Time- and space-resolved dynamics of ablation and optical breakdown induced by femtosecond laser pulses in indium phosphide

Jörn Bonse, Guillaume Bachelier, Jan Siegel, Javier Solis, and Heinz Sturm

Citation: J. Appl. Phys. 103, 054910 (2008); doi: 10.1063/1.2885105
View online: http://dx.doi.org/10.1063/1.2885105
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v103/i5
Published by the American Institute of Physics.

Related Articles
Negative effect of crystallization on the mechanism of laser damage in a HfO2/SiO2 multilayer

Anomalous transport of Sb in laser irradiated Ge

Pulsed laser operated high rate charging of Fe-doped LiNbO3 crystal for electron emission

Formation of nanostructured TiO2 by femtosecond laser irradiation of titanium in O2

Finite element calculations of the time dependent thermal fluxes in the laser-heated diamond anvil cell

Additional information on J. Appl. Phys.
Journal Homepage: http://jap.aip.org/
Journal Information: http://jap.aip.org/about/about_the_journal
Top downloads: http://jap.aip.org/features/most_downloaded
Information for Authors: http://jap.aip.org/authors
Time- and space-resolved dynamics of ablation and optical breakdown induced by femtosecond laser pulses in indium phosphide

Jörn Bonse,1,a) Guillaume Bachelier,2,b) Jan Siegel,2 Javier Solís,2 and Heinz Sturm3

1Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Strasse 2A, D-12489 Berlin, Germany
2Laser Processing Group, Instituto de Optica, CSIC, Serrano 121, E-28006 Madrid, Spain
3Bundesanstalt für Materialforschung und -prüfung, Unter den Eichen 87, D-12205 Berlin, Germany

(Received 18 October 2007; accepted 19 December 2007; published online 13 March 2008)

Femtosecond time-resolved microscopy has been used to analyze the structural transformation dynamics (melting, ablation, and solidification phenomena) induced by single intense 130 fs laser pulses in single-crystalline (100)-indium phosphide wafers in air on a time scale from ~100 fs up to 8 ns. In the ablative regime close to the ablation threshold, transient surface reflectivity patterns are observed by fs microscopy on a ps to ns time scale as a consequence of the complex spatial density structure of the ablating material (dynamic Newton fringes). At higher fluences, exceeding six times the ablation threshold, optical breakdown causes another, more violent ablation regime, which reduces the energy deposition depth along with the time of significant material removal. As a consequence, ablation lasts longer in a ring-shaped region around the region of optical breakdown. This leads to the formation of a crater profile with a central protrusion. In the melting regime below the ablation threshold, the melting dynamics of indium phosphide has been quantified and subsequent superficial amorphization has been observed upon solidification on the ns time scale leading to amorphous layer thicknesses of the order of a few tens of nanometers. © 2008 American Institute of Physics. [DOI: 10.1063/1.2885105]

I. INTRODUCTION

Indium phosphide (InP) is a III-V compound semiconductor that is finding ever increasing applications in the field of ultra-high-speed optoelectronics. Recently, the behavior of this material upon irradiation with femtosecond laser pulses has been studied by different groups using complementary in situ2–4 and ex situ techniques.5–13 During the course of these experiments, a particular morphological feature has been observed by two different groups in the single-pulse ablation regime whose origin has not been unambiguously identified yet.6,11 In a previous publication, some of us reported a characteristic permanent ring pattern in the ablation craters which exhibited a threshold behavior and which was related to a local recrystallization process of the residual melt pool on the semiconductor surface.6 Later, Borowiec et al. associated the existence of this feature with a second ablation regime and noted that in this regime the intensity for plasma formation is overcome.11

The purpose of this paper is to provide a detailed study of the dynamics of the ablation process in single-crystalline indium phosphide upon ultrashort laser pulse irradiation. Using fs-time-resolved microscopy we have investigated the temporal and spatial evolution of the surface ablation process induced by single fs laser pulses. This technique allows snapshots of the surface reflectivity to be recorded at different time delays after the pulse has reached the sample surface, providing sub-ps temporal and micrometer spatial resolution covering a time span up to 8 ns. The application of this technique along with complementary optical and scanning force microscopic characterization allows us to reveal the origin of the particular ablation feature and its relation to the conventional ablation regime reported.

II. EXPERIMENTAL

The laser used for irradiation provided linearly polarized pulses of 130 fs duration at 800 nm (λpump). At this photon energy (1.55 eV), a direct interband transition can be induced in single-crystalline (100)-InP by linear absorption (American Xtal Technology, band gap energy 1.35 eV, n-type, S-doped). The 400 μm thick polished wafers were cleaned in an ultrasonic bath using methanol prior to irradiation. The irradiation was performed in air and each surface region was irradiated only once. The s-polarized laser beam was focused onto the sample at an angle of incidence of 54° to a Gaussian elliptical spot size of 100 × 60 μm² (1/e² diameter). The temporal and spatial evolution of the surface reflectivity upon laser irradiation was measured at the C.S.I.C. using a fs-time-resolved microscopy (fs-TRM) setup described in detail elsewhere.14 Briefly, a fraction of the pump pulse was frequency-doubled to 400 nm (λprobe) and used as a low-intensity probe pulse to illuminate the sample at normal incidence. The sample surface was then imaged onto a 12-bit charge coupled device camera using a long working distance microscope objective (20X, numerical aperture=0.42) and a tube lens (f =200 mm), with a 10 nm bandpass filter centered at λprobe placed in the imaging path. The reflectivity images corresponding to different delays (τ) have been normalized by the
The temporal resolution of the fs-TRM setup is since the Fresnel reflectivity of the surface is increased for amorphized area contrast. The black dotted line in image sequence is encoded in a common linear gray scale with an optimized threshold is quantitatively consistent with the estimated experimental uncertainty in at the probe-wavelength via 

\[ R(R) = \frac{R_{\text{mol}}} {R_{\text{amorph}}} \] 

Concerning the reflectivity increase, it has been shown in previous publications\(^1\) that nonthermal melting (NTM) can take place in InP for fluences already exceeding 1.4 \( \times \Phi_{\text{abl}} \) (corresponding to an estimated carrier density of \( \sim 3 \times 10^{22} \) cm\(^{-3} \), i.e., the generation of an electron-hole plasma with high carrier densities leading to a destabilization of the lattice structure within hundreds of femtoseconds.\(^17\) Given the peak fluences used in Fig. 1 [(a) 1.5 \( \times \Phi_{\text{abl}} \), ... (c) 8.5 \( \times \Phi_{\text{abl}} \)], NTM is expected to occur in the center of the irradiated spots even if, given the time-resolution of 500 fs of our fs-TRM setup, we are not able to distinguish here between a reflectivity increase due to laser-generated carriers or due to nonthermal melting.

At 1 ps delay, the same qualitative picture is seen at all three peak fluences, but the reflectivity has significantly raised toward the level of molten InP, indicating that the phase transition takes place. Between 1 and 10 ps, the surface reflectivity starts to decrease in the center of the irradiated spots (peak fluence-dependent behavior). This decrease is indicative of the onset of ablation.\(^18\) Moreover, the dark ring of decreased reflectivity seen immediately after excitation around the central region of increased reflectivity vanishes between 1 and 100 ps due to thermal melting in that low-fluence region.\(^19\) Additionally, this vanishing can be affected by nonradiative Auger recombination at such high excitation levels close to the melting threshold, by surface recombination, and by carrier diffusion (the latter two are expected to be less dominant on that time scale).\(^20\)

At 100 ps delay, a very dark central region can be seen where almost no light is reflected since absorption and scattering in the ablating material shield the surface from the probe beam radiation. This central region is surrounded by a bright ring of molten material that exhibits an increased reflectivity. The borderline between both regions coincides with the edge of the ablation crater, which is visible at long time delays (several seconds, Fig. 1, \( \infty \)).

At delay times between 100 ps and 1 ns, a characteristic transient ring pattern is visible in the region where ablation takes place (see, for instance, Fig. 1, 100 ps and 1 ns). The nature of these rings has been studied already in detail in other materials. It has been associated with an optical inter-
ference effect (dynamically moving Newton fringes). The corresponding interference fringes are visible during the formation and spatial movement of a complex material density profile after fs laser pulse irradiation of semiconductors and metals. The resulting density profile consists, at the air side of the expanding material, of a thin ablation layer with nearly solid state material density and a thickness smaller than the optical penetration depth in this optically excited ablating layer. The partial reflections at this dynamically moving layer and the reflection at the remaining surface underneath then allow interference effects to occur transiently.

Interestingly, the fringe pattern is seen only in a certain fluence range in the ablative regime [below $\approx 0.42 \text{ J/cm}^2$], compare (a)–(c) at 1 ns delay in Fig. 1. Moreover, the transient ring pattern disappears for delay times between 1 and 8 ns. Both observations are consistent with the results obtained in other semiconductors. However, the surface reflectivity is still decreased compared to the permanent reflectivity images, indicating that the probe beam radiation is still interacting with ablating material (Fig. 1, 8 ns). As it has been shown in a previous publication for germanium, the origin of the disappearance of the ring pattern at high fluences or long delay times ($\approx 1\text{ ns}$) lies in the decreasing sharpness of the interfaces of the ablating layer.

At 8 ns delay, a striking difference between spots irradiated at different peak fluences can be seen. At low fluences [0.44 J/cm$^2$, Fig. 1(a), and 0.66 J/cm$^2$, Fig. 1(b)], the central ablation area appears relatively uniform. Increasing the peak fluence, another ablation regime appears. This is visible at the highest fluence value [2.56 J/cm$^2$, Fig. 1(c)], where the time span of strong ablation is reduced in the center of the spot. In comparison, ablation lasts longer in an annular shaped region around it. At this peak fluence value and delay (8 ns), another distinct transient feature can be observed in the reflectivity image around the irradiated spot [marked by “SW” in Fig. 1(c)], which is caused by the ablation induced formation and radial expansion of a pressure or shock wave in the surrounding air. This further confirms that at such high fluences another ablation regime of more violent ablation of InP is reached.

The images of the permanent surface modification taken several seconds after the pump pulse irradiation (Fig. 1, $\infty$) show the sharp borderline of the ablation crater [marked by white vertical dashed lines in (a) and (c)]. Around this crater (labeled with region B), a ring of permanently decreased reflectivity can be seen [region A, marked by black vertical dotted lines in (a)]. As it will be shown later in Sec. III B, it is caused by a thin amorphous layer with a thickness of a few tens of nanometers formed on the surface as a consequence of melting and rapid solidification. From an analysis of the diameters of those amorphous rings (see Ref. 6), a threshold fluence value of $\Phi_{\text{th}}(54^\circ)=0.20 \text{ J/cm}^2$ is found here for melting and subsequent amorphization.

Interestingly, at the highest peak fluence value of 2.56 J/cm$^2$, an additional elliptically shaped permanent feature is observed in the center of the crater [region C, outer extent marked by a white dash-dotted line in Fig. 1(c)]. This feature exhibits a sharply defined threshold fluence of 1.76 J/cm$^2$ [consistent with the value of 1.3 J/cm$^2$ (Ref. 6) at normal incidence]. Its diameter coincides with the inner boundary of the ring of material still ablating after 8 ns delay.

To quantitatively follow the time evolution of the reflectivity, we have plotted in Fig. 2 the normalized surface reflectivity change $\Delta R/R$ as a function of the delay time. The reflectivity change has been evaluated in three different locations marked in the spot already shown in Fig. 1(c) for 8 ns delay, corresponding to representative locations in regions A, B, and C, respectively. This data representation is the equivalent to a point-probing conventional fs-pump-probe experiment at local fluences of 2.56, 1.35, and 0.25 J/cm$^2$.

All discussed stages of melting, ablation, and a partial recovery of the reflectivity can be seen in curve B (1.35 J/cm$^2$) and curve C (2.56 J/cm$^2$). The initial reflectivity increase on the sub-picosecond to picosecond scale reaches values of $\Delta R/R \approx 0.2$. The onset of ablation after tens of ps then reduces the normalized reflectivity change to values approaching $\approx 0.9$ at position C after 100 ps, which means that the probe beam radiation is almost completely absorbed or scattered in the excited surface region. After one nanosecond, a partial reflectivity recovery is seen in curve C, finally reaching a permanent normalized reflectivity change of $\approx 0.04$. In curve B, the reflectivity recovery is delayed and takes place after 8 ns delay (not accessible by our fs-TRM setup), leading to a small permanent reflectivity decrease of $\approx 0.06$.

This behavior in the ablation regime is contrasted by the evolution of the surface reflectivity change in the narrow ring of molten material around the crater (curve A, 0.25 J/cm$^2$). After the reflectivity increase in sub-ps and ps time scales to $\Delta R/R \approx 0.24$, the relative reflectivity change stays at a value of $\approx 0.15$ before solidification takes place between 1 and 8 ns, leading to an amorphous layer of slightly reduced reflectivity ($\Delta R/R \approx 0.04$).

B. Numerical simulation of the observed reflectivity changes

For the semiconductor InP it was already reported that the solidification of a fs laser-induced melt layer occurs interfacially from the solid/liquid interface and the solidifying material turns into an amorphous state when a critical speed in the order of 1–4 m/s is exceeded for the velocity of the
resolidification front. At such velocities, there is not enough time for the nucleation of a crystalline phase, which leads to the formation of the amorphous material.

The evolution of the reflectivity in such a scenario has been modeled by considering a thin film of molten or amorphous material with variable thickness on top of a crystalline substrate. The optical model used takes into consideration the fully coherent superposition of Fresnel reflections at all interfaces [air/liquid(amorphous), liquid(amorphous)/crystalline] for the given probe wavelength of 400 nm at normal incidence. The optical constants \(n + ik\) for the different material phases [c-InP, a-InP, and \(\ell\)-InP] used for the thin film optical calculations are summarized in Table I. Since the complex refractive index of liquid InP is not known at \(\lambda_{\text{probe}}\), we have used the values corresponding to liquid GaAs, since these materials have very similar band structures in the solid phase. For direct comparison with the experimental results, the absolute reflectivity values \(R\) have been normalized by the value of the crystalline material \(R_c\) via \(\Delta R / R = (R - R_c) / R_c\), with \(R_c(0^\circ, 400 \text{ nm}) = 0.454\).

The calculations for a thin liquid layer on crystalline material [Fig. 3(a)] show a maximum value for \(\Delta R / R\) of 0.27 for a molten layer thickness of \(\sim 25\) nm. This maximum corresponds to a constructive interference effect during the propagation of the melt front into the solid material. For melt depths larger than approximately 80 nm, the reflectivity change saturates when the molten layer becomes optically thick, showing a value of \(\Delta R / R \sim 0.15\). The maximum value and the saturation level are in excellent quantitative agreement with the experimental data shown in Fig. 2 (curve A, associated with region A in Fig. 1, below the ablation threshold). The saturated reflectivity level of +0.15 is consequently indicative of the formation of an optically thick molten layer after 1 to 10 ps which exists for 1 to 8 ns. Moreover, we can conclude that at 400 nm wavelength the reflectivities of bulk \(\ell\)-GaAs and \(\ell\)-InP coincide, indicating that the optical constants of both liquids should be very similar.

The solidification process, corresponding to the formation of a thin amorphous layer on top of the surface, has been modeled in Fig. 3(b). In this case, the simulation shows some oscillations for increasing thickness due to the different optical constants of a-InP (see Table I). By comparing the simulated values with the final reflectivity value (\(\Delta R / R = -0.04\)) in Fig. 2 (curve A), we can infer the formation of an amorphous layer with a thickness of \(\approx 20\) nm. This value confirms the results of a previous time-resolved study at a different probing wavelength, where amorphous layer thicknesses of less than 50 nm were found.

### C. Post-irradiation analysis

In order to reveal the origin of the particular features observed at high fluences and long delays, some selected ablation morphologies (obtained for normal incident single fs laser pulse irradiation) were characterized by means of scanning force microscopy (SFM) and by complementary optical microscopy (OM) employing a differential interference contrast method (Nomarski mode). Figure 4 shows two different images of such an ablation crater generated in an InP surface (0\(^\circ\)) by a single 130 fs laser pulse at a peak fluence of \(\Phi_0 = 2.4 \text{ J/cm}^2\) (approximately ten times the ablation threshold fluence). Besides the SFM-surface topography [Fig. 4(a)] and an optical micrograph [Fig. 4(b)], a topography cross-section through the center of the crater [Fig. 4(c)] and the corresponding spatial fluence distribution [Fig. 4(d)] are given.

The same characteristic permanent ring structures as previously seen in Fig. 1(c) \((\infty)\) are visible in both, the optical
As a consequence, the deepest crater regions are located through superimposing the Gaussian-like crater profile in region A to explain the shape of crater profiles of GaAs ablated by 2.56 J/cm² found here for the material InP.

The SFM-topography clearly indicates that the crater region B, where significant ablation lasts longer [see Fig. 1(c)], also exhibits a somewhat bigger ablated depth than the central part of the crater (region C). All observations, i.e., (i) the ablation dynamics at long time scales, (ii) the crater profile, and (iii) the threshold behavior for the occurrence of the central feature (region C), can be explained by optical breakdown at the surface and the formation of a high density plasma during the pulse: The cumulative effect of linear and nonlinear absorption along with impact ionization leads to a drastic decrease of the effective energy deposition depth of the fs laser radiation. A very large amount of the laser pulse energy is deposited in a very thin layer close to the InP surface. Due to the high energy density within this layer, the material is rapidly carried away from the surface, leaving behind less-excited material underneath, which does not significantly ablate anymore at longer time scales. Consequently, a shallower crater is formed in the central region exceeding the optical breakdown threshold. Recently, a similar scenario has been proposed by Stojanovic et al. in order to explain the shape of crater profiles of GaAs ablated by single fs laser pulse in air (620 nm, 100 fs, 45°). Their threshold value of 1.2 J/cm² is very close to the threshold of 1.3 J/cm² found here for the material InP.

This explanation is furthermore consistent with our observations that the ablation process lasts less time at 2.56 J/cm² than at 1.35 J/cm² (Fig. 2) because the ablation velocity of a high density plasma produced by optical breakdown is expected to be much faster than in the case of linear absorption.

It should be noted that in complementary SFM studies of the ablation of InP induced by tightly focused visible femtosecond laser pulses in a rough vacuum (105 fs, w₀ = 5 μm, 0.1 mbar) two different regimes of ablation have been reported for single pulse irradiation. Interestingly, the central ring feature C was observed too at high fluences exceeding = 0.55−1.3 J/cm² (depending on the wavelength). Due to the normal incident fs-laser pulses, the central feature reported in that work was nearly perfectly circular, similar to the shape of the region C shown in Fig. 4. But in contrast to our conditions (loose focusing and irradiation in air), no step-like protrusion has been reported in the central region of the crater. Most likely the atmosphere plays an important role in the morphologies observed upon optical breakdown. On the other hand, a second ablation regime was reported in this fluence regime, which significantly deepens the ablation crater (in vacuum) and simultaneously increases the rim volume surrounding the central region C feature. The latter observation could be explained by the large recoil pressure of the ablating material in the region where the optical breakdown occurs. The importance of the ablation pressure in the fluence regime where the central feature C is formed is indirectly supported by the observation of an atmospheric pressure/shock wave in the fluence regime of optical breakdown (see Fig. 2). Other factors such as the absolute size of the irradiated spots or the doping of the samples might additionally play an important role and could explain the particular surface morphological differences between the present work and the results reported in Ref. 11.

Interestingly, in a previous study (under similar conditions as here), it was found by micro-Raman spectroscopy that the molten InP in region C solidifies in a polycrystalline state underneath a thin amorphous top layer. Such a polycrystalline resolidification has not been observed in region A (amorphization without ablation) or in region B (ablation and superficial amorphization). Moreover, the surface roughness is significantly reduced in region C (Rrms ≈ 4 nm) when compared to region B (Rrms ≈ 11 nm). Both observations suggest that, along with a reduction of the ablation depth in the spot center, the optical breakdown also increases the thickness and lifetime of the residual molten layer underneath and consequently affects the solidification behavior of the melt pool and its residual surface roughness. A reduced supercooling of the molten material prior to solidification should facilitate the formation of the polycrystalline phase. The increased thickness of the melt pool in region C can be additionally affected by the large ablation pressure acting on the sample surface upon optical breakdown. This pressure would lower the melting temperature of the material and therefore transiently increase the depth of the melt pool.

IV. CONCLUSIONS

In summary, we have studied the temporal dynamics of melting, ablation, and resolidification upon single titanium:sapphire femtosecond laser pulse irradiation of single-crystalline indium phosphate. Femtosecond time-resolved microscopic imaging allowed a characterization of the process dynamics in a time span covering more than four orders of magnitude (100 fs up to 8 ns). Our results confirm and extend the few previous studies on ultrafast phase transitions in indium phosphate and provide on longer time scales additional insights in the ablation process due to the fs-time-resolved imaging technique: for laser pulses with fluences...
slightly exceeding the ablation threshold, reflectivity oscillations (caused by a transient Newton-fringe pattern) have been observed which vanish between 1 and 8 ns (even if ablation still takes place). At high fluences exceeding six times the ablation threshold, evidence is presented that optical breakdown occurs at the surface, which effectively reduces the energy deposition depth of the fs laser radiation and leads to shallower ablation craters in the center of the spots. Due to the high energy content within the excited region, this finally leads to large velocities of the high density ablation plasma and consequently to a reduced duration of ablation in the central region of the irradiated spot. In the melting regime below the ablation threshold, experimental data for the optical reflectivity of molten InP at 400 nm wavelength are presented and the formation of a few tens of nm thick amorphous top-layer is observed upon solidification on the ns time scale.

ACKNOWLEDGMENTS

This work has been partially supported by the EU in the frame of the TMR Project FLASH (Grant No. MRTN-CT-2003-503641). G.B. acknowledges the funding in the frame of the same project. J.B. acknowledges the funding of the C.S.I.C. through a contract in the frame of the I3P program of the same project. J.B. acknowledges the funding by the German Science Foundation (DFG, Grant No. RO 2074/5-1, 2006–2007) and Professor J.M. Wrobel (University of Kansas City, USA) for his courtesy in providing the samples.

15The elevated angle of incidence (54°) leads to an increase of the threshold by a certain factor due to a higher Fresnel reflectivity. For c-InP at 800 nm wavelength, this factor can be estimated as \( [1-\tan(54°)]/[1-\tan(0°)] \approx 1.374 \) (for the model see Ref. 4).
19This is most pronounced in Fig. 1(a), where an increase of the diameter of the region of elevated reflectivity can be seen for delays between 1 and 10 ps.
22This value is obtained from the spatial extent of the ring-free central region in Fig. 1(a, 1 ns) by using the known Gaussian fluence profile; for details see Ref. 25.
27J. P. Callan, A. M. T. Kim, L. Huang, and E. Mazur, Chem. Phys. 251, 167 (2000), values taken 8 ps after excitation with a femtosecond laser pulse at a fluence of 1.6 times the melting threshold.
31Choi and Grigoropoulos (Ref. 23) reported pressures of the ablating shock wave front exceeding tens to hundreds of atmospheres during several tens of ns upon ultrashort laser pulse irradiation (80 fs, 800 nm) of silicon at fluences between 1 and 1.5 J/cm².
32An equilibrium pressure of 100 kbar lowers the melting temperature of InP by approximately 290 K (Ref. 33).