{ik_0^2}{2k}F \ . \tag{29}$$

This is correct to lowest order in F. Part of this reflected wave then crosses the interface and hence the total reflected wave is

$$\mathcal{E}_x^{(r)} = (r_0 + t_0 r_1 \tilde{t}_0 e^{2ikz'})\mathcal{E}_0 e^{i(-k_0 z - \omega t)} \ , \tag{30}$$

where $\tilde{t}_0$ is the transmission coefficient from the film into vacuum, i.e.,

$$\tilde{t}_0 = \frac{2k}{k_0 + k} \ . \tag{31}$$

If we now consider the more general case of an arbitrary $\Delta\epsilon(z',t)$ we find that the reflection coefficient r is

$$\begin{aligned} r &= r_0 + \frac{ik_0^2}{2k}t_0\tilde{t}_0 \int_0^\infty dz'\, e^{2ikz'}\Delta\epsilon(z',t) \\ &\equiv r_0 + \Delta r \ . \end{aligned} \tag{32}$$

The change in reflectivity is

$$\Delta R = |r_0 + \Delta r|^2 - |r_0|^2 \ , \tag{33}$$

and from (27)

$$\Delta\epsilon(z,t) = 2(n + i\kappa)\left[\frac{\partial n}{\partial \eta_{33}} + i\frac{\partial \kappa}{\partial \eta_{33}}\right]\eta_{33}(z,t) \ . \tag{34}$$

Combining these results and simplifying, we find that the change in reflectivity correct to first order in the strain is

$$\Delta R(t) = \int_0^\infty f(z)\eta_{33}(z,t)dz \ , \tag{35}$$

where

$$f(z) = f_0\left[\frac{\partial n}{\partial \eta_{33}}\sin\left[\frac{4\pi nz}{\lambda} - \phi\right] + \frac{\partial \kappa}{\partial \eta_{33}}\cos\left[\frac{4\pi nz}{\lambda} - \phi\right]\right]e^{-z/\zeta} \ , \tag{36}$$

$$f_0 = 8\frac{\omega[n^2(n^2+\kappa^2-1)^2 + \kappa^2(n^2+\kappa^2+1)^2]^{1/2}}{c[(n+1)^2+\kappa^2]^2} \ , \tag{37}$$

$$\tan\phi = \frac{\kappa(n^2+\kappa^2+1)}{n(n^2+\kappa^2-1)} \ . \tag{38}$$

λ is the light wavelength in free space, ζ is the absorption length ($\zeta = \alpha^{-1} = c/2\omega\kappa$), and ϕ lies between 0 and $\pi/2$.

The "sensitivity function" f determines how strain at different depths below the surface of the film contributes to the change in the reflectivity. We will discuss f for several materials in the next section. The general form of f is an exponentially-damped oscillation with nonzero phase at the surface $z=0$. The periodicity of f is half the wavelength of light in the material. The range of f is determined by the absorption length $\zeta(=\alpha^{-1})$ of the light.

It is straightforward to use the same method to calculate $\Delta R(t)$ for a film whose thickness d is comparable to, or even less than ζ, as well as the change in transmission $\Delta T(t)$.

III. EXPERIMENT

Photoinduced reflectivity measurements were made using the picosecond pump and probe technique.[14] The pump pulse in our experiments induces changes in the optical constants n and κ which are monitored by the probe pulse as a function of the mechanically adjusted delay time between pump and probe. We use a passively mode-locked colliding-pulse ring dye laser[15] with a photon energy of 2 eV, a pulse length of 0.2 psec, and an energy per pulse of 0.2 nJ. The repetition rate of the laser is 110 MHz, the pump beam is chopped at 4 MHz with an acousto-optical modulator. The probe light reflected from the sample surface is detected by a Si diode, whose output is preamplified and fed into a phase sensitive amplifier locked to the chopping frequency. The magnitude of the fractional changes $\Delta R/R$ we measured were in the range of 10^{-6}—10^{-3}. The sample was mounted in an optical Dewar; the sample temperature could be varied from 40 to 300 K.

A. Semiconductors

We have made a detailed study of the generation and detection process in films of a-As_2Te_3. Results for the photoinduced change $\Delta R(t)$ of the reflectivity of a 2200-Å a-As_2Te_3 film dc sputtered onto a sapphire substrate are shown in Fig. 4. The response can clearly be divided into the sum of two components. The first component consists of a rapid increase in ΔR just after $t=0$, followed by a slower relaxation to a negative value. For times longer than those shown in Fig. 4, this negative ΔR in turn relaxes back towards zero. This component has a contribution from electronic relaxation phenomena as previously observed in other materials.[16] There may also be a significant contribution from thermal effects. The layer in which the light is absorbed is heated, and the change in n and κ in this layer gives a change in reflectivity. This reflectivity change slowly disappears as the heat diffuses into the interior. The second component in the signal is the series of equally spaced pulses. Each pulse corresponds to one round trip of the acoustic pulse in the film.

The decrease in amplitude of the acoustic pulses is partially due to attenuation of the stress pulse as it propagates in the film, and partly because some of the pulse is transmitted across the film-sapphire interface. The acoustic reflection coefficient r_{FS} at this interface is calculated from standard acoustic-mismatch theory[4,17] to be 0.59. A similar film of a-As_2Te_3 deposited on a quartz substrate showed no acoustic echoes. This was consistent with the small (0.07) acoustic reflection coefficient predicted for this interface.

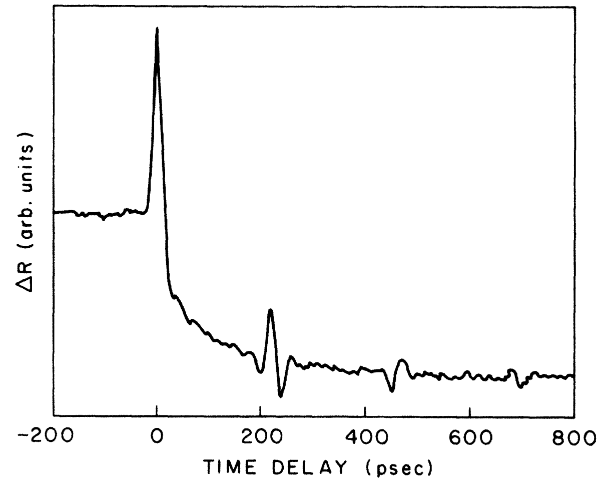

FIG. 4. Photoinduced changes in reflectivity of a 2200-Å film of As_2Te_3 sputtered onto a sapphire substrate.

The successive echoes in Fig. 4 are inverted with respect to each other. This is consistent with the boundary conditions at the two surfaces of the film. At the free surface there is a phase change of π, and at the sapphire interface there is no phase change because sapphire has a higher acoustic impedance than the film.

We now want to compare the shape of the detected pulses with the predictions of the theory. Consider first the spatial form of the acoustic pulses. For the moment, we assume that the pulse is generated by the thermal expansion mechanism. From the time spacing of the echoes and the measured film thickness, we find a sound velocity in a-As_2Te_3 of 2.0×10^5 cm sec^{-1}. The absorption length ζ for light of our wavelength is[18,19] ~ 300 Å. We do not have an accurate value for the thermal diffusivity, but for a typical nonmetallic glass D is $\sim 10^{-2}$ cm^2 sec^{-1}. Thus the parameter $D/v\zeta$ is 0.017, and the effect of heat conduction on the pulse shape will be very small (see Fig. 3), and can be neglected. Thus, the pulse shape is as shown in Fig. 2. When this pulse returns to the free surface of the sample the strain near the surface is given by the sum of the returning pulse and the reflection of this pulse at the surface. Thus, from (7) the strain near the free surface is given by[20]

$$\eta_{33}(z,t)=(1-R)\frac{Q\beta}{A\zeta C}\frac{1+\nu}{1-\nu}r_{FS}\left[\tfrac{1}{2}e^{-|z+vt|/\zeta}\mathrm{sgn}(z+vt)+\tfrac{1}{2}e^{-|z-vt|/\zeta}\mathrm{sgn}(z-vt)\right], \qquad (39)$$

where time is measured relative to the time of arrival of the midpoint of the pulse at the free surface of the film. Note that for fixed z the strain is an even function of time, and that the strain is always zero at $z=0$.

Consider now the sensitivity function f. We have measured the optical reflectivity and used this to find $n=3.7$. Then (37) and (38) give $f_0=0.83(\omega/c)$ and $\phi=0.46$ rad. To evaluate f we also need to know $\partial n/\partial\eta_{33}$ and $\partial\alpha/\partial\eta_{33}$. Experimental values for these quantities are not available so we use the following approach. An accepted model for the absorption edge of a number of amorphous semiconductors is[21]

$$\alpha(E)=\begin{cases} a(E-E_g)^2/E, & E>E_g \\ 0, & E<E_g \end{cases} \tag{40}$$

where a is a constant. For a-As$_2$Te$_3$ the experimental value[19] of a is 5.4×10^5 cm^{-1}eV^{-1}. We assume that α changes with strain only because of the variation of the energy gap with strain, i.e., we neglect $\partial a/\partial\eta_{33}$. Then, we obtain

$$\frac{\partial\alpha}{\partial\eta_{33}}=\begin{cases} -\dfrac{2a(E-E_g)}{E}\dfrac{\partial E_g}{\partial\eta_{33}}, & E>E_g \\ 0, & E<E_g\,. \end{cases} \tag{41}$$

Using the Kramers-Kronig relation between $n(\omega)$ and $\alpha(\omega)$, we find

$$\frac{\partial n}{\partial\eta_{33}}=-\frac{a\hbar c}{\pi E}g(E_g/E)\frac{\partial E_g}{\partial\eta_{33}}\,, \tag{42}$$

where

$$g(x)=(1+x)\ln|1+x|-(1-x)\ln|1-x|-2x\ln x\,. \tag{43}$$

For a-As$_2$Te$_3$, E_g is 0.8 eV.[18,19] The sensitivity function $f(z)$ can be expressed as

$$f(z)=b\frac{\partial\ln E_g}{\partial\eta_{33}}\cos\left[\frac{4\pi nz}{\lambda}-\psi\right]e^{-z/\xi}\,, \tag{44}$$

where $b=-2.8\times10^5$ cm^{-1}, and $\psi=1.14$ rad. This function is plotted in Fig. 5. The dimensionless quantity $\partial\ln E_g/\partial\eta_{33}$ should be of the order of unity, but the actual value is not known. In plotting Fig. 5 we have set it equal to 1.

To make the comparison with experiment we calculate the convolution (35) of the sensitivity function (44) with the strain (39). When this is done we find a result which has a time dependence very similar to the experimental result, but has the opposite sign. This indicates that either $\partial\ln E_g/\partial\eta_{33}$ is in fact negative, or the sign of the strain pulse is opposite to that we have calculated. Studies of other chalcogenide glasses indicate that dE_g/dP is usually negative, and so $\partial\ln E_g/\partial\eta_{33}$ should be positive. Thus, we are led to the conclusion that the sign discrepancy is due to the sign of the strain pulse, not the sign of the sensitivity function. Inspection of the relative magnitudes of the electronic and phonon contributions to the stress [Eqs. (17) and (18)] shows that this conclusion is reasonable.

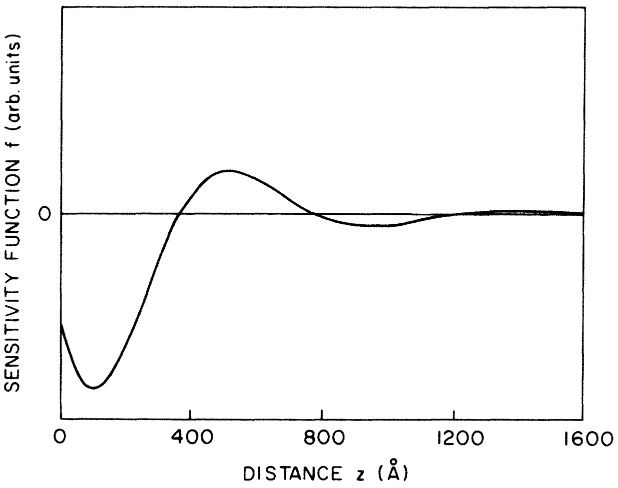

FIG. 5. The sensitivity function f [Eq. (44)] for a-As$_2$Te$_3$ plotted versus distance z into the film.

The ratio of the electronic to the phonon stress is

$$\frac{\sigma_{ii}^e}{\sigma_{ii}^p}=\frac{C}{3\beta}\frac{dE_g}{dP}\frac{1}{E-E_g}\,. \tag{45}$$

The linear expansion coefficient β is[22] 1.9×10^{-5} K^{-1}, and C is estimated[23] as 1.3 J cm^{-3}K^{-1}. Thus, we find

$$\frac{\sigma_{ii}^e}{\sigma_{ii}^p}=190\frac{dE_g}{dP}\,, \tag{46}$$

where dE_g/dP is in eV kbar^{-1}. Values of dE_g/dP of -0.01 and -0.013 have been measured[24] for As$_2$S$_3$ and As$_2$Se$_3$, respectively. If we assume that the value in As$_2$Te$_3$ is similar, Eq. (46) predicts that the electronic contribution to the stress is larger than the phonon contribution (thermal expansion) and is of opposite sign. This then gives a sign change in the total stress and strain, and agreement with experiment. In Fig. 6 we compare the experimental and theoretical signal shapes. We have adjusted the amplitude of the theory to fit the experimental data. The agreement is extremely good.

We have performed similar experiments with a 2800-Å film of a-Ge sputtered on to a sapphire substrate. The shape of the first acoustic echo as detected by reflectivity

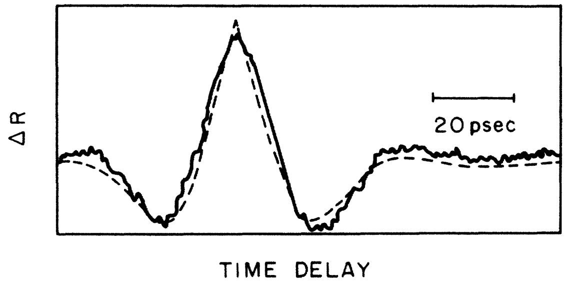

FIG. 6. The first acoustic echo in a-As$_2$Te$_3$. The solid line is the experimental result, and the dashed line the theoretical. The magnitude of the theoretical result has been adjusted to match the experimental data.

is shown in Fig. 7. From the arrival time of the first echo we calculate a longitudinal sound velocity of 4.6×10^5 cm sec^{-1}. The error is ±10% and is due to the uncertainty in the film thickness. To within experimental error the velocity is in agreement with the measurement of Rothenfusser *et al.*[25] We have not attempted to make a detailed fit of the pulse shape to theory. The shape is very similar to that observed in a-As$_2$Te$_3$, but is narrower by about a factor of 1.7. For a-Ge, n is 5 and ζ is 300 Å,[26] so these values are quite similar to those for a-As$_2$Te$_3$. If we take the sensitivity function to be the same in both materials, the width (in time) of the detected echo will be reduced simply by the ratio of the sound velocities in the two materials. This ratio is 2.3, and thus gives reasonable agreement with experiment.

The sign of the detected echo in a-Ge is the same as in a-As$_2$Te$_3$. This is as expected. In a-Ge, dE_g/dP is positive[24] and so the electronic and phonon contributions to the stress add. Thus, the sign of the stress is opposite compared to a-As$_2$Te$_3$. However, the different sign of dE_g/dP means that the sign of the sensitivity function is also reversed, and therefore the detected change in reflectivity should have the same sign in the two materials.

We have looked for acoustic echoes in a-Si:H and have not found any. Both the thermal expansion coefficient and dE_g/dP are much smaller in this material than in a-As$_2$Te$_3$ or a-Ge. In a-As$_2$Se$_3$ we see an interesting effect[27] (Fig. 8). These data were taken with a bulk sample (4 mm thick), and thus the observed oscillations in reflectivity (period 44.8 psec) are not related to acoustic echoes. Their origin is as follows. In a-As$_2$Se$_3$ the absorption length for light is long (see below), and hence the sensitivity function undergoes many oscillations before it damps out. The acoustic pulse generated at the surface propagates through these oscillations of the sensitivity function, and gives the observed oscillations in reflectivity. The period τ of the oscillations is from (35)

$$\tau=\frac{\lambda}{2nv}\ . \tag{47}$$

For As$_2$Se$_3$, n is 3.7,[28] and so the measured τ gives a sound velocity of 1.9×10^5 cm sec^{-1} in good agreement with other measurements.[29] The attenuation of the reflectivity oscillations is principally due to the decay of the sensitivity function, but there may also be a small contribution from the attenuation of the acoustic pulse.[30] If the acoustic attenuation is ignored, then the reflectivity change must be of the form [see (35)]

$$\Delta R(t)\propto\cos\left[\frac{4\pi nvt}{\lambda}-\delta\right]e^{-z/\zeta}\ , \tag{48}$$

where δ is some phase shift. We can make a good fit to the data with a light absorption length $\zeta(=\alpha^{-1})$ of 2000 Å (Fig. 8). This absorption is stronger by a factor of ~2.5 than the value measured previously,[31] but is not surprising since we have observed a significant photodarkening with the high light intensity used in our experiments. The fit uses the value 1.46 rad for the phase δ.

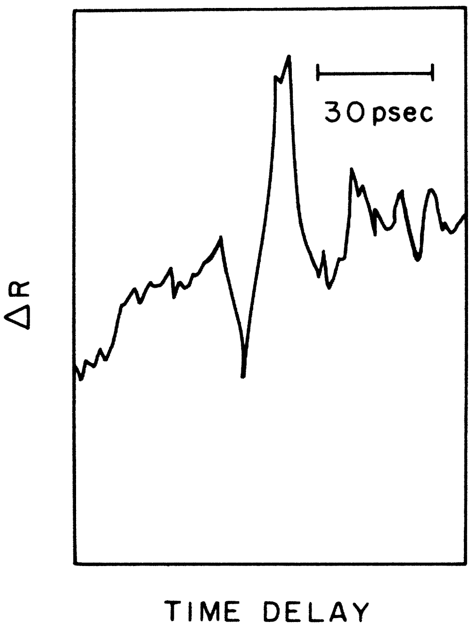

FIG. 7. The first acoustic echo in a film of a-Ge.

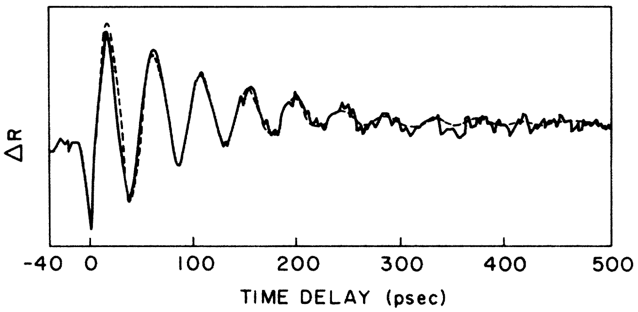

FIG. 8. Reflectivity measurements on a bulk sample of a-As$_2$Se$_3$. The dashed curve is a fit to the data described in the text.

B. Metals

In Fig. 9 we show measurements we have made for a film of nickel of approximately 1200 Å thickness deposit-

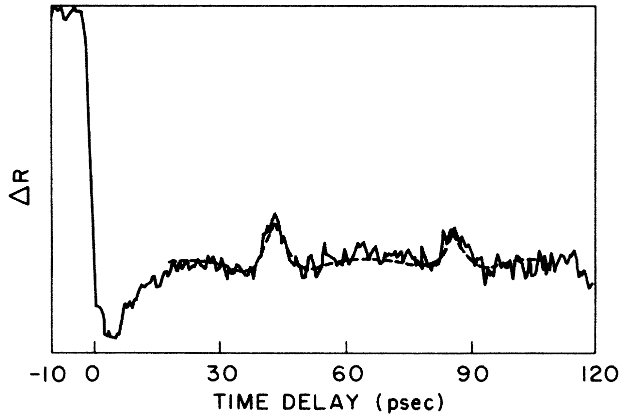

FIG. 9. Acoustic echoes observed in a nickel film. The dashed curve is a theoretical fit described in the text.

ed onto a fused quartz substrate. Unlike in As_2Te_3 and Ge, the second acoustic echo is not inverted with respect to the first; this is because the acoustic impedance of nickel is larger than the impedance of the quartz substrate. The ratio of the amplitudes of the two echoes agrees to within the accuracy of the experiment with the theoretical acoustic reflection coefficient between nickel and quartz (0.66).

For nickel the sound velocity[32] is anisotropic[33] and varies between 5.3 and 6.3×10^5 cm sec^{-1}. The refractive index n is[34] 1.93 and $\zeta=135$ Å. We do not know $\partial n/\partial\eta_{33}$ and $\partial\kappa/\partial\eta_{33}$ entering into Eq. (36), and do not even have a good model to estimate the ratio $(\partial n/\partial\eta_{33})/(\partial\kappa/\partial\eta_{33})$. We have used the ratio as an adjustable parameter, and the resulting fit to the data using the value 0.5 is shown in Fig. 9. This fit has ignored the effect of thermal diffusion on the acoustic pulse shape. For nickel at room temperature $D=0.23$ cm^2 sec^{-1}, and so $D/v\zeta$ is 0.3. This amount of diffusion does give a significant change in the theoretical echo shape, but given the lack of knowledge of the derivatives of the optical constants and the noise in the data, we cannot make a serious test of the theory.

We have also detected acoustic echoes in films of copper and aluminum; these materials are potentially interesting because of the high thermal diffusion. In magnesium, zinc, molybdenium, and tin we were unable to detect acoustic echoes. We did not identify the origin of these differences but we note that the technique is applicable if the sensitivity of the optical constants to stress is sufficiently large. In crystalline solids, strong responses are expected in regions close to a singularity in the optical spectrum.[35,36] In a metal, strong responses occur in the region of the plasma edge and at singularities of interband transitions, while the responses are weak in the region where the optical properties are only determined by nearly-free electrons. A general trend, seen also in amorphous solids, is that in regions where the reflectivity depends weakly on frequency the responses are weak. It should be advantageous to select the probe frequency in a spectral region where the piezo-optical constants of the studied material are large.

C. Sound velocity and attenuation measurements

A measurement of the ratio of amplitudes of successive echoes can be used to measure acoustic attenuation. It is necessary to allow for the partial transmission of sound into the substrate. To make a quantitative attenuation measurement, the acoustic frequency must be specified. Let us suppose that the first returning strain pulse is[37] $g^{(1)}(t+z/v)$. If we choose the origin of time at the moment when the center of this pulse reaches $z=0$, then the reflection of the pulse at the free surface is $-g^{(1)}(t-z/v)$. Thus, the change in reflectivity will be

$$\Delta R^{(1)}(t)=\int_0^\infty f(z)[g^{(1)}(t+z/v)-g^{(1)}(t-z/v)]dz \; . \tag{49}$$

We Fourier decompose the pulse shape $g^{(1)}$ according to

$$g^{(1)}(t)\equiv\int_{-\infty}^{\infty} d\Omega\, g^{(1)}(\Omega)e^{-i\Omega t} \; . \tag{50}$$

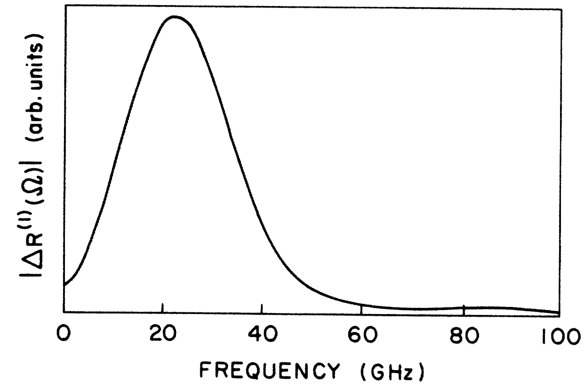

FIG. 10. Magnitude of the Fourier transform of the first acoustic echo in a 4150-Å film of a-As_2Te_3.

Then, the Fourier transform $\Delta R^{(1)}(\Omega)$ of $\Delta R^{(1)}(t)$ is given by

$$\begin{aligned}\Delta R^{(1)}(\Omega)&=(2\pi)^{-1}\int_{-\infty}^{\infty} dt\, \Delta R^{(1)}(t)e^{i\Omega t}\\ &=\tilde{f}(\Omega)g^{(1)}(\Omega) \; ,\end{aligned} \tag{51}$$

where

$$\tilde{f}(\Omega)\equiv-2i\int_0^\infty dz\, f(z)\sin(\Omega z/v) \; . \tag{52}$$

For the second acoustic echo the Fourier transform of $\Delta R(t)$ will be

$$\Delta R^{(2)}(\Omega)=\tilde{f}(\Omega)g^{(2)}(\Omega) \; . \tag{53}$$

Let us suppose that the Fourier component of the acoustic pulse at frequency Ω is attenuated at a rate $\gamma(\Omega)$ per unit distance. Then

$$g^{(2)}(\Omega)=-g^{(1)}(\Omega)r_{\mathrm{FS}}\exp[2id\Omega/v-2d\gamma(\Omega)] \; , \tag{54}$$

where r_{FS} is the reflection coefficient at the film-substrate interface. Thus

$$\gamma(\Omega)=\ln|r_{\mathrm{FS}}\,\Delta R^{(1)}(\Omega)/\Delta R^{(2)}(\Omega)|/2d \; . \tag{55}$$

This gives a quantitative method to determine the attenuation at a definite frequency from the reflectivity measurement. In Fig. 10 we show $|\Delta R^{(1)}(\Omega)|$ for an

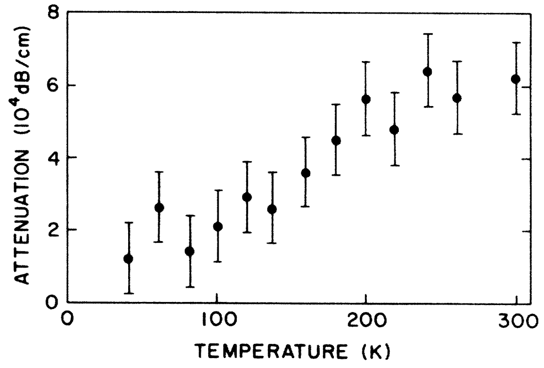

FIG. 11. Acoustic attenuation at 30 GHz in a-As_2Te_3.

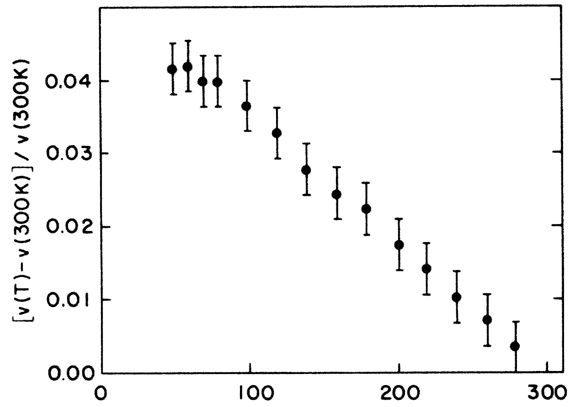

FIG. 12. Temperature dependence of the sound velocity in a-As$_2$Te$_3$.

echo in a 4150-Å film of a-As$_2$Te$_3$. The spectral content has a maximum of $\sim$25 GHz. Figure 11 shows the attenuation as a function of temperature at 30 GHz found from Eq. (55). The general order of magnitude of this attenuation, and its temperature dependence are similar to results found in other glasses in this temperature and frequency range.[38] In Fig. 12 we show results for the temperature dependence of the sound velocity measured in the same example. These results neglect the change in path length associated with thermal expansion.

IV. SUMMARY

We have given a theory of the generation and detection of acoustic pulses by picosecond optical techniques. We have observed these pulses in several materials, and in a-As$_2$Te$_3$ we are able to make a quantitative comparison with the theory. These methods that we have described appear to be a promising new tool for the study of high-frequency phonons. Unlike several other techniques, such as superconducting tunnel junctions, this technique can be applied to study phonons at room temperature. The excellent time resolution means that measurements can be made even in samples only available as thin films. The frequency range which can be studied in the present type of experiment is determined by the spectral content of the acoustic pulses; this spectrum peaks at a frequency ν of roughly $v/2\zeta$. In the experiments described here we have generated and detected the phonons in a single film, and have measured the attenuation in this same film. We are currently performing experiments in which we measure the acoustic attenuation in one film by generating and detecting the phonons in another film (transducer) in which the optical properties depend strongly on strain.

ACKNOWLEDGMENTS

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