Strong oscillations detected by picosecond ultrasonics in silicon: Evidence for an electronic-structure effect

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We present the results of picosecond ultrasonic experiments performed at different laser wavelengths in different samples all grown on silicon (100) substrates. In the blue range we report on strong oscillations in the reflectivity curves. We present experimental and numerical results that identify the origin of these oscillations in a strong acousto-optic interaction in the silicon substrate. Then we propose to explain the high amplitude of these oscillations by a relation with direct interband transitions in silicon which fall in the same range. This explanation is supported by two other experimental evidences: First, sudden changes in the phase of the detected signal are observed as the laser wavelength is tuned around the interband transitions. Second, we report on a shift of this phase change as the substrate is heated. This study shows that the effect of interband transitions on picosecond ultrasonic studies we had first demonstrated in thin metallic films can be extended to semiconductors.

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I. INTRODUCTION

Picosecond ultrasonics is a technique that makes ultrasonic measurements at very high frequency (up to several hundred GHz) possible. The conventional transducers used in acoustics for generating and detecting ultrasonic waves can not reach these frequencies. Thomsen *et al.* were the first to show that picosecond acoustic pulses could be generated and detected using ultrashort optical pulses.[1,2] The spatial extension of these pulses can be less than a few tens of nanometers so that they lend themselves very well to the characterization of thin films. In particular picosecond ultrasonics has been used to access to thicknesses, sound velocities, attenuation measurements in sub-micron thick films and multi-layers.[3–6]

Several studies have revealed a strong wavelength dependence of the echoes detected in picosecond ultrasonics. Our group has demonstrated that these changes observed in the echoes shape can be used to study some of the electronic interband transitions in thin metallic films.[7,8] Bosco *et al.* have also recently reported wavelength effects in the picosecond ultrasonic response of NiFe/NiO/Si samples.[9] Among their results they have suggested that a silicon interband transition may play a role in some of the observed wavelength effects. As this transition was out the tuning range of their laser source they could not check the accuracy of this assumption.

Here we present similar wavelength effects which complete these pioneer works: First we have observed similar effects in much different samples which only have in common the chemical nature of the substrate. Second we scan over a wavelength range, wide enough to probe around the involved interband transition. That reveals sudden changes in the phase of the detected signal. Third we present results obtained at different substrate temperatures that support this interpretation. From all of these results we deduce that in semiconductors as in metals, interband transitions may strongly influence picosecond ultrasonics studies.

The paper is organized as follows: In the first part we come back on picosecond ultrasonics and its connection with electronic structure. Then we describe the experimental setup. In a third part we present the first experimental results from which we establish that the detected oscillations come from an acousto-optic interaction in the silicon substrate. Then we propose an interpretation of these results which involves well-known interband transitions of silicon and present complementary results that support it. That let us conclude about the general effect of interband transitions in semiconductors on picosecond ultrasonics.

II. PICOSECOND ULTRASONICS AND INTERBAND TRANSITIONS

A. Picosecond ultrasonics

A schematic diagram of a picosecond ultrasonic experiment is shown in Fig. 1. A first optical pulse (the pump

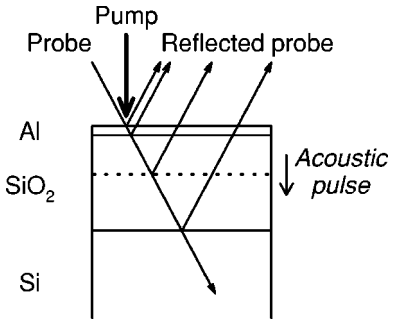

FIG. 1. Schematic diagram of the experiment. The pump light pulse generates a longitudinal acoustic pulse from the Al layer that propagates inside the sample. A small part of the probe is reflected by the acoustic pulse and interferes with the light reflected by the interfaces of the sample.

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 the particular case of a metal, absorption can be very strong, giving a length of a few nanometers. As this dimension is much smaller than the spot size (typically a few tens of microns in diameter) one can consider basically that only longitudinal waves are excited by the pump pulse. The resulting pulse propagates in the film at the longitudinal sound velocity typically a few nanometers per picosecond that explains how absorption can generate picosecond acoustic pulses. The strain pulse is reflected onto the film-substrate interface and the resulting echo returns to the surface and modifies in 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. Usually, these echoes are used to measure thicknesses of thin films, sound velocities, attenuation, and so on.[3]

B. The detection mechanism and its sensitivity to interband transitions

The detection mechanism of such an experiment is based on the modification of the optical properties of materials as they are strained. This modification affects the reflection of the probe beam. A detected echo is not the strain pulse itself but instead a measure of its impact on the optical properties of the film. The interaction between the strain wave and the optical refraction index is measured by the piezo-optic couplings. We have shown that their values strongly influence the qualitative shape of echoes.[7] As they are very sensitive to electronic interband transitions we have suggested that interband transitions may be detected by studying the shape of acoustic echoes.

In the case of a layer which is partially transparent for the probe beam, the acousto-optic interaction acts in the whole layer and the short acoustic pulse is replaced by a decaying oscillation.[10] In fact when the strain pulse is propagating in a medium where the probe light is also propagating interferences appear between the probe reflected onto the optical interfaces and the light which is partially reflected onto the acoustic pulse as shown in Fig. 1. As the pulse is propagating at the sound velocity the phase relation between both beams is changing with the delay between pump and probe and oscillations result. By applying the Bragg's condition to these interferences the period of these so-called Brillouin oscillations may be written as

$$T = \frac{\lambda}{2nv\cos\theta}, \tag{1}$$

where λ is the probe wavelength, n is the index of refraction at this wavelength, v is the sound velocity and θ is the angle of incidence. One should notice that the physical origin of Brillouin oscillations is the same as acoustic echoes which are detected in absorbing materials like metals. That implies that the phase and the amplitude of these oscillations also reflects the value of the piezo-optic couplings. Following the previous study on metallic thin films, these oscillations are expected to vary strongly near the onset of a direct interband transition. That is what is demonstrated here in silicon.

III. EXPERIMENTAL DETAILS

A. Experimental setup

The experiment is based on a conventional pump and probe setup associated with a tunable titanium:sapphire oscillator [Coherent MIRA 900f (Ref. 11)]. The laser produces 120 fs optical pulses at a repetition rate of 76 MHz centered at a wavelength adjustable between 700 and 990 nm. The laser output is split to provide pump and probe beams with crossed polarizations. The probe pulse can be delayed with respect to the pump pulse by an optical delay line based on a translation stage. Both beams are focused on the same point of the sample by a 60 mm lens. The maximum incident fluence of the pump beam is 1 J/m^2. The ratio between the pump and probe intensities is close to 1000:1. To improve the signal-to-noise ratio, the pump beam is chopped using an acousto-optic modulator and the output of the photodiode, which monitors the reflected probe, is amplified through a lock-in scheme. Fluctuations in the probe intensity were normalized by splitting the probe into signal and reference beams and monitoring the difference between the signals detected in identical photodiodes.

Most of experiments were performed with a blue probe obtained by focusing the laser beam into a 2 mm β-barium borate (BBO) crystal to generate the initial second harmonic.

Some experiments were also performed at different temperatures. In that cases the samples were bound on a conventional hot plate with a thin layer of thermal silicon grease.

B. Description of the samples

The results we present here involve samples which have the same structure (Al/X/Si where X is a transparent layer) that means composed of a transparent layer deposited onto a (100) silicon substrate. For each sample a 120 Å thick film of polycrystalline aluminum has been evaporated on the transparent layer in order to generate and detect acoustic waves with the laser. In the following we present results obtained in three samples. The first two samples are composed of an amorphous silicon dioxide (SiO_2) layer as transparent layer and differ in the thickness of this layer (respectively, 430 and 150 nm). These silica layers were deposited using plasma-enhanced chemical-vapor deposition (PECVD). In the third sample the transparent layer is composed a 548 nm thick layer of silicon nitride (Si_3N_4) deposited using low pressure chemical-vapor deposition (LPCVD).

IV. FIRST RESULTS

A. A basic experiment

Figure 2(a) reproduces the transient reflectivity signal measured in the Al/SiO_2(430 nm)/Si sample. Both pump and probe pulses are centered at 804 nm. The signal is first composed of a jump at zero time that is the electronic con-

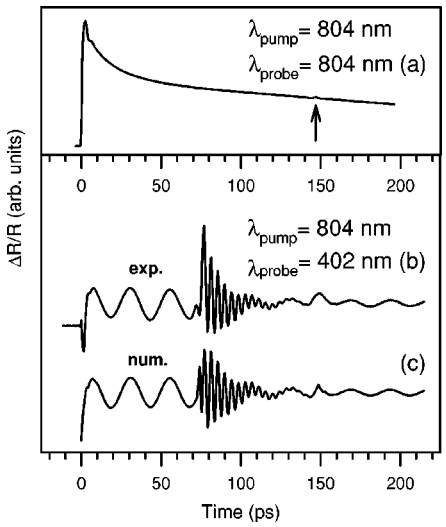

FIG. 2. (a) Reflectivity measurement on a $Al/SiO_2(430\ nm)/Si$ sample with pump and probe both centered at 804 nm. (b) Reflectivity measurement on the same sample with the same pump wavelength but with a probe centered at 402 nm. One should remark the high amplitude oscillations starting near 75 ps to which this paper is devoted. (c) Numerical result which well reproduces all the observed oscillations in part (b).

tribution to the pump-probe signal. A few picoseconds later, the pump energy is converted into heat, which diffuses on a larger time scale. This leads to a slow decrease of reflectivity. Figure 2(a) also shows an acoustic echo that appears near 150 ps. It corresponds to one round trip of the strain pulse as expected from the mechanical properties of the 430 nm thick SiO_2 layer.

B. Giant oscillations

Figure 2(b) reproduces the signal obtained in the same sample using a blue probe and an infrared pump. This result has been obtained using the same laser wavelength for the pump beam as in previous experiment [Fig. 2(a)] and the second harmonic beam for the probe. One first notes that the signal has greatly changed: The electronic, thermal and acoustic contributions have been strongly affected by the change in the probe wavelength. Concerning the acoustic part one observes a structure near 150 ps, which corresponds as in the previous experiment to the first acoustic echo detected in the Al layer.

Figure 2(b) also reveals strong oscillations: The first starts at $t=0$ and has a low frequency ($T \simeq 24$ ps). The second starts near 70 ps and has a much higher frequency ($T \simeq 5$ ps). As explained in Part II B, such oscillations may result of an acousto-optic interaction, respectively, in the SiO_2 layer and in the Si substrate. After the generation of the strain pulse in the Al layer it enters in the SiO_2 layer leading to an acousto-optic interaction in that medium. As silica is transparent one expects undamped oscillations starting at $t=0$. The expected period of this acousto-optic interaction can be deduced from Eq. (1). We get a period of 23 ps using $v=5.97$ nm/ps and $n=1.47$.[12] This value is close to the measured period of the low frequency oscillations which also start at $t=0$ and present no damping. This leads us to ascribe the low frequency oscillations to an acousto-optic interaction in the SiO_2 layer. When the strain pulse reaches the substrate another acousto-optic interaction can act in silicon. The resulting oscillations should differ from the first one by three parameters. First they should start when the pulse enters in the substrate and not at $t=0$. The corresponding delay can be deduced from the time position of the echo detected in the first experiment (75 ps). Second the absorption in silicon at such a wavelength is strong so that one expects damped oscillations. Finally the oscillations' period can be evaluated using the same Eq. (1) and literature values.[13,14] This leads to a period close to 4.3 ps. As all of these three particulartities are in good agreement with the experimental signal visible on Fig. 2(b) we ascribe the high frequency oscillations to an acousto-optic interaction in the silicon substrate.

To go further we have reproduced both oscillations by a numerical calculation visible on Fig. 2(c). The calculation is based on an analytical model which includes an instantaneous generation process for the strain pulses, limited to the Al layer, and governed by the refraction indexes. The curve displays first order calculation results for the reflectivity, with contributions arising from all the sample layers, and fitted to the experiments scale. For simplification purpose, the model assumes no ultrasonic damping. The values chosen for the SiO_2 and Al thicknesses are consistent with the deposition chambers calibration data. Optical and mechanical parameters were taken from the literature except for the piezo-optical coupling coefficients.[12–14] The model reproduces very well the experimental curve except two localized portions discussed thereafter. The period of the oscillations, as well as their phase, attenuation, and amplitude fit almost perfectly the experimental curve. It confirms our interpretation about their origin.

On Fig. 2(b) the first oscillations come from the detection process in silica while the strain pulse launched in Al travels through it. Then, close to 75 ps, the pulse is divided in two parts when it reaches the SiO_2/Si interface. The first part is transmitted into the Si substrate and causes the high frequency oscillations. While the pulse is going further deep into the substrate, the part of the probe reflected by this pulse crosses a thicker layer of silicon. Even though the pulse amplitude remains constant, the reflected probe is more and more absorbed by the substrate. As a consequence, the oscillations detected in silicon are damped. The second part of the initial pulse is reflected, and comes back to the surface through silica, giving low frequency oscillations again. This explains the low frequency oscillations that interfere with silicon's oscillations. The echo—defined as the detection of the backward pulse in the layer where it was created, here Al—appears near 150 ps as expected, although narrower. After the echo, the pulse goes back in silica and we see again low frequency oscillations. One may notice the difference between the amplitudes of these low frequency oscillations before and after 75 ps. It is due to the partial acoustical reflection at the interface SiO_2/Si. All these points can be easily verified by arbitrary changes in the calculation parameters. Differences between experiments and calculation occur near 75 and 150 ps. Since they take place when pulses are

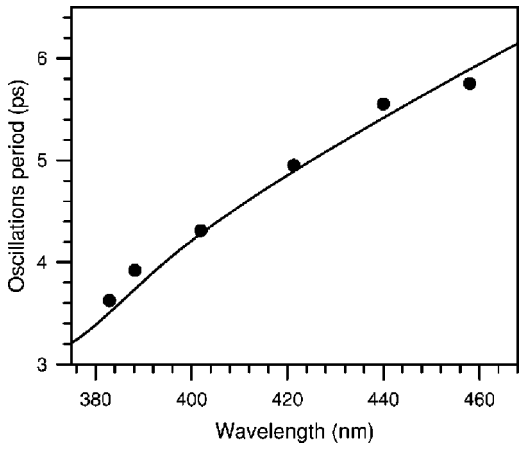

FIG. 3. The measured (symbols) and calculated periods of the Brillouin oscillations detected in the silicon substrate at different laser wavelengths. The solid line represents the values calculated using Eq. (1) and literature values for all physical parameters.

close to interfaces, this experiment might detect imperfect interfaces.

Another confirmation of this interpretation can be found in the effect of a change in the laser wavelength on the oscillations' period. Figure 3 presents the evolution of the experimental period with the probe wavelength and a theoretical curve obtained by using the Eq. (1) and literature values of the index of refraction of silicon.[13] One should notice the excellent agreement we have obtained.

Similar effects were observed in other samples as shown in Figs. 4(a) and 4(b) (respectively, in $Al/Si_3N_4(548\ nm)/Si$ and $Al/SiO_2(150\ nm)/Si$). As expected, one retrieves the same high frequency oscillations starting at different probe delays which correspond to the arrival of the strain pulse in the substrate.

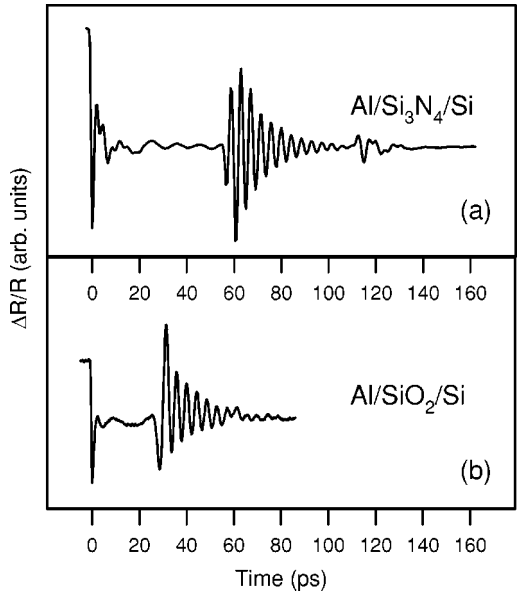

FIG. 4. Similar experiments (infrared pump and blue probe) made on samples with different transparent layers: $Al/Si_3N_4/Si$ (a) and $Al/SiO_2(150\ nm)/Si$ (b). In both curves high amplitude oscillations begin when the acoustic pulse enters the silicon substrate.

All these results finish to demonstrate that the high frequency oscillations correspond well to Brillouin oscillations detected in the Si substrate.

V. DISCUSSION AND COMPLEMENTARY RESULTS

We have presented picosecond ultrasonic experiments performed at different laser wavelengths in $Al/SiO_2/Si$. We have detected a strong oscillatory contribution of the Si substrate when the probe is tuned in the blue range. We have observed similar oscillations in other samples which have the same structure ($Al/X/Si$ where X is a transparent layer). We have also detected such oscillations in a sample which had no transparent layer (i.e. Al/Si). The oscillations detected by Bosco *et al*. are found to be of the same nature.[9] In fact their samples are composed of a thin absorbing film deposited on a transparent layer itself sputtered on a silicon substrate. This confirms the key role of the substrate in the amplitude of the oscillations. Experiments performed with a red-infrared probe in the same sample did not reveal such a signal. In both experiments, the acoustic pulse is the same since the pump beams are identical. The relative probe intensities inside the Si substrate are smaller in the blue case whereas a higher contribution is observed. The only way of understanding such results is thus to involve a strong change in the value of the detection coefficients. So we conclude that the acousto-optic parameters of silicon should be strongly dependent with the probe wavelength in the blue range. Here again the detection mechanism involved in picosecond ultrasonics is found to be strongly dependent with the laser wavelength. As in the previous studies we can rely this to an interband transition in the electronic structure of the studied material. Due to the nature of the detection mechanism, picosecond ultrasonics is sensitive to the derivatives of optical properties of materials: The derivatives of the real and imaginary parts of the index of refraction with respect to the strain. An interband transition produces a small irregularity on the optical index of a solid but a discontinuity of the first-derivative response, which could thus affect the detection mechanism in picosecond ultrasonics. The band structure of Si presents several direct interbands transitions which may be responsible for our observations. The lowest direct energy gap usually labeled E_0' is located at the Γ point in the Brillouin zone.[15] It is nearly degenerated with many other direct interband transitions labeled E_1 acting between bands which are parallel along the $\Gamma-L$ directions. At room temperature, E_0' and E_1 are close to 3.4 eV (365 nm) and are responsible for the strong absorption of silicon in this wavelength range. It should be noticed that they fall precisely in the wavelength range where we have made our observation.

When we get close to these transitions, the damping of the oscillations becomes so important that we can not measure their period anymore. As expected, the silicon is more and more opaque as the photons energy get closer to the direct gap. Nevertheless, the amplitude of the signal remains very important as shown on Fig. 5, and the curve shape then looks like an echo localized at the time when the strain pulse enters in the silicon layer, say at half the time of a round-trip. This metamorphosis of an oscillation into an echo illustrates the

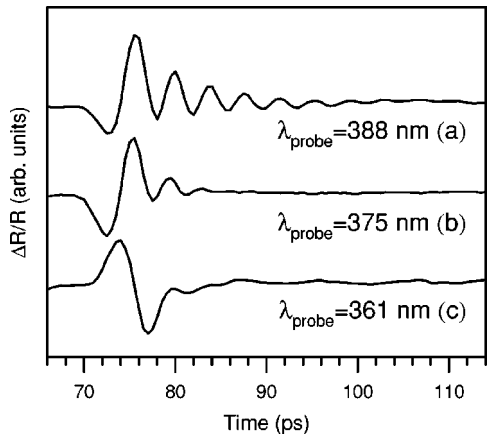

FIG. 5. Acousto-optic contribution of the silicon substrate obtained in the $Al/SiO_2(430\ nm)/Si$ sample at different laser wavelength near the onset of the 3.4 eV interband transitions. One should remark the increase of the damping of the oscillations as the wavelength decrease. One should also notice the sudden phase change which appears between 375 and 361 nm (Parts (b) and (c)).

fact that they both correspond to the same physical mechanism (see Sec. II B). This point justifies the interest for the transparent layer in our samples. In a Al/Si sample the acoustic contribution of the substrate at such wavelengths is localized in time near $t=0$ delay at which other contributions exist (in particular oscillations due to the ringing of the Al layer which frequency is close to the period of the Brillouin oscillations) and a mixing of all contributions results. When one uses a transparent layer the acoustic contribution of the substrate is still detected but starts at a longer probe delay where no other oscillations similar in frequence exists.

Figure 5 also reveals a sudden change in the phase of the signal obtained in the $Al/SiO_2(430\ nm)/Si$ sample between 375 and 361 nm. It should be noted that it is the first report of such a phenomenom in Si. Bosco *et al.* have also reported a change in the phase of the oscillations they had detected in the silicon substrate at a higher wavelength. This effect was attributed to an interference effect of the probe beam in the transparent layer. This interpretation was supported by the fact that the thickness of the layer was close to the optical wavelength of the probe in the dielectric. This is not the case for the samples studied here: The probe optical wavelength in SiO_2 is close to 250 nm whereas the thickness of the SiO_2 layer in the concerned sample is 430 nm. Another important point is the fact that we observed the same change in the acoustic signal for both samples $Al/SiO_2/Si$ whose SiO_2 thicknesses are strongly different and this happened at the same wavelength (near 365 nm).

This last observation is similar to what we had reported in copper and aluminum.[8] In fact we had observed sudden sign changes in the acoustic echoes detected in thin metallic samples when the probe wavelength was tuned around an interband transition. As we did at that time, we may compare our results to those obtained many years ago in piezomodulation. The detection mechanism of such experiments is very similar to ours even if geometry and experimental setup have nothing in common. Such experiments performed in silicon have revealed peaks near 3.4 eV (365 nm) which were attribuated to E_0' and E_1.[16] This wavelength falls precisely in the range where we have observed a phase inversion of the acoustic contribution of the Si substrate. This is another argument in favor of the role of the same interband transitions in the present observation.

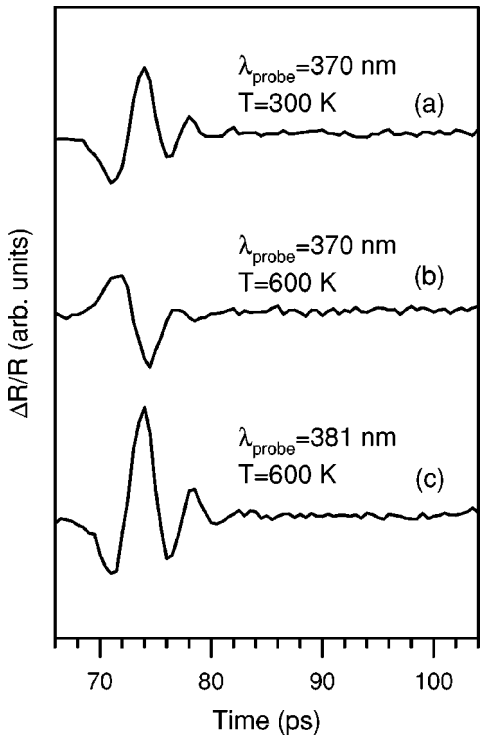

FIG. 6. Acoustic echo shape detected in silicon at different temperatures and probe wavelengths. Parts (a) and (b) reveal that temperature and wavelength have the same effect on the echo phase (see Fig. 5). In the part (c) the probe wavelength has been red-shifted in order to retrieve at high temperature the inital shape of the acoustic echo.

In order to test the proposed interpretation we explored the impact of a change in the substrate temperature on the shape of the acoustic signal detected in silicon. From the theoretical point of view, heating the substrate implies a decrease of the energy of any transition. In particular it means that probing at a fixed wavelength near the involved interband transitions and for different substrate temperatures one should observe similar changes in the echo shape as observed when we have changed the wavelength. Figure 6 presents our results obtained for a heating of 300 K above room temperature. On Figs. 6(a) and 6(b) one first observes the signals detected at the same wavelength but measured at two temperatures in the $Al/SiO_2(430\ nm)/Si$ sample. In the hot case, the echo shape seems to be as if the wavelength was tuned down the interband transition. Figure 6(c) gives the experimental signal obtained at high temperature and at a different wavelength for which the acoustic signal retrieves its inital shape. It shows that a transition effect is still present but with a red-shift of the transition as expected. From the corresponding probe wavelengths, we can estimate the change induced on the transition energy by the heating to 0.1 eV. This value can be compared to the results obtained by Lautenschlager *et al.* who have proposed a law for de-

scribing the evolution of both transitions E_0' and E_1 above 350 K.[17] Using their expression we find a change of 0.12 eV in the energy of the involved transitions with our experimental heating. This good agreement confirms the origin of our observations.

VI. CONCLUSION

We have presented experimental results that confirm the connection that exists between picosecond ultrasonic experiments and electronic structure. We started from the observation of strong oscillations in the transient reflectivity for an $Al/SiO_2/Si$ sample. Complementary experiments have demonstrated that these oscillations come from a strong change in the piezo-optic couplings of silicon near 370 nm. We have then relied the high amplitude of these oscillations to the direct band gap of silicon which falls in the same wavelength range. Similar results have been obtained in many different samples which only have in common the nature of the substrate. As previously observed in metal thin films, sudden changes in the detected signal are observed when the laser wavelength is tuned around the involved transition. Temperature was found to produce similar changes in the detected signals as expected from a theoretical point of view. Our previous experiments made on polycrystalline metals did not display such important changes in the amplitude of the probe response. That should first come from the crystalline nature of the sample. One may also suggest that it could be related to the degeneracy of E_0' and E_1 interband transitions. This raises the question of the respective role of both transition in our observations. The answer should result of similar experiments performed at low temperatures: From Ref. 17, at 100 K both transitions are separated by more than 10 nm. Such experiments could be performed in other semiconductors, in particular we are currently looking for similar effects in germanium.

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