Time of Flight Mass Spectroscopy of Femtosecond Laser Ablation of Solid Surfaces

A. Cavalleri, K. Sokolowski-Tinten, J. Bialkowski, D. von der Linde

Institut für Laser und Plasmaphysik, Universität-GHS-Essen, Germany

Abstract. Velocity distributions of evaporated particles from laser irradiated GaAs and Silicon give a temperatures in excess of 3000 K at the ablation threshold. The results suggest that explosive boiling causes material removal.

After excitation with femtosecond laser pulses, ablation can be achieved at the surface of an absorbing solid. While for lower fluences normal evaporation/sublimation causes particle desorption from the surface, above a fluence threshold $F_a$ macroscopic removal of material takes place and craters are left on the surface.

By means of time-of-flight (TOF) mass spectroscopy, we measure the velocity distributions of gallium and silicon particles from GaAs and Si surfaces, respectively. A quadrupole mass spectrometer (QMS) provides the TOF distribution of a given particle mass after excitation with a 100 fs, 620 nm laser pulse. In order to provide information on single shot ablation, the sample is translated after every exposure. The ablation threshold $F_a$ is measured independently by means of post mortem analysis.

Figure 1 shows the total number of particles as a function of normalised laser fluence. Below $F_a$, the number of particles depends on the specific surface, consistent with what expected for normal desorption from a hot semiconductor surface.

![Graph](image_url)

**Fig. 1** Number of detected particles from GaAs and Silicon as a function of normalised laser fluence. The ablation threshold corresponds to $F/F_a=1$
Above threshold the total number of detected particles shows instead a common behavior for both Si and GaAs, suggesting that a process of general nature is taking place. The step observed at $F_a$ in the total number of particles, together with the abrupt creation of a 20 nm crater, suggest that ablation is a bulk effect.

The measured velocity distributions have been quantitatively analysed taking into account the relevance of mutual interaction of the released particles. If the density of desorbed particles is low, no interaction occurs and a free flight model of the TOF signal can be applied (equation 1). Since the desorption probability is an exponential function of the surface temperature, the measured $T_0$ provides a good approximation of the maximum surface temperature $T_{s\text{\,(max)}}$ [1].

$$f_{\text{free}}(t) = A / t^4 \exp\left[\frac{-m}{2k_bT_0} \frac{L^2}{t^2}\right]$$  \hspace{1cm} (1)

Figure 2 shows the result of our fits below the threshold for ablation. In both cases the measured maximum surface temperature increases monotonically from the respective melting temperatures at the corresponding fluences $F_m$ to a value in excess of 3000 K at $F_a$.

![Figure 2](image_url)

**Fig. 2** Fitted maximum surface temperature for laser fluences below the ablation threshold

For higher laser fluences ($F>F_a$) the density in front of the sample increases. Mutual interaction is responsible for the development of a "full range" Maxwellian distribution [2,3]. Two flow parameters are then required to describe TOF distributions, temperature $T_d$ and drift velocity $v_d$.

$$f_{\text{full}}(t) = A / t^4 \exp\left[\frac{-m}{2k_bT_d} (L - v_d t)^2 / t^2\right]$$  \hspace{1cm} (2)

$L$ is the flight distance before detection, $m$ for the particle mass and $k_b$ is the Boltzmann constant. Figure 3 shows the corresponding fitting results for gallium atoms, $T_d$ decreases towards approximately 1800 K, whereas $v_d$ reaches values of
the order of 600 m/sec. For F>F_a we interpret only the results on Ga (GaAs), where only monomers are detected.

![Graph showing temperature and drift velocity](image)

**Fig. 3** Temperature and drift velocity resulting from a Full-range-Maxwellian fit of the velocity distributions of gallium particles for F>F_a

Ablation starts from a hot liquid surface whose temperature is below the critical temperature (approx 5000 K in silicon). Optical data [4] suggest that rapid phase decomposition (explosive boiling) occurs after creation of a hot, liquid layer of about 20 nm. The initial phase of the expansion, where formation of the gas phase occurs, is to be described within a hydrodynamic picture [4]. Upon dilution however, the system goes through a phase where the description as a continuum is not appropriate anymore and single collisions between the particles occur on a timescale which is comparable with that of the expansion. A Knudsen layer, corresponding to that region in front of a sample where collisions are relevant, is formed. After further dilution, the particles become ballistic and fly towards the mass spectrometer where they are detected. According to Knudsen layer theory [2] the relationship between the two fitted parameters should be \( v_d = \left( \frac{\gamma k_B T_d}{m} \right)^{1/2} \), where \( \gamma = C_p/C_v \) in the Knudsen layer. Above 2.5*F_a, the theoretical relationship between \( v_d \) and \( T_d \) holds within less than 5% with \( \gamma = 5/3 \).

In conclusion we have measured the maximum temperature of GaAs and silicon surfaces irradiated with visible femtosecond pulses for several fluences below the ablation threshold. We find peak temperatures at F_a of 3200-3500 K. Phase decomposition occurring at the beginning of the expansion process results eventually into a dense vapor in which a Knudsen-layer is formed.

**References**
