Phase transformations of an InSb surface induced by strong femtosecond laser pulses

I. L. Shumay and U. Höfer

Max-Planck-Institut für Quantenoptik, D-85740 Garching, Germany

Phase transformations of InSb(211) induced by 130-fs laser pulses at 800 nm have been time resolved in a wide range of laser fluences. The pump-probe technique has been used, where both optical reflectivity and reflected second-harmonic generation (SHG) from the probe pulses are monitored as functions of probe versus pump pulse delay. The results are indicative of InSb undergoing a phase transition to a centrosymmetric state in a few hundred femtoseconds at sufficiently high laser fluences, similar to GaAs studied earlier. The initial ultrafast drop of the second-harmonic signal following excitation in the high-fluence regime occurs within the same time interval for both InSb and GaAs, suggesting that these changes are governed by electronic excitation effects. Subsequent studies of the InSb sample surface morphology and of the reflectivity imply the formation of an amorphous layer on the surface following laser-induced melting. It is argued that a metastable metallic phase does not appear on the surface of InSb under femtosecond laser excitation at room temperature. [S0163-1829(96)01623-2]

I. INTRODUCTION

The problem of laser-induced phase transitions in semiconductors has been the scope of intensive experimental and theoretical studies ever since the discovery of pulsed-laser annealing.[1] Of particular interest is the dynamics of phase transitions induced by ultrashort femtosecond light pulses, which are capable of depositing energy into a solid on a time scale short compared to fundamental energy relaxation times. Indeed, femtosecond laser pulses interacting with metals or semiconductors produce a large number of nonequilibrium hot carriers that strongly modify the properties of the excited surface layer of the material during the time it takes for the carriers to transfer energy to the lattice, i.e., before electronic and phonon temperatures become equal.

At sufficiently high absorbed laser fluences the surface layer of the material melts. Then, the questions are how fast one can melt a semiconductor crystal with an ultrashort light pulse, in what way the initially hot and dense electron-hole plasma may influence the dynamics of this laser-induced phase transition, and what is the interplay between thermal and nonthermal mechanisms of experimentally observed ultrafast structural phase transition (on a subpicosecond time scale) of crystalline semiconductors with either diamond (Si), (Refs. 2 and 3) or zinc-blende (GaAs) (Refs. 4–11) lattice structure induced by strong femtosecond laser pulses.

In the above experimental studies, reflected optical second-harmonic (SH) generation[12,13] has been used as a probe of the lattice structure in the near-surface layer, providing the required high temporal resolution limited only by the duration of the available laser pulses. Changes of the SH intensity were compared with the simultaneously measured changes of linear reflectivity. The observed ultrafast drop of the SH intensity following laser excitation at high laser fluences (several times higher than the threshold value) was suggestive of the material losing crystalline order within, typically, 200 fs. Since the time required for this phase transition was too short to be attributed to the usual thermal melting, implying energy transfer from excited carriers to phonons followed by its thermalization between phonon modes, the hypothesis of a plasma-assisted phase transition[14,15] has been used to explain the experimental results. In this model, when a sufficient number of valence electrons (about 10%) is excited from bonding valence-band states to antibonding conduction-band states, covalent bonding is no longer able to support the tetrahedrally coordinated crystal structure, and within a few hundred femtoseconds after excitation the semiconductor evolves into a liquid metallic state possessing inversion symmetry.[5,6] The change of the atomic coordination associated with this transition requires a time approximately equal to the reciprocal of the lattice vibrational frequency. Indeed, femtosecond time-resolved studies of reflectivity[8,9,11] have shown that at fluences 2.5–3 times the threshold value the temporal evolution of the dielectric constants of GaAs is consistent with the collapse of the band gap, leading to GaAs attaining metallic properties in just about 300 fs.

Based on the results of the experimental studies, this hypothesis has been used recently as a basis for a detailed theoretical consideration of how the lattice of a cubic semiconductor can be transferred into a metallic state in the presence of a dense hot electron-hole plasma.[11] It was shown that the lattice structure of semiconductors with diamond or zinc-blende symmetry (for example, Si or GaAs, respectively) becomes unstable with respect to the β-tin structure under these conditions, and that this instability, together with an effective repulsive potential, facilitates a structural phase transition into a centrosymmetric phase on a subpicosecond time scale. Specifically, the calculations predict that in silicon the displacement of atoms can be as large as 1 Å, and that atoms can have a kinetic energy of 0.4 eV within just 120 fs after the laser pulse; the gap between valence and conduction bands vanishes, and the material attains metallic properties. Subsequently, the crystal rapidly melts because of the high kinetic energy of the atoms. Similar results were obtained for GaAs, the time of the phase transition being longer (about 200 fs) because of the smaller phonon frequency in GaAs.

However, some controversy still remains concerning the nature of the transient nonequilibrium state existing within

the first several hundred femtoseconds after excitation. In particular, a question to be answered is whether the semiconductor crystal structure evolves directly into a disordered liquid state, or whether there is a transient nonequilibrium centrosymmetric crystalline phase preceeding the liquid metallic phase.[16,17]

Another problem is related to interpretation of the experimental data. The time-resolved SH data corrected for changes of the dielectric function at the fundamental frequency indicate a very steep drop of the second-order nonlinearity of GaAs on a time scale comparable with the pulse duration.[10,11] This initial drop has been attributed either to purely electronic effects (bond-charge depletion and band-gap shrinkage), which occur in structurally intact solid,[11] or to structural disordering of the crystal's lattice[10] caused by strong electronic excitation. The laser-induced reflectivity changes in GaAs have also been alternatively interpreted as being caused mainly by changes in the electronic band structure,[9] or by free-carrier effects.[11]

Then, in order to clarify the remaining questions, it would be interesting to study the dynamics of the laser-induced phase transition in some other material with a structure similar to that of GaAs, for example, InSb, and compare the results with those obtained for GaAs under similar experimental conditions. One may expect different dynamics of the laser-induced phase transition into a centrosymmetric metallic phase in this material. First of all, because of the narrow band gap of InSb (the fundamental band gap in InSb at room temperature is only 0.18 eV), 1.55-eV photons delivered by a femtosecond Ti-sapphire laser system can excite electrons high into the conduction band with large excess energy, resulting in a very high initial electronic temperature. Then, it will take longer time for the highly excited electronic subsystem of the semiconductor to relax to thermal equilibrium with the lattice, since the phonon emission rate in polar semiconductors essentially saturates at high electronic energies even at high carrier densities.[18] Simultaneously, an electronic temperature much higher than the band gap will result in a higher rate of impact ionization. This would tend to keep the electron-hole plasma density high by counterbalancing the Auger recombination.[19] These conditions would favor an electronic mechanism of the phase transformation.

On the other hand, the characteristic dynamics of the phase transition into a metallic phase, when the conditions for the phonon instability are satisfied, depends on a microscopic composition of the material. Thus, larger masses of atoms composing the InSb lattice and a larger lattice constant are both expected to slow down the transition into a centrosymmetric β-tin structure, compared to GaAs.[16]

There is another reason to believe that InSb is a particularly attractive material for studying ultrafast laser-induced phase transitions. It was found earlier that excitation of InSb immersed in liquid nitrogen with 10-ns pulses of a Nd:YAG (yttrium aluminum garnet) laser with the energy fluence of 0.06 J/cm^2 results in a structural phase transition of InSb into a metastable metallic state with β-tin structure,[20] supposedly without melting of the crystal. The authors suggested that a plasma-assisted mechanism accounts for this phase transition. However, the density of the electron-hole plasma produced by a nanosecond laser pulse was insufficient for such a mechanism to be effective, and the authors

had to suggest in addition that condensation of electron-hole droplets and an inhomogeneous coupling of the laser beam with the sample surface could be responsible the required high carrier density in their experiments. The fact that the metastable phase could only be produced at initial sample temperatures below 190 K has been attributed to higher carrier densities, which could be achieved without melting the sample, and also to transient hardening. Obviously, femtosecond laser pulses generating much higher carrier densities (above 10^{22} cm^{-3} in the present experiments) and large transient strain accompanying the formation of a dense electron-hole plasma would facilitate observation of such solid-to-solid phase transition in InSb.

We report here on fs time-resolved optical studies of fast laser-induced phase transformations in InSb. We used a pump-and-probe technique, where both the optical reflectivity and the reflected SHG intensity were monitored as functions of probe versus pump pulse delay. The measurements were made in a wide range of pump fluences. The results we obtained at the laser fluences several times higher than the threshold where permanent modification of the surface morphology occurs after excitation can be interpreted in terms of the plasma-assisted lattice instability model assuming an ultrafast melting via a plasma-assisted structural phase transition. However, in the high-fluence regime the fall time of the SH intensity observed with InSb was found to be about the same as that measured for GaAs under the same experimental conditions and is limited by the pulse duration (130 fs). This observation contradicts the hypothesis that structural changes govern the ultrafast fall of the SH intensity and are more consistent with the assumption that purely electronic excitation effects are responsible for the ultrafast initial changes of the SH intensity.

Permanent changes of the surface morphology and the optical reflectivity of the InSb sample after it was illuminated with laser pulses of the same wavelength and fluence but different pulse duration, as well as the results of the pump-probe measurements at low laser fluences, are more consistent with the formation of an amorphous layer on the surface than with a phase transition into a metastable metallic state.

II. EXPERIMENT

In the experiments, we used pulses at 800 nm delivered by the laser system consisting of a femtosecond self-mode-locked Ti-sapphire laser oscillator (Spectra-Physics, Tsunami) and a CPA (chirped-pulse amplification) regenerative amplifier pumped by a cw-pumped, Q-switched, internally frequency-doubled Nd:YLF (lithium yttrium fluoride) laser (Quantronix). The system provided a uniform nearly Gaussian beam profile and high stability of the output pulse energy and duration. Typically, the pulse duration measured from the cross correlation of the pump and probe pulses on the sample was 130 fs.

For the pump-probe measurements, a small fraction of the pump pulse was split off and was used to probe the laser-induced changes in both the optical reflectivity and the reflected SH intensity after introducing a variable optical delay.

We used mirror-quality polished p-type wafers of InSb(211). A p-polarized probe beam was incident on the

surface at an angle of 34°, whereas an *s*-polarized pump beam was incident on the surface at an angle of 27°. Polarizations of the two beams were made orthogonal in order to reduce their coherent interaction near zero delay.[4] The pump pulse energy could be varied with a half-wave plate and a polarizer. The SH radiation produced by the probe beam was properly filtered out spatially, so that no signal originating from the stronger pump beam was seen by the detection system (a monochromator with an attached photomultiplier was used for measuring the SH intensity, and a photodiode was used for detecting changes in reflectivity). The pump and probe pulses overlaping in time and space on the surface gave rise to the SH signal generated in the direction bisecting the angle between specular reflected pump and probe beams; this signal was used for adjusting both the probe versus pump delay and for optimizing the superposition of the two beams on the surface. The beam spot diameters on the surface were measured to be 50 μm for the probe beam, and 180 μm for the pump beam. In addition, a small diaphragm was installed in the diverging reflected probe beam to ensure that a homogeneously excited central portion (10%) of the pump-illuminated surface area was seen by the detection system. The probe pulse fluence was kept constant at about 0.01 J/cm^2. The laser was operated with a repetition rate of 0.3 Hz, and the sample was moved between the shots to avoid accumulation of damage.

It should be noted that InSb supplies additional difficulties for an experimentalist. First, it is a very soft material, so that it is not easy to get a mirror-quality polished surface, as in the case of Si or GaAs. This problem has been solved by averaging the signal over a few dozen laser shots. Second, the available samples are small in size (typically, about 1–2 cm^2). Third, the high coefficient of absorption [about 10^5 cm^{-1} at 800 nm (Ref. 21)] and relatively low melting temperature (800 K), combined, make it difficult to study changes of the reflectivity and the second harmonic in the low-fluence range (below the threshold of the phase transition).

III. RESULTS AND DISCUSSION

First, we analyze the results of the pump-probe measurements.

The reflected SH intensity and the reflectivity as functions of the probe pulse delay are shown in Figs. 1 and 2, respectively. The amplitude of changes seen at time delays of up to 4 ps depends on laser fluence. The curves depicted in Figs. 1 and 2 were taken at pump pulse fluences above the threshold of the laser-induced permanent changes of the surface morphology (see below). A crude estimate based on the value of the laser fluence and the coefficient of absorption, assuming that pump photons are absorbed by electronic transitions from the valence band to the conduction band shows that even at a laser fluence of 0.013 J/cm^2 the density of the photoexcited electron-hole plasma reaches values above 10^{22} cm^{-3}.

At low fluences (less than 0.05 J/cm^2) the second harmonic shows a fast drop within several hundred femtoseconds followed by slower changes on a time scale of picoseconds. At higher fluences the second harmonic drops faster, and eventually goes down to zero within the first picosecond
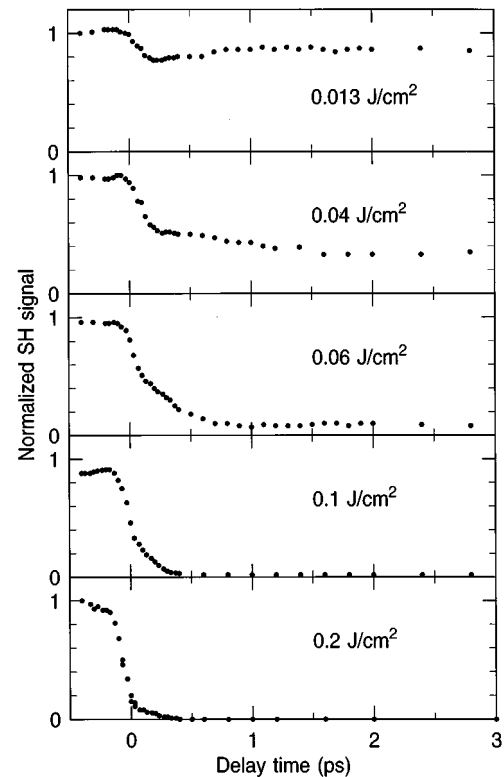

FIG. 1. The SH signal from the probe pulse as a function of delay time with respect to the pump pulse for different pump fluences. Unity corresponds to the SH signal in the absence of pump pulses.

after excitation. Interestingly, at fluences above 0.06 J/cm^2 one can clearly see that the initially very fast step in the SH signal is followed by a slower tail at time delays of several hundred femtoseconds. At the pump fluence of 0.2 J/cm^2 the second harmonic disappears within less than 300 fs. However, the slow component is still there. We also note that the initial fast decay of the second harmonic is in fact limited by the finite duration of the probe pulse.

The fall of the second harmonic is accompanied by the rise of the optical reflectivity measured at the fundamental frequency (Fig. 2). At pump fluence of 0.013 J/cm^2 the reflectivity shows only minor changes of several percent, which develop on a time scale of several picoseconds. As the pump fluence gets higher, there appears an initial fast rise followed by slower changes. Simultaneously, the height of the fast step in reflectivity increases at higher fluences, until at fluences of more than 0.2 J/cm^2 it saturates at about 60% of the unperturbed value. Also, the characteristic time of the fast changing component of reflectivity gets shorter at higher laser fluences. Nevertheless, at a pump fluence of 0.2 J/cm^2 the 10%–90% changes of reflectivity develop within 450 fs, whereas similar changes of the second harmonic occur within 240 fs.

It is also clearly seen that at low and medium laser fluences there is an initial small rise of the second harmonic and a corresponding drop of the reflectivity near zero delay. This feature is similar to that observed earlier in GaAs (Ref. 7) and disappears at higher laser fluences.

Generally, the above behavior of the reflected second harmonic and the linear reflectivity observed with InSb re-
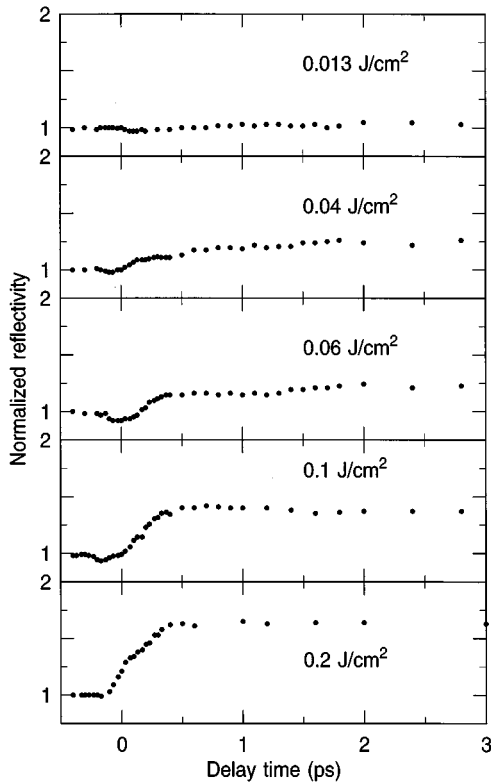
FIG. 2. Reflectivity of InSb at 800 nm as a function of delay for different pump fluences. These data were measured simultaneously with the second harmonic data of Fig. 1. Unity corresponds to the sample reflectivity in the absence of pump pulses.

FIG. 3. Time-resolved relative changes of the reflectivity and the SH intensity for InSb and GaAs at high laser fluences (0.2 J/cm^2 for InSb and 0.6 J/cm^2 for GaAs). Also shown is the cross correlation of the pump and probe pulses. The solid curves are drawn to guide the eye.

sembles that observed previously with GaAs.[4–11] Thus, given the structural similarity of the two semiconductors, one can use the similar arguments in explaining the results obtained.

It has been understood in a recent series of experiments[7–11] that the large modification of the linear dielectric function at both the fundamental and the SH frequencies can cause substantial changes in the SH signal, especially, in the range of low and medium pump fluences. Indeed, the SH intensity is governed not only by the second-order nonlinear optical susceptibility $\chi^{(2)}$, which reflects the spatial symmetry of the crystalline lattice but also by the Fresnel's factor.[12] On a subpicosecond time scale after excitation, the laser-induced changes of the dielectric function result from an electronic excitation and are thus characterised by an ultrafast response time. Consequently, when analyzing the SH data, one should take into account that this effect may mask the actual changes of the nonlinear-optical susceptibility.

The slow changes of the SH intensity and of the optical reflectivity at lower pump fluences can be attributed to thermal and electon-hole plasma effects influencing the dielectric constants. Although we could not find optical parameters of a molten InSb in the literature, the high reflectivity of the sample after several hundred femtoseconds at high excitation fluences is most probably indicative of the formation of a metallic liquid on the surface of the crystal. This conclusion is also supported by subsequent studies of the surface morphology (see below).

At high excitation fluences the SH signal disappears completely within several hundred femtoseconds. This behavior
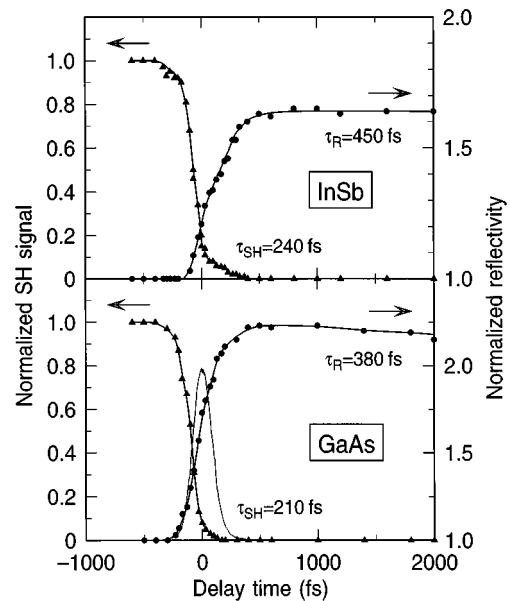
cannot be attributed to changes of the Fresnel factor and implies that the bulk dipole second-order nonlinear-optical susceptibility $\chi^{(2)}$ goes to zero on this time scale.[10] The drop of the second-order bulk nonlinearity was usually explained in terms of the hypothesis that the near-surface layer of the semiconductor undergoes a structural phase transition into a centrosymmetric state where SHG is symmetry forbidden in the electric-dipole approximation. Since the rise of the linear optical reflectivity and the corresponding fall of the second harmonic in this fluence range of the pump pulses occur too fast to be explained by normal thermal melting of the semiconductor, by analogy with GaAs, this fast structural phase transition can be attributed to electronic mechanism, that is, plasma-induced lattice instability facilitating phase transition into a metallic phase.[16] The time of this phase transformation is inversely proportional to phonon frequency. Consequently, it should be longer for the InSb lattice, which is composed of much heavier atoms than that of GaAs [LO phonon wave number in GaAs is 285.0 cm^{-1}, compared to 196.7 cm^{-1} in InSb (Ref. 22)].

Keeping in mind that at high pump fluences the characteristic fall time of the SH signal saturates as a function of the pump fluence,[6] we have compared the time scales of pump-induced changes of the linear reflectivity and the second harmonic in the high fluence range for GaAs and InSb *in exactly the same* experimental arrangement (pump fluences where fast changes dominate the SH response were a factor of 3 higher in the case of GaAs). It turned out that the characteristic times of the fast changes (between 10% and 90% of the initial values) of the second harmonic of the two semiconductors are the same within 10% (Fig. 3). Moreover, if one compares only the steep initial fall of the second harmonic, without taking into account the tail that is observed in the case of InSb, then the changes of the second harmonic for the two semiconductors are exactly the same and are, in fact,

limited by the probe pulse duration. These findings are similar to the results of others: with shorter laser pulses the initial drop of the second harmonic appears to occur faster,[5–7,10,11] but it is still limited by the laser pulse duration.

The changes of the optical reflectivity always develop slower than the corresponding changes of the SH signal (Fig. 3). This fact can be interpreted as being due to the high sensitivity of SHG to laser-induced structural changes (the value of the second-order susceptibility is very sensitive to the long-range order of the lattice, the characteristic spatial scale being the optical wavelength[4,10]) and to the laser-induced changes of the linear dielectric functions at both the fundamental and the SH frequencies.[7–11]

The fact that the reflected SH intensity drops equally fast for InSb and GaAs is in obvious contradiction to theoretical expectations based on the lattice instability model.[16] Similarly, characteristics of the phase transformation in silicon and gallium arsenide have been found to be very much alike.[11] Based on this fact, the authors of Ref. 11 suggested a phenomenological two-step model of the laser-induced phase transition. In this model, there is an initial excitation stage during which the changes of the SH signal and of the optical reflectivity are caused by an electronic excitation of a structurally intact solid material. This excitation stage is followed by a transition stage during which the material undergoes a structural change towards a disordered liquid phase. The excitation stage is limited by the duration of the laser pulse, whereas the transition stage develops on a longer time scale of several hundred femtoseconds or longer, depending on laser fluence. It was suggested that the principal physical effects responsible for the changes of the optical parameters of the material during the excitation stage are state and band filling, renormalization of the band structure, and free-carrier effects, the latter being the dominant factor determining the linear optical response.[11]

In order to explain the initial ultrafast decay of the SH signal, it was suggested in Ref. 11 that strong electronic excitation induces changes in the value of the microscopic nonlinear optical susceptibility $\chi^{(2)}$, the major effects being saturation of the optical transitions involved in absorption of the pump pulses (bond-charge depletion) and band-gap shrinkage. Both of these effects could cause the decrease of the $\chi^{(2)}$ in GaAs at the probe photon energy of about 2 eV used in the previous experiments.[11] The plasma-assisted type of the structural phase transition was assumed to occur only at high pump fluences (a factor of 3 or more higher than the threshold value) and would account for the complete disappearance of the SH signal in a few hundred femtoseconds.

From this point of view, the initial ultrafast decay of the SH signal in our experiments with InSb and GaAs, which is limited by the probe pulse duration, can be attributed to electronic excitation, whereas the tail that is present in the SH data for InSb but is absent in those for GaAs is due to the slower structural dynamics of the InSb lattice, in qualitative agreement with the electronically induced lattice instability model.[16]

However, the band-gap shrinkage in InSb in our case should have an opposite effect on $\chi^{(2)}$ compared to GaAs. Indeed, the second-order nonlinearity of GaAs has a maximum at the probe wavelength of 2 eV used in Ref. 11, and a minimum at 2.5 eV. Consequently, the band shrinkage would

cause a reduction of the second-order nonlinear-optical susceptibility.[11] On the contrary, at our probe photon energy of 1.55 eV $\chi^{(2)}$ of InSb is close to minimum[23,24] and should increase if the band gap shrinks. Thus, band-gap shrinkage cannot be a dominant effect of the electronic excitation that reduces the value of $\chi^{(2)}$.

However, bond-charge depletion, or saturation of optical transitions coupled by the laser field at a high level of excitation should have an effect on $\chi^{(2)}$ causing its reduction. For example, optical pump-induced saturation of surface states plays a dominant role in the decrease of the nonlinear-optical response of clean Si surfaces.[25]

It was suggested in Ref. 10 that strong electronic excitation may result in a transient disordering of the crystal lattice even below the threshold of the plasma-induced structural phase transition. These structural changes cause a loss of the long-range order of the lattice and thus can also account for the fast decrease of the second-order nonlinear optical susceptibility. However, one may expect that the time scale of these structural changes would be different for different semiconductors.

Thus, our experimental data provide further evidence that purely electronic effects are likely to be responsible for the ultrafast initial drop of the SH intensity induced by strong femtosecond-laser excitation, followed by structural changes that occur on a time scale of several hundred femtoseconds (in the high-fluence regime of excitation), possibly via a plasma-induced lattice instability mechanism.[16] However, to our knowledge, a detailed theoretical calculation of the effect of an electronic excitation on SHG, as well as the effect of the transient lattice disordering,[10] is missing at the present moment.

As mentioned above, another interesting aspect of studying femtosecond-laser-induced phase transitions in InSb is trying to detect a metastable metallic phase that at room temperature must live several hours after laser excitation. This phase observed by Gromov *et al.*[20] has a β-tin lattice symmetry and is thus *exactly* the phase into which a zinc-blende lattice of InSb is expected to evolve according to the plasma-assisted mechanism of the phase transition.[16] It was claimed in Ref. 20 that a phase transition into this metastable metallic phase can be induced at laser fluences below those required for melting of the surface layer. The new phase is centrosymmetric (body-centered tetragonal lattice with D_{4h} symmetry), and its reflectivity mesured at 632.8 nm was found to be 30% higher than that of normal InSb. Consequently, phase transition into this state would result in a decrease of the reflected SH intensity and in an increase of the linear optical reflectivity. With this in mind, we carefully studied the dynamics of the phase transition, together with the laser-produced changes of the surface morphology at low fluences.

Consider first the results of the time-resolved studies at the pump fluence of 0.013 J/cm^2. If the plasma-induced transition into a metastable metallic phase takes place, then the fast drop of the second harmonic by 20% could be attributed to partial metallization of the surface (in Ref. 20 several laser pulses were required to achieve complete metallization of the surface). This step should then persist for a long time (about 15 h at room temperature[20]). However, although the step in the SH signal and the rise of reflectivity measured with this pump fluence and with a time delay of 130 ps were essen-
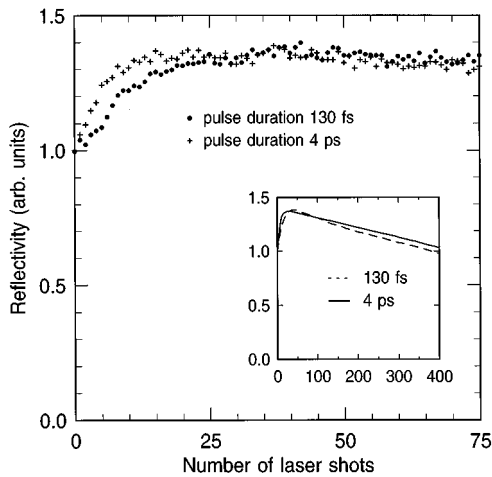
FIG. 4. Changes of reflectivity of InSb as a function of the number of the absorbed laser pulses with the fluence of 0.03 J/cm^2 and the pulse repetition rate 0.3 Hz. The data are presented for two pulse durations: ●, 130 fs; +, 4 ps. Reflectivity of the sample is normalized to its nonperturbed value. The behavior of the reflectivity on a larger scale is shown in the inset: dashed line, for 130-fs pulses; solid line, for 4-ps pulses.

FIG. 5. Reflected SH signal from InSb as a function of the number of the absorbed laser pulses with the fluence 0.03 J/cm^2 and the repetition rate 0.3 Hz. The data are presented for two pulse durations: ●, 130 fs; +, 4 ps. These data were measured simultaneously with the second harmonic data of Fig. 4. The data are normalized to nonperturbed values of the second-harmonic signal. The behavior of the SH on a larger scale is shown in the inset: dashed line, data for 130-fs pulses; solid line, those for 4-ps pulses.

tially the same as those measured at a time delay of 2 ps, these changes were completely recovered before the arrival of the next probe pulse in a time interval of 0.3 s.

We then studied accumulation of the laser-produced permanent surface modification. In these measurements, a single laser beam was used with the incident fluence of 0.03 J/cm^2 and the pulse repetition rate of 0.3 Hz. Position of the sample was not changed between laser shots. The experiment was done for two pulse durations: 130 fs and 4 ps (pulse duration could be conveniently changed by simply introducing a frequency chirp with the help of an optical compressor, without disturbing experimental arrangement or changing pulse energy). The accumulation of the surface modification seen by the next arriving pulse is shown in Figs. 4 and 5, where changes of the sample reflectivity and of the reflected SH intensity, respectively, are shown as functions of the number of the absorbed laser shots for two different pulse durations.

It is seen that the reflectivity rises as the sample is exposed to more and more laser pulses and gradually reaches a value that is about 38% higher than the nonperturbed reflectivity of InSb. The surface was found to remain flat at this stage. However, after some time the reflectivity starts to decrease. This decrease of reflectivity corresponds to accumulation of surface damage with the formation of a crater leading to large light scattering. The SH signal drops on the same time scale as the rise of the reflectivity and levels off at a value amounting to several percent of the nonperturbed value. If the laser fluence was decreased, accumulation of surface modification slowed down. However, an interesting feature to note is the obviously faster accumulation of the surface modification induced by 4-ps laser pulses compared to those induced by 130-fs pulses of the same fluence. This effect is exactly opposite to what one would expect if permanent changes of the reflectivity and the second harmonic were due to a plasma-assisted phase transition of the InSb surface layer to a metallic state, because the plasma density
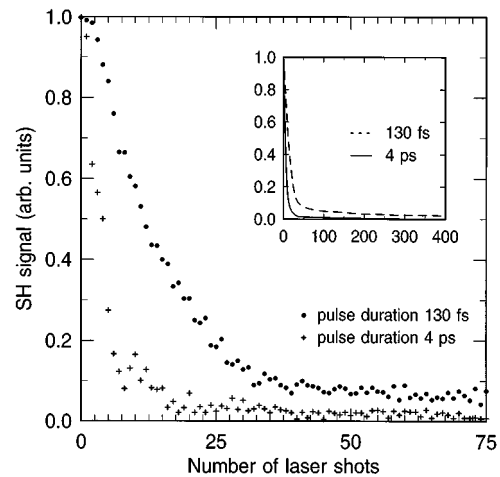
is higher for femtosecond excitation (carrier diffusion can be neglected), whereas the phase transition is expected to occur within only several hundred femtoseconds after excitation.

The question to be answered is what is the nature of the phase with high reflectivity. Examination of the surface under an optical microscope shows that the phase with increased reflectivity starts to appear at pump fluences above 0.01 J/cm^2. Initially, there appears a small spot in the center of the illuminated surface area. As the laser fluence is increased, the size of the spot with higher reflectivity increases, then, at still higher fluence, the central part of the spot becomes darker than the surrounding nonexposed surface and is surrounded by a ring with increased reflectivity. These findings are similar to the laser-induced modification of an InSb surface observed earlier.[26] Finally, at fluences higher than 0.06 J/cm^2 the surface no longer remains flat, and there appears a typical crater of laser-produced damage.

The above observations precisely resemble the picture of surface amorphization observed under picosecond laser excitation of Si (Ref. 27) or GaAs (Ref. 28). Indeed, amorphous InSb has a larger dielectric constant at our probe wavelength of 800 nm than an InSb crystal,[29] which can explain the observed rise of the optical reflectivity. The large absorption coefficient of InSb results in a steep gradient of the laser intensity penetrating into the bulk of the sample, so that a very thin molten layer appears on the surface at fluences exceeding the threshold by a small amount. Rapid cooling of this layer prevents an epitaxial growth of the crystalline lattice, and the semiconductor solidifies in an amorphous state. Amorphization naturally explains the fall of the SH signal in Fig. 4. Note that the large gradient of the laser intensity in the near-surface layer of the sample also contributes to the fact that the laser-induced changes of the reflectivity and of the second harmonic observed in our time-resolved measurements (Figs. 1 and 2) are strongly fluence dependent.

To summarize the above observations, permanent changes

of reflectivity induced on the surface of InSb can be explained naturally by a surface amorphization induced by ultrashort light pulses. The facts that the increased reflectivity does not relax after several days, that the dependence of accumulation dynamics on pulse duration favors longer pulses, and that permanent changes of reflectivity appear only when there is a larger preceding transient rise of the reflectivity and a corresponding fall of the second harmonic, as seen in time-resolved measurements, are inconsistent with the model of a plasma-assisted solid-solid phase transition of InSb surface into a metastable metallic state.

IV. CONCLUSION

We have studied femtosecond-laser-induced phase transformations of a crystalline InSb by simultaneously measuring the optical reflectivity, and the SH signal generated at the surface as functions of the probe pulse delay after excitation, and of the pump pulse fluence.

The general picture we obtained is similar to that previously observed with GaAs. At high pump fluences, the second harmonic and the reflectivity change very fast, on a time scale of several hundred femtoseconds, suggesting an electron-hole plasma-assisted mechanism of the phase tran-

sition, rather than a thermal one. The ultrafast initial fall of the reflected SH intensity at high excitation fluences was found to have about the same duration for InSb and GaAs and is limited by the laser pulse duration. This circumstance suggests that this fall is governed by purely electronic effects.

The conditions for the onset of permanent laser-induced changes of the reflectivity are more consistent with a laser-produced amorphization of the surface layer than with an appearance of a metastable centrosymmetric metallic phase. However, in order to make a final conclusion, the structure of the phase with a permanently high reflectivity which is produced on the surface of InSb by a femtosecond-laser excitation should be studied directly by using other structure-sensitive techniques, for example, by Raman microprobe analysis,[30] or particle scattering, or x-ray diffraction.

[1] See, for example, S. A. Akhmanov, N. I. Koroteev, and I. L. Shumay, *Nonlinear Optical Diagnostics of Laser-Excited Semiconductor Surfaces*, Laser Science and Technology. An International Handbook, Vol. 2, edited by V.S. Letokhov, C.V. Shank, Y.R. Shen, and H. Walther (Harwood, Chur, Switzerland, 1989), and references therein.

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