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Femtosecond laser ablation of gallium arsenide investigated with time-of-flight mass spectroscopy

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We have investigated femtosecond laser-induced ablation of gallium arsenide using time-of-flight mass spectroscopy. At the ablation threshold, we estimated surface temperatures on the order of 3500 K. We observed a clear thresholdlike effect in the number of detected particles and with increasing fluence free flight desorption transforms into a collisional expansion process. Above the ablation threshold, the behavior of gallium particles can be quantitatively described through Knudsen-layer theory. © *1998 American Institute of Physics.* [S0003-6951(98)03919-9]

It has been shown that femtosecond laser pulses offer some advantages in laser processing of materials.[1] However, at the present time the physical mechanisms of femtosecond laser-induced removal of material from solids (laser ablation) is not fully understood. In the case of metals and strongly absorbing semiconductors, laser ablation near threshold can be described in terms of thermal processes even when femtosecond pulses are used. After deposition and thermalization of the laser energy the material melts. Vaporization, boiling or phase explosion may contribute to the material removal, depending on the maximum temperature and the cooling time.[2] However, concerning the detailed dynamics of femtosecond laser ablation there is still some uncertainty. For example, it has been suggested[1,3] that the material would not undergo melting because sublimation occurs on a time scale shorter than the time for the formation of the liquid phase. On the other hand, it is widely accepted that in covalent semiconductors rapid nonthermal melting does occur on a subpicosecond time scale.[4–7] Recent optical measurements on a wide variety of semiconductors show that indeed a solid–liquid phase transition takes place and that the optical properties of the surface remain those of the liquid for several picoseconds after excitation.[8]

Information on the temperature of the surface close to the ablation threshold, to date still lacking, may help in better understanding the process. The surface temperature of laser-heated materials has previously been studied, among other things, by time-of-flight (TOF) measurements of evaporated particles.[9,10] In the context of laser ablation a comparison of TOF distributions below and above threshold could provide useful insight into the physical mechanisms of the mass transport away from the surface.

We report experimental results on GaAs, which is well suited for the present experiment because of several reasons. First, the energy deposition mechanisms in the femtosecond time domain have been widely studied[4–7] and uncertainties in the heating process are therefore minimized. Second, the dynamics of ultrafast laser melting in GaAs is also quite well understood. Third, because of the high vapor pressure of Ga and As, the particle yield is relatively high also in the range below the ablation threshold. Our results show that the nonthermally initiated melting of GaAs results in a liquid surface at a temperature well above the melting point. There is also a clear indication of the formation of a full Knudsen layer in front of the ablated surface at about $2\,F_{\mathrm{th}}$ (ablation threshold fluence).

The experiments were performed in ultrahigh vacuum at pressures below 10^{-10} mbar. TOF distribution of the various laser-desorbed particles were measured using a quadrupole mass spectrometer (QMS) as a particle detector. Desorbed neutrals were ionized at the entrance of the mass filter by means of an electron beam. The laser system consisted of a three-stage-amplified dye laser (colliding pulse mode-locked oscillator) providing 100 fs visible pulses (620 nm). GaAs [100] surfaces, where irradiated with pulses of less than 1 mJ of energy, focused with a lens of 50 cm focal length. The energy densities in our experiment ranged from less than 100 to about 500 mJ/cm^2, the melting and ablation threshold being 100 and 175 mJ/ cm^2, respectively (p polarization, 45° angle of incidence). The ablation threshold was measured by plotting the ablated surface area as a function of the logarithm of the incident fluence.[11] The QMS output, representing the TOF distributions, were recorded with the help of a digital oscilloscope. By suitably translating the GaAs sample after each laser pulse the recorded distributions were always obtained from a fresh surface area. Below the ablation threshold, the measurement of a TOF distribution required averaging over several thousand laser pulses.

Figure 1 shows a plot of the number of detected Ga particles as a function of excitation fluence. Note that across the fluence corresponding to the ablation threshold the number of desorbed particles increases by more than a factor of 2 for a fluence variation of ±3%.

Figure 2(a) shows a typical TOF distribution of Ga particles obtained *below* the ablation threshold at 160 mJ/cm^2. Such a curve can, in principle, be described by two different models depending on the relevance of collisions. A situation in which collisions between desorbed particles is negligible can be modeled with a ''free flight'' half range Maxwellian:[9,10]

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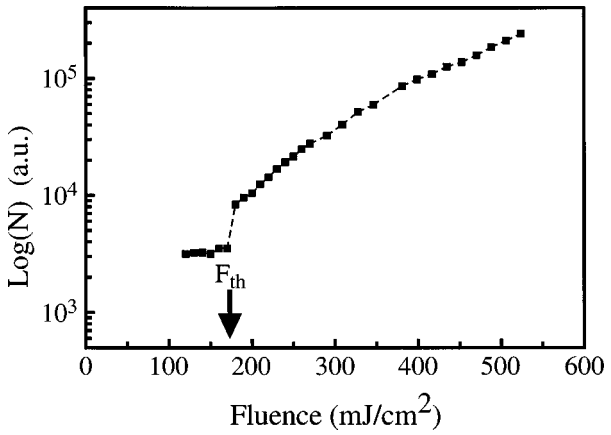

FIG. 1. Relative number of detected particles (arbitrary units) as a function of laser fluence. Black arrow: independently measured ablation threshold.

$$f(t)=A/t^4\exp[-(m/2k_bT_0)L^2/t^2], \tag{1}$$

where L stands for the distance traveled before ionization, k_b is the Boltzmann constant and T_0 represents the characteristic temperature of the distribution. Fitting the measured distribution [Fig. 2(a)] with (1), leaving A and T_0 as free parameters and taking into account the drift time between ionization and detection, yields a temperature of approximately 2500 $\pm$100 K. If one assumes instead that collisions between desorbed particles are significant, the appropriate model is that of a ''full range'' drifted Maxwellian, where the velocity distribution contains the center of mass velocity v_d:[12]

$$f(t)=A/t^4\exp[-(m/2k_bT_d)(L-v_dt)^2/t^2]. \tag{2}$$

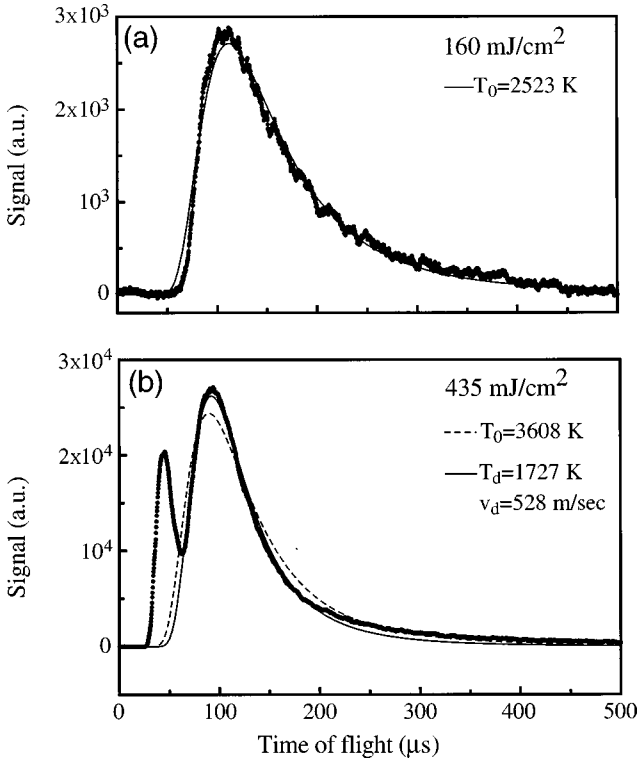

FIG. 2. (a) Time-of-flight distribution below the ablation threshold (160 mJ/cm^2). Continous curve: ''half range'' Maxwellian fit. (b) Distribution above the ablation threshold. Dashed curve: ''half range'' Maxwellian. Continous curve: drifted Maxwellian.

The result for temperature and drift velocity from a fit of the data [Fig. 2(a)] using (2) was barely distinguishable from the preceding result (T_d=2470$\pm$100 K, v_d=23$\pm$30 m/s), confirming the applicability of the free flight hypothesis under these conditions.

Figure 2(b) shows a typical distribution for fluences well *above* the ablation threshold. At shorter time delays an additional peak can be seen. This feature did not disappear when the ionizer in the QMS was turned off, indicating that it is due to the presence of ions in the ablation plume.[13] Taking into account the efficiency of the ionizer, the ion-to-neutral ratio was estimated to be less than 1/1000.

The slow part of the distribution, which represents the neutral particles, has been analyzed also using both (1) and (2). In this case the two different fits give significantly different results. The ''half range'' Maxwellian (1) fits the measured distribution poorly and gives a temperature in excess of 3500 K. On the other hand, a satisfactory result is obtained by fitting the data to a drifted distribution, T_d=1727 K and v_d=528 m/s.

The overall behavior of the temperature and drift velocity as a function of laser pulse energy is shown in Fig. 3. Below threshold the ''half range'' Maxwellian model is the most suited to describe the TOF distributions. With increasing pump fluence we observe a monotonic increase of the fitted temperatures from 1860 K for 120 mJ/cm^2 to about 3050 K at the ablation threshold (175 mJ/cm^2), where it stabilizes to some temperature plateau. Comparing the results of both fitting procedures above threshold we find good agreement (no drifting) up to approximately 1.5 F_{th}.

Above 270 mJ/cm^2 the two models provide very different results. The nondrifted Maxwellian gives progressively unsatisfactory fits [see Fig. 2(b)], with further apparent increase of the temperature. On the other hand, the drifted Maxwellian fits the measured time-of-flight distributions very well, indicating a drop in T_d and a monotonic increase of the drifting velocity v_d. For what concerns the desorption and ablation of arsenic, we detected molecules up to As_4, suggesting that the single molecule desorption picture cannot be applied. Crack products generated by electron impact on arsenic species in the ionizer further complicate the interpretation of the arsenic data.

Our interpretation of the results proceeds along the following lines. The laser energy is deposited in the sample on a time scale shorter than that necessary for any structural transformation. Below the ablation threshold particle desorption is due to normal vaporization. Being in ultrahigh vacuum, the net desorption from the sample is positive at any temperature, and the total number of desorbed particles can be calculated using the Clausius–Clapeyron equation.[2] The number of desorbed particles is sufficiently small that the gallium atoms suffer almost no collisions after detaching from the surface. Therefore, the measured particle temperature represents the surface temperature. With the desorption probability being exponentially dependent on the temperature, one expects that most of the particles are released from the center of the heated area when the temperature reaches its highest value.[9,10] Model calculations show that the measured particle temperature only slightly underestimates the maximum surface temperature in the center of the irradiated spot.

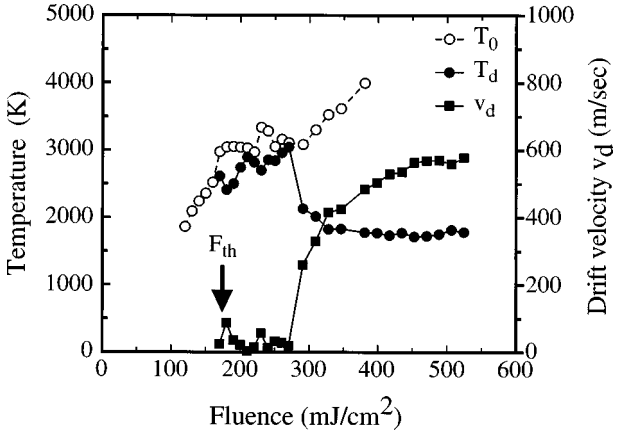

FIG. 3. Curve fit results with both half range and full range Maxwellians. Empty circles: half range temperature fit. Full circles: full range Maxwellian temperature (error bars corresponding to a systematic error of ± 100 K are omitted for clarity). Full squares: drifting velocities of the full range Maxwellian.

The error is calculated to range from 150 to 400 K for maximum surface temperatures of 1500 and 3000 K, respectively. We measure temperatures increasing from 1860 to 3050 K for fluences ranging from 1.2 times the melting threshold to F_{th}. This indicates that the liquid surface is heated significantly above the melting point of GaAs($T_M = 1511$ K), reaching a maximum value of approximately 3500 K at the ablation threshold.

As shown in Fig. 1 the number of particles increases significantly above F_{th}, and the increase of the signal with laser fluence becomes steeper. Interference microscopy of the ablated surface area reveals an ablated layer of about 10–20 nm in depth even for fluences slightly above F_{th}. This is a clear indication of the occurrence of a thresholdlike *bulk* effect such as explosive boiling. Under these conditions the simple ''free flight'' hypothesis fails to describe the mass transport, and one expects[2,12] to observe the appearance of some drift velocity, according to (2). This expected behavior is indeed observed in the measured TOF distributions as the laser fluence is increased well above its threshold value. Slightly above threshold neither of the two models gives reliable results, since the observed distribution represents a spatial average over the central area where ablation occurs, and outer areas below threshold where particle emission is due to desorption. Figure 1 shows that just above the ablation threshold the total number of particles amounts to about 2–3 times that measured below, suggesting that ablation and desorption contribute with comparable amounts to the measured signal. When the fluence reaches about 1.5 F_{th} we estimate that more than 90% of the total number of detected particles are due to ablation. Therefore, we assume that in this case (2) provides a reliable model.

As optical measurements show,[8] ablation starts from a *bulk liquid* and is likely to be initially accompanied by expansion, phase decomposition and eventual transformation into a dense gas. Collisions in the gas are likely to be responsible for the formation of a Knudsen layer[12] after the material has decomposed in the new phase. For a fully formed Knudsen layer the drift velocity should be given by $v_d = (\gamma k_b T_d / m)^{1/2}$, where $\gamma = C_p / C_v^{12}$. Above the ablation threshold T_d stabilizes around 1800 K, whereas v_{d} reaches a value slightly below 600 m/s. Assuming $\gamma = 5/3$ (ideal gas) the Knudsen layer theory predicts values for v_d which are within 5% of the measured drifting. This relationship is strictly fulfilled only above about 2.5 F_{th} possibly because of a lower effective value of γ close to the ablation threshold. It is important to stress that T_d represents only a flow parameter and it is neither the surface temperature nor the temperature of the expanding gas.[14] Nevertheless, a formal relationship exists between T_d and v_d, the fulfillment of which indicates the formation of a full Knudsen layer in front of the sample.

Quantitative connection between asymptotic and initial behavior is, however, not trivial and the transition between condensed and gas phase is, from the present results, unaccessible. Further experimental information on temperature and density evolution in the early stage of expansion would be very desirable in order to better understand the ablation process.

In conclusion we have performed TOF spectroscopy on [100] GaAs surfaces irradiated with femtosecond laser pulses. We observe an increasingly hot liquid surface below the ablation threshold from which a step like the ablation process originates. The highest measured temperature below the ablation threshold is about 3050 K, corresponding to an expected maximum temperature of approximately 3500 K. Our TOF distributions transform from half range into full range Maxwellian, and the quantitative relationship between temperature and drift velocity can be described within an excellent approximation with the model of Knudsen layer formation in an ideal monoatomic gas.

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