Wavelength dependence of the single pulse femtosecond laser ablation threshold of indium phosphide in the 400–2050 nm range

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Abstract

We present single pulse femtosecond laser ablation threshold measurements of InP obtained by optical, scanning electron, and atomic force microscopy. The experiments were conducted with laser pulses 65–175 fs in duration, in the wavelength range from 400 to 2050 nm, covering the photon energy region above and below the bandgap of InP. The ablation thresholds determined from depth and volume measurements varied from 87 mJ/cm² at 400 nm to 250 mJ/cm² at 2050 nm. In addition, crater depths and volumes were measured over a range of laser fluences extending well above the ablation threshold.

1. Introduction

Femtosecond laser ablation of semiconductors has been an area of intense fundamental and applied research for about two decades. A large amount of work has been reported on the study of dynamics and the analysis of the final state of the material, see e.g. [1–7]. However the majority of femtosecond ablation studies on semiconductors published to date were performed with light pulses centered around the peak wavelengths of Ti:sapphire and dye lasers, ≈800 and ≈620 nm respectively. Analysis of the ablation of materials over a broader range of wavelengths can provide important information about the absorption processes and serve as experimental tests for advanced theoretical models. In this work, we present systematic measurements of the wavelength dependence of the ablation threshold of InP in the range of 400–2050 nm,
covering photon energies above and below the bandgap of InP, $E_g = 1.34$ eV, which corresponds to a wavelength of $\lambda = 925$ nm. In addition, details on the crater dimensions were obtained for a wide range of laser pulse energies. The measurements were performed by optical microscopy (OM), scanning electron microscopy (SEM) and atomic force microscopy (AFM).

### 2. Experimental setup

A commercial Ti:sapphire regenerative amplifier was used to produce pulses at $\approx 800$ nm (Spectra-Physics, Spitfire LCX). Second harmonic beams at $\approx 400$ nm were obtained by frequency doubling the fundamental beam in a 0.3 mm thick nonlinear optical crystal (BBO). Pulses in the near infrared (NIR) were obtained from an optical parametric amplifier (Spectra-Physics, OPA-800) pumped by another commercial Ti:sapphire regenerative amplifier (Spectra-Physics, sub-50 fs Spitfire). Typically the signal and idler beams were centered at wavelengths of 1330 and 2050 nm, respectively. Finally the pulses at 660 nm were produced by frequency doubling the OPA signal beam in a 2 mm thick BBO crystal. The n-InP(1 0 0) samples were irradiated under a rough vacuum $\approx 0.1$ mbar base pressure. The laser was focused on the sample at normal incidence by a $5 \times$ microscope objective. A set of thin, reflective neutral density filters was utilized to adjust the pulse energy on the sample. The pulse energy in the wavelength range of 400–1000 nm was measured with a semiconductor power meter (Ophir PD300-3W) while a surface absorbing head (Ophir 2A-SH) was used for power measurements at 1330 and 2050 nm. The experiments were conducted with femtosecond pulses of 65–175 fs in duration. The pulse duration at each wavelength was measured with a scanning, second order intensity autocorrelator and fitted to a Gaussian temporal profile. The pulse durations for each wavelength are given in Table 1. At each wavelength sets of craters produced by single pulses were prepared and analyzed by OM operated in the Nomarski mode, SEM, and AFM operated in the contact mode. Since AFM scans are very time consuming, craters were grouped in arrays of 5 (Fig. 1) and analyzed individually after the scan. Images of the sets of five craters contain $512 \times 512$ points. Several factors contribute to the uncertainties in the AFM measurements including calibration errors, the effects of finite pixel size, and the AFM tip geometry limitations in measuring sharp features.

### 3. Results

In the SEM and OM analysis the damage threshold and the spot size on the sample surface were obtained from measurements of the peak fluence dependence of crater diameters. Irradiation with pulse energies exceeding the modification threshold leads to the formation of several characteristic morphological regions, such as melting and ablation zones, rims, etc. [6]. In all cases presented in this study the crater diameter was measured to the outside of the crater rim. This feature was most easily identified under all three microscopy techniques. The diameter $D$ of each crater was measured as a function of pulse energy $E$ by SEM, OM and AFM. By fitting the data to the equation...
The maximum crater depth $h_m$ was measured as a function of peak fluence $\phi_0$, and fitted to the logarithmic expression

$$h_m(\phi_0) = h_0 \ln \left( \frac{\phi_0}{\phi_{th}} \right),$$

where $\phi_{th}$ and $h_0$ are the fit parameters. In the ablation of metals the parameter $h_0$ is often interpreted as an optical penetration depth in the low fluence regime.

The expression for the fluence dependence of the crater volume was derived following simple considerations analogous to those used to obtain Eq. (3) [9]. The fluence at radius $r$ and depth $h$ below the surface is given by

$$\phi(r, h) = (1 - R)\phi_0 \exp \left( -\frac{2r^2}{\omega_0^2} - \alpha h \right).$$

Assuming that the absorption coefficient $\alpha$ is constant and independent of intensity, the energy absorbed per unit volume is given by $-d\phi/dh = \alpha \phi$. If all material which receives an energy density in excess of $H$ (J/cm$^3$) is ablated the crater profile $h(r)$ is defined by the condition $\alpha \phi(r, h) = H$ and yields

$$h(r, \phi_0) = \frac{1}{\alpha} \ln \left( \frac{\phi_0}{\phi_{th}} \right) - \frac{2r^2}{\omega_0^2}, \quad \text{where}$$

$$\phi_{th} = \frac{H}{\alpha(1 - R)}.$$

The maximum crater radius $r_m$ is found by setting $h(r_m, \phi_0) = 0$ and leads to an expression equivalent to Eq. (1). The ablated volume is given by

$$V(\phi_0) = 2\pi \int_0^{r_m} h(r, \phi_0) r \, dr$$

$$= V_0 \left( \ln \left( \frac{\phi_0}{\phi_{th}} \right) \right)^2,$$

where $V_0 = \pi\omega_0^2/4\alpha$. This equation, based on very simple assumptions, provides the functional form for our data analysis. The crater volume $V$ (the volume beneath the original surface), and the rim volume (the volume above the original surface), were measured as a function of peak fluence $\phi_0$ and fitted to Eq. (6). In all cases the square root of volume was plotted as a function of log($\phi_0$).

Fig. 1(a)–(d) show the examples of OM images of ablation craters produced by irradiation with 660 nm pulses. The corresponding crater profiles for selected
craters obtained from the AFM scans are shown on the right side of Fig. 1. Fig. 2 presents data collected for craters irradiated at a laser wavelength of 660 nm. Fig. 2(a) shows the $D^2$ measurements obtained by SEM, OM and AFM along with fits to Eq. (1). The spot size $\omega_0$ was taken as the average value obtained from the three fits and used in all fluence calculations at a given wavelength. Fig. 2(b) shows the AFM measurements of the crater depth dependence on fluence. Two distinct regimes, with different slopes and thresholds can be fitted to the data in the low ($\phi_0 \leq 800 \text{ mJ/cm}^2$) and high ($\phi_0 \geq 800 \text{ mJ/cm}^2$) fluence regions. The onset of the high fluence regime was taken as the intercept of the two fit lines in Fig. 2(b). At the other wavelengths, the high fluence regime onset varied from about 1000 to 3000 mJ/cm$^2$. The high fluence regime is characterized by a substantial increase in the slope of the depth versus fluence for the ablation craters. The value of the fit parameter $h_0$ for the higher fluence regime is approximately 300 nm for all wavelengths in the opaque region, and 590 nm at a wavelength of 1300 nm. At 2050 nm the maximum pulse energy was insufficient to investigate the high fluence regime. In the high fluence regime the crater profiles develop increased curvature (Fig. 1(a) and (b)), and debris resembling resolidified liquid droplets is visible in the vicinity of some craters (Fig. 1(a)). Note the discontinuity in the crater depth data in the low fluence regime. We fit Eq. (3) only to the low fluence data points above the discontinuity. The parameters $h_0$ and $\phi_{h, th}^V$ thus obtained are considered simple numerical fit values. We take the fluence at the discontinuity as the effective depth ablation threshold. At fluences below this newly defined threshold $\phi_{h, th}^V$, surface modification was still evident, however, the loss of material was minimal with crater depths in the range of 1–3 nm. Fig. 2(c) shows the AFM measurements of the crater and the rim volume dependence on fluence. The straight line represents a fit to Eq. (6). As in the fluence dependence of the crater depth, the discontinuity in the crater volume data is observed in the low fluence regime, although it is not as pronounced. Similarly, the values of $V_0$ and $\phi_{h, th}^V$ obtained are considered numerical fit values. We take the fluence at the discontinuity as the effective volume ablation threshold $\phi_{h, th}^V$. Note that the fluence at the discontinuity of crater volume is the same as for the crater depth data. Two regimes analogous to those seen in Fig. 2(b) are clearly visible in the fluence dependence of the rim volume and to a lesser extent in the fluence dependence of the crater volume. Due to the AFM limitations in measuring droplets and other sharp features, the uncertainties in the rim volume measurements are expected to be substantially larger than for crater volume determination. Fig. 2(d) shows the plot of the difference between the crater and the rim volume.

The wavelength dependence of $\phi_{h, th}^V$ (or equivalently $\phi_{h, th}^D$) obtained from AFM measurements is shown in Fig. 3. Also, the average values, $\phi_{h, th}^D$(avrg),

![Fig. 2. Data analysis of single pulse ablation craters produced by 105 fs, 660 nm pulses showing (a) squared diameter measured by ( сраз) SEM, (olecule) OM and (bullet) AFM, (b) crater depth, (c) square root of crater (square) and rim (round) volume, and (d) square root of the difference between crater and rim volume, plotted as a function of peak laser fluence.](image-url)
obtained from a large number of SEM measurements performed over a course of several months are included in the same graph. The straight line represents a linear fit to the $\phi^D_{th}(avrg)$ data points at wavelengths of 400, 660 and 800 nm, including the origin. Fit parameters for AFM data are summarized in Table 1. The superscripts $h$, $V$, and $D$ are used to distinguish the respective fit parameter values. The uncertainty in the absolute threshold fluences is estimated to be about $\pm 25\%$, and is attributed to uncertainty in power and spot size measurements, as well as the fit uncertainties. The relative uncertainties for values measured at different wavelengths are expected to be less than the absolute uncertainty.

The AFM data provide additional information about the morphology and geometry of the ablation craters. Selected results of crater profiles obtained under 800 nm irradiation, as well as results for the depth versus fluence for all the laser wavelengths in the low fluence regime are illustrated in Fig. 4. The first two AFM profiles in Fig. 4(a) show the removal of a very small layer, and in the second case, just below the threshold $\phi^D_{th}$, a peak is clearly evident in the center. Upon surpassing the threshold (center, Fig. 4(a)) the crater depth becomes substantial, typically some tens of nanometers. The crater depth is fairly uniform in the lateral directions as seen in the crater profiles in Fig. 1(d) and the three highest fluences in Fig. 4(a). The profiles of craters in the low fluence regime clearly deviate from the shape predicted by Eq. (5).

With an increase of fluence above about 550 mJ/cm$^2$ (at 660 nm), a new surface morphological feature emerges in the center of the craters in Fig. 1(b). The inner feature is almost perfectly circular and is surrounded by a pronounced rim. This rim is significantly higher and thicker than the outer rim in the low fluence regime. The threshold fluence for emergence of this particular feature was estimated by $D^2$ fitting. The threshold fluence varied with wavelength from approximately 550 to 1300 mJ/cm$^2$, however there was no simple wavelength dependence. The effective spot size determined from the slope of the $D^2$ fit to the inner feature was 5.9 $\mu$m, whereas the spot size determined by a $D^2$ fit to the entire crater in the low fluence regime (Fig. 2(a)) was 4.3 $\mu$m. At all wavelengths, a fit to the inner feature resulted in a larger spot size.

4. Discussion

The discontinuity in the fluence dependence of the crater depth and crater volume, hence the onset of significant material removal, was associated with the
the damage threshold with wavelength was observed, ranging from about 300 mJ/cm$^2$ at 800 nm to 800 mJ/cm$^2$ at 2200 nm. The silicon results are qualitatively consistent with our findings for InP. The wavelength dependence of the ablation threshold was addressed by Gamaly et al. [16] who derived simple analytical expressions for the theoretical values of the ablation threshold for metals and dielectrics. Their two expressions predict linear dependences of the ablation threshold on the laser wavelength. The theory was in good agreement with experimental results obtained by Perry et al. [17] on fused silica. Simanovskii et al. [18] have recently reported mid-infrared (4.7–7.8 μm) optical breakdown measurements in narrow-bandgap (ZnS, ZnSe) and wide-bandgap (LiF, MgF$_2$, CaF$_2$, BaF$_2$) dielectrics. For the wide-bandgap dielectrics, they found a substantial decrease in the breakdown thresholds with increasing wavelength in the mid-infrared region, while corresponding values for the narrow-bandgap materials were essentially independent of wavelength. In the visible region, the threshold for wide-bandgap dielectrics increased with wavelength, while in the same region the values for ZnSe were largely independent of the wavelength.

The theoretical analysis of the wavelength dependence of the ablation threshold requires consideration of the absorption and transport processes. The absorption processes determine the “initial” density and the spatial profile of the excited carriers. The primary mechanisms for carrier generation and energy deposition in semiconductors are single and multiphoton excitation as well as free carrier absorption and impact ionization. Two-photon absorption is particularly important in irradiation with intense femtosecond pulses [19–21]. If the effects of free carriers are neglected, the effective absorption coefficient can be written as [21–24]:

$$\alpha_{\text{eff}} = \alpha_{\text{lin}} + \beta I_0 (1 - R),$$

where $\alpha_{\text{lin}}$ and $\beta$ are one and two-photon absorption coefficients, $I_0$ is the incident laser intensity, and $R$ the small signal reflectivity. In the presence of two-photon absorption the effective absorption coefficient increases and can lead to deposition of the energy over a significantly shorter distance. For example, using the optical constants of InP at 800 nm [25], $\beta \approx 90 \text{ cm/GW}$ [23,26], and $I_0 \approx 10^{12} \text{ W/cm}^2$, yields $\alpha_{\text{eff}}^{-1} = 100 \text{ nm}$, which is smaller than linear optical penetration depth at 800 nm ($\alpha_{\text{lin}}^{-1} = 303 \text{ nm}$ [25]). Free carrier absorption under near-ablation threshold
fluences can be expected to lead to characteristic depths of the same order as given above, and hence must be included in a quantitative analysis. In addition to optical absorption, the subsequent carrier dynamics will influence the ablation threshold [21,27]. For example, Bulgakova et al. [28] have recently treated electronic transport and its implications for ultrafast laser ablation in a wide range of material types. In particular, they point out the distinction of dielectrics versus metals and semiconductors in terms of the laser-induced charging under femtosecond laser irradiation of materials.

Several interesting morphological features were observed in the AFM analysis. A peak seen in Fig. 4(a) just below the ablation threshold can be related to melt flow as discussed by Bonse et al. [6] and Bennett et al. [29]. We observed similar features at other wavelengths near the ablation threshold. An important aspect of the AFM data is the pronounced discontinuity in the fluence dependence of the crater depth in the vicinity of the ablation threshold (Fig. 4). A sudden increase in the ablation rate just above threshold has been previously reported, for example, after single pulse ablation of GaAs [30]. The final state of the material follows the behavior expected on the basis of ultrafast time-resolved microscopy studies [31]. Hashida et al. [32] reported rather rapid changes in the ablation rate of copper near thresholds under multi-pulse irradiation conditions. In studies utilizing time of flight mass spectroscopy the threshold of ablation was characterized by a sharp increase in the number of detected particles [33,34]. Several theoretical investigations of laser-induced melting and ablation have utilized molecular dynamic (MD) simulations [35–39]. Schäfer et al. [38] have studied the ultrafast laser ablation of metals using a hybrid approach involving MD and heat conduction. In their simulation they obtained an ablation rate which rose very rapidly when the ablation threshold was exceeded. This increase was attributed to a spallation process. Perez and Lewis utilized a two-dimensional MD model to study ablation mechanisms [39]. The authors identified several processes of material removal, including spallation, phase explosion, fragmentation and vaporization. The discontinuity in the fluence dependence of the crater depth near the ablation threshold was also attributed to ejection of material by spallation. Our results on InP are similar to those obtained via MD models; for example, see Fig. 21 in Ref. [39]. However, the model was not believed to adequately describe nonthermal melting of covalent solids. More recently the MD simulations of ablation processes in Si were presented [40]. The authors concluded that phase explosion is the primary mode of femtosecond laser-based material removal in semiconductors at fluences close to the ablation threshold.

An inner surface feature, similar to that seen in Fig. 1(b) for \( \phi_0 \geq 550 \text{ mJ/cm}^2 \), has previously been reported in femtosecond ablation of InP with 800 nm pulses [6]. The morphology and structure of this feature were studied by optical and micro-Raman spectroscopy, and the authors associated the formation of this feature with the recrystallization of the molten semiconductor. The threshold fluence, determined by \( D^2 \) fitting, was 1300 mJ/cm\(^2\). \( D^2 \) fitting of our data at 800 nm yields a threshold fluence for the inner feature of 770 mJ/cm\(^2\). The threshold values are in reasonable agreement, considering the experimental uncertainties and the different experimental conditions as discussed above. As noted in Section 3, \( D^2 \) fitting of the inner feature gives a larger spot size than \( D^2 \) fitting to the outside crater diameter in the low fluence regime. This discrepancy is most likely a result of mass transport. As the fluence is increased, a significantly larger volume of material is melted. Tight focusing leads to steep temperature gradients in the lateral dimensions, and due to the possibility of hydrodynamic flow [29], the final surface morphology is not expected to be an accurate representation of the local fluence.

The existence of low and high fluence ablation regimes has previously been reported in femtosecond laser ablation of metals [41–43], ceramics [44,45], and semiconductors [10,46,47]. For example, in our earlier work on the micromachining of grooves in InP with 800 nm laser pulses [10], fit parameters were obtained for two ablation regimes, and the onset of the high fluence regime was apparent for values \( \sim 1000 \text{ mJ/cm}^2 \). However, the previous studies were based on multiple pulse irradiation, while the results presented in this study indicate that the two ablation regimes are also observed with single pulse irradiation. Although the current evidence is not generally as compelling as observed in the machining of grooves, it seems to rule out the cumulative effects, which play an important role in multiple pulse ablation [46,48]. Ablation in the
second fluence regime was not studied in detail and the understanding of the underlying physics is still lacking. The two ablation regimes have been discussed for metals in the framework of the two-temperature model [41] where the final depth of the crater is related to characteristic depth of the energy deposition. According to the model the energy deposition profile in the low and the high fluence regimes is determined respectively by the optical penetration depth and electronic heat conduction depth. For semiconductors, Bonse et al. [23] have reviewed multi-pulse data for ablation of Si and InP over a wide fluence range and suggested various physical mechanisms for the enhanced ablation yield at the higher fluences. It should be noted that our high fluence data reaches intensities associated with plasma formation [31,34,49]. Recently, Roeterdink et al. [49] presented the analysis of time of flight ablation of Si(1 1 1) (160 fs, 800 nm) in the fluence range $>1000$ mJ/cm$^2$. The authors presented experimental evidence of Coulomb explosion and plasma formation. In contrast, theoretical calculations and experimental results of other authors [28,50] suggest that Coulomb explosion only occurs in ablation of dielectrics. Discussions of the physics and experimental interpretations are on-going [51,52].

5. Summary

In summary, we presented the first detailed measurements of the wavelength dependence of the ablation threshold of InP over a wide photon energy range. Based on the discontinuity in the maximum crater depth (and equivalently the crater volume versus fluence), the ablation threshold was found to vary from $87$ mJ/cm$^2$ at 400 nm to $250$ mJ/cm$^2$ at 2050 nm. This data can provide benchmarks for theoretical work aimed at predicting the wavelength dependence of the ablation threshold for compound semiconductors. A sharp discontinuity of the depth-versus-fluence behavior observed at all wavelengths is analogous to a number of other experimental results, and to recent results obtained from MD simulations showing spallation effects for femtosecond laser irradiated materials. Finally, our results provide evidence for a two-regime description for the ablation of InP over a wide range of laser fluences.

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Reference
