Evidence of Laser-Wavelength Effect in Picosecond Ultrasonics: Possible Connection With Interband Transitions

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We have studied the effect of wavelength change on picosecond acoustic pulses generated using a femtosecond laser. For the first time, we show that the pulse shape can be strongly influenced by the laser wavelength. The results are in excellent agreement with a calculation based on a thermoelastic model which connects them to significant changes in the piezo-optical constants. There are similarities between the present study and stress modulation spectroscopy, which allows us to ascribe the observations to interband transitions and suggests thus a new potentiality of picosecond ultrasonics.

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The development of ultrafast pulsed-laser techniques has enabled time-resolved studies of the dynamics of photoexcited carriers in semiconductors or metals [1–3]. The electron dynamics is, in general, fully resolved after a few hundred femtoseconds. On a larger time scale, Thomsen *et al.* have first shown that photoexcited electrons can generate picosecond acoustic pulses which lead to the study of the acoustic or thermal properties of thin films [4,5]. With this so-called picosecond ultrasonics technique, it is possible to generate acoustic waves whose frequency is so high (up to several hundred GHz) that they suit very well thin films charaterization. It has been used to access thicknesses, sound velocities, and attenuation measurements using ultrasonics in a frequency range that is inaccessible by conventional techniques [6]. It has also motivated fundamental studies concerning the elastic properties of multilayers [7,8], electronic diffusion, and electron-phonon coupling in metals [9,10].

In the particular case of a metallic film deposited on a substrate, one can describe a picosecond ultrasonics experiment as follows. A first optical pulse (the pump pulse) is incident at the sample surface where it is absorbed and the resulting dilatation generates a strain pulse whose extension is related to the absorption length. In a metal, absorption can be very strong giving a length of a few nanometers. Such a mechanical pulse propagates into the sample at the sound velocity (typically a few nanometers per picosecond), which explains how absorption can generate picosecond acoustic pulses. This pulse is reflected onto the film-substrate interface and the resulting echo comes back to the surface and modifies this way the dieletric constant of the film. These changes can be detected by another optical pulse (the probe pulse) whose reflection or transmission is affected by the presence of the strain wave. By adjusting the delay between pump and probe pulses it becomes possible to monitor the successive echoes due to the strain generated by the pump pulse.

From this scheme, two conditions are needed to do such an experiment. First, the pump pulse must be absorbed by the sample. Second, the probe pulse must be affected by an acoustic pulse. This last point involves a change in the optical constants due to strain which is related to piezo-optic coefficients of the sample. Both conditions can be affected by the laser wavelength. The absorption may be enhanced by selecting a wavelength which lies in an absorption peak. As first suggested by Thomsen *et al.* [4], it should also be advantageous to choose a probe frequency in a spectral region where the piezo-optic couplings are large. Nevertheless, to our knowledge, the effect of laser wavelength on acoustic echoes has never been examined either theoretically or experimentally.

In this Letter we report the first observation of significant changes in the acoustic echo shape due to a wavelength change of the laser source. Complementary experiments based on a two-color pump and probe setup reveal that this effect is due to the detection process. Simulations of detected echoes using a photoelastic model relate this to strong changes in the piezo-optic couplings with the wavelength, which is known to appear near interband transitions. This work demonstrates the possibility for picosecond ultrasonics experiments of studying the electronic structure of thin films.

Several experimental conditions have permitted such an observation. First, experiments were performed on a tungsten film sputtered on a silicon substrate. Tungsten has so high an acoustic impedance compared to the substrate that a significant part of the incoming acoustic energy is reflected at the interface, which has favored the observation of echoes. Second, the improvement of the tunable femtosecond laser sources has greatly simplified the production of very short pulses whose wavelength can be easily changed. Third, our experimental setup was developed to detect signal changes $\Delta R/R$ of a few 10^{-7} which is crucial for the investigation of the precise structure of acoustic echoes.

Our picosecond ultrasonics experiment is based on a conventional pump and probe setup [4] associated with a tunable Ti:sapphire oscillator (Coherent MIRA 900f [11]).

The laser produces 120 fs optical pulses with a repetition rate of 76 MHz centered at a wavelength adjustable between 720 and 980 nm. Most experiments have been done using the same wavelength for the pump and the probe beam. Nevertheless several experiments have involved a frequency doubled beam (pump or probe) obtained using a 2 mm beta barium borate crystal. The optical pulse duration is much shorter than the strain pulses to be neglected even in the case of second-harmonic pulses which are longer than in the single frequency case.

A typical experimental result obtained in a 170 nm thick tungsten film sputtered onto a silicon substrate is reproduced in Fig. 1. It represents the reflectivity change of the probe beam as a function of the delay between pump and probe both centered at 820 nm. Such a signal is composed of three main parts. The first one is the sharp peak localized at $t = 0$ which corresponds to the absorption of the pump pulse by the electron gas of the metallic film. On a larger time scale, the change in reflectivity slowly disappears as the heat diffuses into the sample. The last point concerns echoes resulting from the successive reflections of the acoustic pulse at the film-substrate and air-film interfaces. Using literature value for the velocity of polycrystalline tungsten [12], $v = 5.19$ nm/ps, the time interval between echoes (65 ps) yields a thickness of 168 nm, very close to the thickness measured by scanning electron microscopy (170 nm), which confirms the accuracy of the sound velocity which will be used in the following. Several echoes are well defined due to the high constrast in acoustic impedance seen by longitudinal acoustic waves at the film-substrate interface.

Let us focus our attention on the precise structure of the first echo. Figure 2 shows the first echo shape obtained at various wavelengths (750, 820, and 920 nm) for similar pump energies. Qualitative changes in the pulse shape are visible. As usually in picosecond ultrasonics, these experiments were performed using the same wavelength for pump and probe beams. To identify the origin of these pulse shape modifications, we have carried out two-color pump and probe experiments using a frequency-doubled beam. The fundamental wavelengths were the same as in the previous results. Figure 3(a) shows the echo shapes obtained in experiments performed with a blue probe and a near infrared pump. In that case no change in the pulse shape can be noticed as the fundamental wavelength changes. The echo detected with a blue probe [Fig. 3(a)] is reduced by half compared to the infrared one (Fig. 2). As in both experiments the pump pulses are the same; the strain pulses should be the same. The observed difference thus reveals that the detection mechanism plays an important role in the shape of the detected echo. Figure 3(b) gives the results of the complementary experiments (near infrared probe and blue pump). The lower intensity of the blue pulse compared to the infrared one explains the reduced signal to noise ratio of these results. In spite of this, they reproduce well the pulse shape modifications observed in Fig. 2. All these results demonstrate that the observed effect is connected to a change of the probe wavelength in the vicinity of 800 nm and that its origin should be searched in the detection mechanism and not in the generation one.

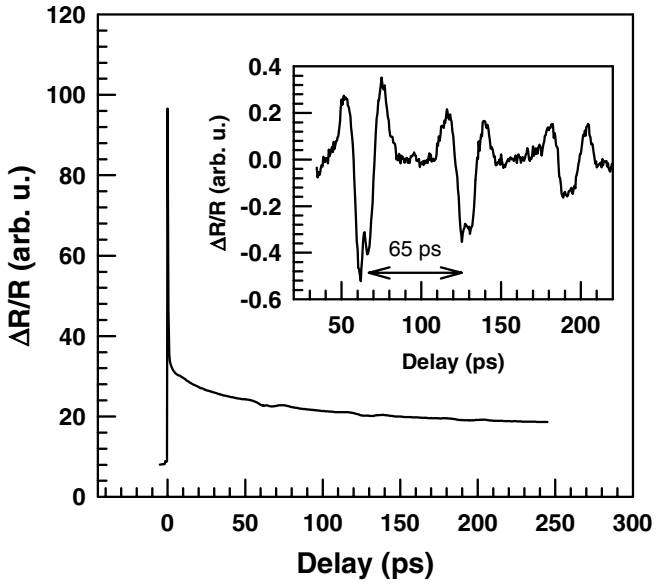

FIG. 1. Transient reflection changes measured in a W film deposited onto a Si substrate versus time delay from the pump pulse. Both pump and probe pulses are centered at 820 nm. The inset shows the first three acoustic echoes after subtraction of the thermal background.

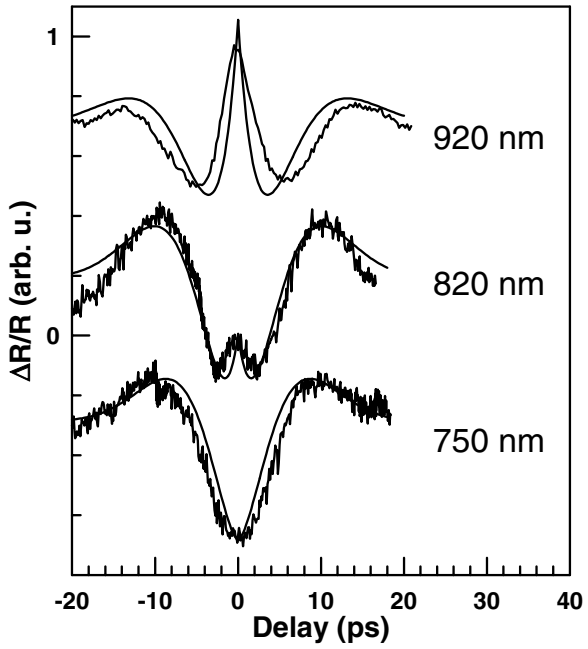

FIG. 2. The first acoustic echo measured in a W film obtained for three laser wavelengths. Simulation results (smooth lines) reproduce well the change in the echo shape with the wavelength by adjusting the piezo-optic couplings.

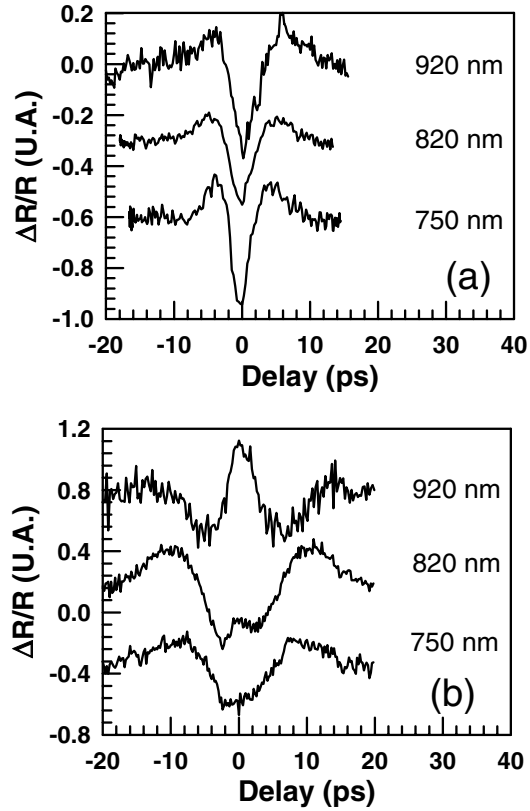

FIG. 3. The first acoustic echo in a film of W obtained for two-color pump and probe experiments: (a) with a near infrared pump and a blue probe and (b) with a blue pump and a red-infrared probe.

For an understanding of the origin of this qualitative change, let us briefly review the photoelastic model which was first established by Thomsen *et al.* [4]. Following the macroscopic point of view used in the introduction, the generation of the strain pulse is derived from the temperature rise due to the partial absorption of the pump pulse. A thermal stress results from this temperature rise which itself leads to a strain. Using Hooke's law and the fundamental law of motion, one finds a propagative term in the resulting strain given by

$$\eta(z,t) = \frac{A}{\zeta}\, e^{-|z-vt|/\zeta}\, \mathrm{sgn}(z - vt), \tag{1}$$

where A contains all physical constants which govern the absorption of the pump pulse by the sample and its transformation in strain and ζ is the absorption length at the pump wavelength. This strain pulse propagates into the sample away from the surface; the part which is reflected at the film-substrate interface is itself reflected at the air-film interface. The strain pulse which will be detected can then be written as

$$\eta(z,t) = \frac{Ar}{\zeta}\,[e^{-|z-vt|/\zeta}\,\mathrm{sgn}(z - vt) + e^{-|z+vt|/\zeta}\,\mathrm{sgn}(z + vt)], \tag{2}$$

where the origin of time is the arrival of the pulse at the air-film interface and r is the reflection coefficient of the longitudinal waves at the film-substrate interface.

The next step is the description of the detection process. The propagating strain given by Eq. (2) is supposed to modify the reflection of the probe beam by affecting the real and imaginary parts of the optical index of refraction (designated, respectively, by n and k). The piezo-optic coupling is here measured by the first derivative of n and k with respect to the strain, $\partial n/\partial\eta$ and $\partial k/\partial\eta$.

Thomsen *et al.* [4] have shown that the change in reflectivity of the probe beam is then given by

$$\Delta R(t) = \int_0^\infty f(z)\,\eta(z,t)\,dz\,, \tag{3}$$

where $f(z)$ is known as a sensibility function given by

$$f(z) = f_0\Big[\frac{\partial n}{\partial\eta}\,\sin\Big(\frac{4\pi nz}{\lambda} - \Phi\Big) + \frac{\partial k}{\partial\eta}\,\cos\Big(\frac{4\pi nz}{\lambda} - \Phi\Big)\Big]e^{-z/\zeta}, \tag{4}$$

$$f_0 = \frac{16\pi}{\lambda}\,\frac{\sqrt{n^2(n^2+k^2-1)^2 + k^2(n^2+k^2+1)^2}}{([n+1)^2+k^2]^2}\,, \tag{5}$$

$$\tan\Phi = \frac{k(n^2+k^2+1)}{n(n^2+k^2-1)}\,. \tag{6}$$

λ is the probe beam wavelength in free space. Combining Eqs. (2) and (3) one can compute the reflectivity change $\Delta R(t)$ produced by the first echo. Usually, this model is implemented numerically and experimental results are reproduced by fitting the piezo-optic couplings [4,6,8], which has demonstrated the efficiency of such a description.

Before doing that, let us use the previous formula to have some general considerations about the effect of the pump and probe wavelengths on the shape of the measured echo. In the present description, the pump wavelength has no effect on the strain pulse shape; only its temporal extension can vary with the absorption length which is itself dependent on the pump wavelength. The probe wavelength acts in the detection process in several ways: it appears directly [Eqs. (4) and (5)], in the optical index of refraction and as a variable of the two piezo-optic couplings ($\partial n/\partial\eta$, $\partial k/\partial\eta$). By integrating Eq. (3) one can write ΔR as

$$\Delta R(t) = \frac{\partial n}{\partial\eta}\,f_1(t) + \frac{\partial k}{\partial\eta}\,f_2(t)\,, \tag{7}$$

where the functions f_1 and f_2 have very different shapes which keep the same for relatively small changes in the index of refraction. The detected signal results from the weight of both functions which is measured by the ratio $(\partial n/\partial\eta)/(\partial k/\partial\eta)$. Keeping first this ratio constant simulations confirm this point since using the literature values of n, k [13], and v [12] one obtains three simulated echoes

which all have the same shape. By adjusting the ratio of the piezo-optic couplings, it is possible to reproduce well the three pulse shapes shown in Fig. 2 using experimental values for the index of refraction [13]. The corresponding ratios are 1 for 750 nm, 3 for 820 nm, and 20 for 920 nm. It should be noticed that simulated echoes are narrower than experimental ones, which has already been attributed to an electron-phonon coupling effect [14]. Thus the photoelastic model confirms that the observed changes are due to a probe effect and more precisely to a significant change of the piezo-optic couplings of W between 750 and 920 nm.

Similar results have been obtained in a 100 nm thick film of aluminum deposited on Si. Aluminum is of particular interest in picosecond ultrasonics since it is usually used as a transducer for studying transparent samples [6]. From 700 to 880 nm, echoes keep the same shape but undergo a strong change near 880 nm. Such strong variations of the first derivatives of the index of refraction can be observed near the onset of direct interband transitions [15]. Modulation spectroscopy has been used for a long time to detect precisely these so-called critical points and more generally to investigate energy band structure of semiconductors and metals [16,17]. It would have been particularly interesting to compare the present results to those obtained in stress modulation. Such an experiment uses a transducer to generate an acoustic wave and detects the changes it induced in the reflection of light. Even if the experimental setups have nothing in common, picosecond ultrasonics and stress modulation both monitor the changes in reflectivity of light induced by a strain field and are thus sensible to the same piezo-optic couplings. Unfortunately, to our knowledge, no such experimental data are available either for W or for Al. In spite of this, the examination of modulation spectroscopy results obtained for noble metals [15–17] reveals that significant modifications can arise in the piezo-optic couplings as the wavelength changes. Moreover, the real and imaginary parts change independently which suggests that strong variations of the ratio of the piezo-optic couplings as we observed are possible. The examination of the reflectivity spectrum of W let us go further in the connection of the observed effect to interband transitions: the first transitions of W are known to appear at 0.43, 0.87, 1.57, and 2.25 eV [13]. It should be noticed that the interband transition localized at 1.57 eV (790 nm) falls precisely in the region where we observed significant changes in the pulse shape. Concerning the Al case, one also could relate the observed changes to the strong interband effects known to appear near 1.5 eV (830 nm) [18].

In summary, we have presented experimental results concerning the shape of acoustical echoes generated and detected in thin films using a tunable femtosecond laser. For the first time, it has been shown that the wavelength of the laser could strongly affect the shape of the acoustic signal. Two-color experiments and simulations based on a photoelastic model have been used to demonstrate that this effect comes from the detection process. Comparison with theoretical predictions let us relate these variations to strong changes in the piezo-optic couplings with the wavelength. Picosecond ultrasonics is then seen as a new way of doing stress modulation measurements in thin films, contactless and without the use of any transducer.

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