Ultrafast phase transitions after femtosecond laser irradiation of indium phosphide

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The structural transformation dynamics of single-crystalline indium phosphide irradiated with 150 fs laser pulses at 800 nm has been investigated by means of time-resolved reflectivity measurements covering a time window from 150 fs up to 500 ns. The results obtained show that for fluences above the threshold of 0.16 J/cm² thermal melting of the material occurs on the time scale of 1–2 ps, while ablation at higher fluences (>0.23 J/cm²) is preceded by an ultrafast phase transition (“nonthermal melting”) occurring within 400 fs after the arrival of the pulse to the surface. The evolution of the reflectivity on a longer time scale shows a resolidification time typically around 25 ns after which an amorphous layer several tens of nanometer thick is formed on the surface.

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I. INTRODUCTION

The dynamics of femtosecond laser-induced phase transitions has been intensively studied in semiconductors such as silicon^{1,2} and the III-V compounds gallium arsenide^{2,3} (GaAs) and indium antimonide⁴ (InSb). Compared to these materials indium phosphide (InP), another III-V compound semiconductor, has a number of beneficial properties which make it interesting for high-frequency optoelectronic applications.⁵ Indeed, with the ever increasing intrinsic speed of photonic devices, InP has the potential to become the dominant material for use in future ultrahigh-speed detectors, optical switches, transistors, etc.⁶ However, only very few studies have investigated the dynamics of phase transitions of InP upon laser irradiation such that, to date, only nanosecond (ns)-laser pulse induced melting has been investigated by time-resolved optical measurements.^{7,8} Furthermore, these two studies do not provide a consistent interpretation of the transient evolution of the surface reflectivity upon melting.

With respect to the work on femtosecond (fs)-laser pulse irradiation, time-resolved measurements probing the carrier dynamics have been reported solely at carrier densities below any structural modification threshold^{9,10} while at higher fluences only static measurements of the final state of the material have been performed.^{11–13} In this paper we report a detailed study of the structural transformation dynamics of single-crystalline InP under fs-laser pulses, covering a time window from 150 fs up to 500 ns. This has allowed us to investigate in detail melting, ablation, and rapid solidification phenomena in this material as well as nonthermal ultrafast phase transitions which occur at large fluences above the melting threshold. Additionally, our study includes the measurements of the reflectivity of liquid InP at two different wavelengths (514.5 and 800 nm) and a quantitative estimation of the carrier density required for inducing an ultrafast nonthermal phase transition in InP.

II. EXPERIMENTAL DETAILS

The samples were 400 μm thick polished (100) InP wafers (American Xtal Technology, Fremont, USA, n -doped). The laser used for irradiation was a chirped pulse amplification Ti:sapphire laser system (Spectra Physics, Spitfire), providing, at the sample, linearly polarized pulses of ~ 150 fs duration at a wavelength of 800 nm. At this wavelength, in the linear absorption regime, the fundamental absorption mechanism in InP (band gap of 1.35 eV) is a direct interband transition.

The temporal evolution of the surface reflectivity upon irradiation has been measured using two different experimental setups with complementary time scales. A standard fs-resolution pump-probe (fs-PP) setup has been used to measure the reflectivity evolution for time delays between 150 fs and 800 ps. For longer times (350 ps–500 ns) real-time reflectivity (RTR) measurements were performed simultaneously by means of a single sweep streak camera and a fast photodiode. In all cases the surface region was irradiated only once.

In the fs-PP experiment (see inset in Fig. 1), the laser pulse from the amplifier is first split into two orthogonally polarized pump and probe pulses. The pump pulse is then focused at normal incidence at the sample surface to a Gaussian spot diameter ($1/e^2$) of ~ 100 μm . After passing through a delay line, the p -polarized probe pulse is focused at an angle of incidence of 12° to a spot diameter of ~ 18 μm in the center of the region irradiated by the pump pulse. The reflected probe signal is then detected with a ns time-resolution photodiode coupled to a sampling oscilloscope. In the RTR measurements, a 1 μs long square pulse from a single-mode Ar⁺ laser operating at 514.5 nm acts as the probe. The respective spot diameters for the pump and probe pulses in this case are ~ 120 μm and ~ 30 μm . The reflected probe intensity is simultaneously recorded by a streak camera (time resolution of 350 ps in a time window of 50 ns) and by a photodiode/oscilloscope detection system (a few ns time resolution in a time window of 500 ns). Further details regarding this RTR setup can be found elsewhere.¹⁴

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FIG. 1. Normalized surface reflectivity change as a function of time measured for three different pump fluence levels (A: $\phi_0 = 1.26 \phi_m$, B: $\phi_0 = 2.06 \phi_m$, C: $\phi_0 = 5.35 \phi_m$). The lines are to guide the eye. The inset shows the experimental scheme of the fs pump-probe experiment.

III. RESULTS AND DISCUSSION

Figure 1 shows the temporal evolution of the reflectivity changes measured in the fs-PP experiment upon irradiation at three different pump peak fluences ϕ_0 above the melting (curve A) and ablation thresholds (curves B and C). In the curves, the reflectivity changes have been normalized to the value of the single-crystalline material ($R_C[800 \text{ nm}] = 0.31$) such that $\Delta R/R = \{R(t) - R_C\}/R_C$, where $R(t)$ corresponds to the measured reflectivity value at a given time delay. The measured melting and ablation thresholds are consistent within the experimental error with those given in Ref. 12 ($\phi_m = 0.16 \text{ J/cm}^2$ and $\phi_{abl} = 0.23 \text{ J/cm}^2$, respectively). At a fluence level exceeding the melting threshold ($\phi_0 = 1.26 \phi_m$, curve A) but below the ablation threshold ($\phi_{abl} = 1.44 \phi_m$), a reflectivity change of more than 100% occurs within 1–2 ps. Subsequently, the reflectivity decreases slightly reaching finally a constant level of $\Delta R/R \sim 0.75$ at ~ 18 ps. This behavior can be interpreted in terms of the formation of a thin liquid layer on the surface that propagates in depth, leading to the formation of an optically thick molten layer for times after ~ 18 ps. The evolution of the reflectivity in such a scenario has been modeled by considering a thin film of molten material with variable thickness on top of a crystalline (c-InP) substrate. The optical model used takes into consideration the fully coherent superposition of all Fresnel reflections at all interfaces (air/liquid and liquid/solid) for the given wavelength (800 nm), angle of incidence (12°), and polarization (p-polarized beam).^{15,16} Unfortunately, the refractive index ($n + ik$) of liquid InP (l-InP) is not known and therefore as a reasonable approach the values for liquid GaAs (which has a band structure in the solid phase very similar to that of InP) have been used. The values used for simulation are thus $(n + ik)(\text{l-GaAs}) = (2.4 + i3.5)$ (Ref. 3) and $(n + ik)(\text{c-InP}) = (3.5 + i0.2)$ (Ref. 17) at the probing wavelength of 800 nm. The simulations show a maximum 100% reflectivity increase for a molten film thickness of ~ 50 nm followed by a saturation value corresponding to an optically thick layer with $\Delta R/R \sim 0.92$ for melt depths larger than ~ 100 nm. This confirms that the observed initial reflectivity

increase up to a maximum of $\Delta R/R \sim 1.0$ (curve A in Fig. 1) corresponds to a constructive interference effect during the propagation of the melt front into the material at a speed close to the longitudinal speed of sound in the solid ($\sim 5000 \text{ m/s}$).¹⁸ The calculated saturation value of 0.92 is somewhat greater than that observed experimentally ($\Delta R/R \sim 0.75$) which indicates that at this wavelength the approximation of using the optical properties of l-GaAs is not fully satisfactory.

At a fluence $\phi_0 = 2.06 \phi_m$ (curve B), sufficient for ablation, a fast increase of the reflectivity can be observed within 450 fs which is significantly shorter than the electron-phonon relaxation time [~ 2 ps (Ref. 19)]. At the highest fluence ($\phi_0 = 5.35 \phi_m$, curve C), the reflectivity maximum is reached within 360 fs. Note that the maximum of curve A is the same as for curves B and C (within the experimental error) although on a longer time scale. The subpicosecond reflectivity increase to a fluence-independent²⁰ value has been observed before in other semiconductors such as silicon and gallium arsenide and interpreted in terms of a phase transition induced by electronic excitation.^{1–3,20} This phenomenon is usually referred to as *nonthermal* melting and is due to the creation of a high-density electron-hole plasma with carrier densities of the order of 10^{21} – 10^{22} cm^{-3} that leads to a destabilization of the lattice structure before a thermal equilibrium with the carriers is achieved.^{21,22} Both the time scale of the reflectivity increase (< 450 fs) in both curves (B, C) and the initial fluence-independent value of the subpicosecond reflectivity maximum are consistent with the formation of a highly excited state of the material driven by electronic excitation. This process occurs *homogeneously* in the excited volume wherever the stability limit is exceeded. Since this volume is determined by the energy deposition depth of the pump pulse in the *solid* material [optical penetration depth $1/\alpha \sim 300$ nm in the present case],¹⁷ the stability limit can be reached simultaneously over a depth much larger than the optical penetration depth of the probe in the *liquid* [$1/\alpha \sim 20$ nm].³ This explains the fluence independence of the initial reflectivity increase which is just a consequence of the formation of a disordered liquid state which can be formed within a few vibrational periods.²⁰ All three criteria, i.e., (i) the reflectivity increase on a subpicosecond time scale, (ii) the fluence independence of this reflectivity level, and (iii) the observed fluence dependence of the time required to reach the high reflective state, clearly evidence the occurrence of nonthermal melting in InP upon fs-laser pulse irradiation.

In curve B, the subsequent decrease of the reflectivity to a minimum at 200 ps is indicative of the onset of ablation.²³ Beyond this point, the reflectivity rises again towards the reflectivity level of the liquid state. In curve C, the ensuing decrease in reflectivity is more pronounced and after ~ 40 ps the probe pulse is almost completely absorbed in the excited surface region. The reflectivity subsequently increases again after ~ 300 ps. The observation of a reflectivity minimum after a few hundred picoseconds is in excellent agreement with measurements of the onset of the ablation process in semiconductors and metals using fs time-resolved

microscopy.²³ In such studies the ablation is observed to be accompanied by the formation of a rarefaction wave inducing a transient Newton ring pattern.

Along with the formation of a rarefaction wave, additional contributions to the appearance of the reflectivity minimum might arise from evaporation/ejection of material from the surface as observed for ns pumping.⁸ This is supported by the fact that the equilibrium vapor pressure of phosphorus in InP increases rapidly above the melting point [~ 27.5 atm at the melting temperature of 1335 K Ref. 24] which also explains why the fluence thresholds for melting and ablation are very close together. Whatever the actual mechanisms of material removal are, atomic force microscopy (AFM) investigations indicate that, at a fluence level of $3.6 \phi_m = 2.5 \phi_{abl}$, a crater with a maximum depth of ~ 80 nm is formed on the surface.¹² The momentum transferred from the evaporating material to the excited surface layer, i.e., the recoil pressure, would also explain the protruding rim structure (height ~ 20 nm and width ~ 100 – 300 nm) bordering the ablation crater as observed by AFM in Ref. 12.

In order to estimate quantitatively the characteristic carrier densities at the surface required for melting and ablation, an analysis of the crater depth reported in Ref. 12 at the fluence $3.6 \phi_m$ can be used. By applying the formalism of Ref. 25 and knowing the crater depth (80 nm) and the linear optical constants of the crystalline phase,¹⁷ the two-photon absorption coefficient β of *c*-InP has first been estimated to be ~ 90 cm/GW at the wavelength of 800 nm. Hence, according to the theory presented in Ref. 26, carrier density values of 2.0×10^{22} and 3.2×10^{22} cm⁻³ have been obtained for melting and ablation, respectively. At the ablation threshold, for example, where the laser intensity I_0 is $\sim 9 \times 10^{11}$ W/cm², both linear and two-photon absorption contribute significantly to the carrier generation in InP after fs-laser pulse irradiation at 800 nm: $\beta I_0 \approx 8.1 \times 10^4$ cm⁻¹ $>$ $\alpha \approx 3.3 \times 10^4$ cm⁻¹, where α and β denote, respectively, the linear and the two-photon absorption coefficients of InP.

For the case of fs-laser-induced melting at fluences below the ablation threshold, RTR measurements have been performed to investigate the resolidification behavior on the ns time scale. Figure 2 shows the temporal evolution of the surface reflectivity (normalized to $R_c[514.5 \text{ nm}] = 0.36$) for a fluence of $1.27 \phi_m$ comparable to that of curve A in Fig. 1. As shown in the streak camera transient of Fig. 2(a), the reflectivity rapidly increases to a level of $\Delta R/R \sim 0.56$ (leading to a value of $R_L[514.5 \text{ nm}] = 0.56$). The thickness of the molten layer exceeds the optical penetration depth at 514.5 nm for a time duration of ~ 15 ns and produces the observed reflectivity plateau. This change ($\Delta R/R \sim 0.56$) at the plateau agrees well with the value of $\Delta R/R \sim 0.60$ obtained by optical simulations employing the refractive indices at 514.5 nm [$(n+ik)(l\text{-GaAs}) = (1.5+i2.7)$ (Ref. 3) and $(n+ik)(c\text{-InP}) = (3.7+i0.5)$ (Ref. 17)]. At this wavelength, the use of the optical constants of *l*-GaAs is a better approximation than in the case of 800 nm. The difference between the optical properties of the liquid phases of InP and GaAs is most likely related to the different numbers of free carriers in the melt that arise from the respective ratios between ionic and covalent bondings.

FIG. 2. Normalized surface reflectivity changes as a function of time for a fluence of $\phi_0 = 1.27 \phi_m$ as measured with (a) streak camera and (b) photodiode. The arrival of the pump pulse to the surface occurs at time $t = 0$. Note different time scales in (a) and (b). The maximum change measured ($\Delta R/R \sim 0.56$) has been indicated in both plots. The dashed vertical lines in (b) mark the resolidification time interval (~ 25 ns). The inset (c) is an optical micrograph over an area of $160 \times 160 \mu\text{m}^2$ corresponding to the laser irradiated spot.

The smooth decrease in reflectivity observed immediately after the plateau [Fig. 2(a)] indicates the onset of resolidification over the optically probed depth. Simultaneous measurements of the reflectivity with the photodiode [Fig. 2(b)] indicate a resolidification time of the order of 25 ns. The observed resolidification times of some tens of nanoseconds after fs-laser-induced melting are, as expected, similar to those observed for ns-laser pulse irradiation.^{7,8} At a time ~ 50 ns after the fs-pulse irradiation, after solid phase cooling, the reflectivity reaches its final level of $\Delta R/R \sim 0.22$, corresponding to the appearance of a bright spot in the irradiated region as shown in the optical micrograph of Fig. 2(c). Optical simulations of the surface reflectivity (514.5 nm, 18° , *s*-polarized beam), modeling a thin amorphous surface layer [$(n+ik)(a\text{-InP}) = (3.9+i1.2)$ (Ref. 27)] on top of a crystalline substrate, show that the final surface reflectivity change of $\Delta R/R \sim 0.22$ is due to the formation of an amorphous layer with a thickness of several tens of nanometers. This is in good agreement with previous micro-Raman spectroscopy investigations which showed the formation of amorphous material upon fs-laser irradiation above the melting threshold.¹²

IV. CONCLUSIONS

In summary, the dynamics of the fs-laser-induced phase transitions in single-crystalline InP has been analyzed by reflectivity measurements over a time scale between 150 fs and 500 ns. At low fluences above ϕ_m , thermal melting of the surface occurs within 1–2 ps and the liquid layer resolidifies within ~ 40 ns forming an amorphous top layer with a thickness of several tens of nanometers. At higher fluences above the ablation threshold, an ultrafast phase transition has been observed to occur within ~ 400 fs. The reflectivity of this phase is fluence independent and shows an absolute value of

$R \sim 0.63$ at 800 nm. An estimation of the carrier density required to induce this phase transition leads to a value of $\geq 3 \times 10^{22} \text{ cm}^{-3}$.

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