

# Short pulse UV laser ablation of solid and liquid gallium

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**Abstract.** UV laser ablation of gallium from the solid (300 K) and liquid (330 K) phase is reported. The ablation is performed by using a 248 nm excimer laser with pulse durations of 15 ns and 0.5 ps. The ablated neutrals are ionised by resonant multiphoton ionization with a time-delayed laser (605 nm, 15 ns) and are detected by time-of-flight mass spectroscopy. The ablation threshold fluences, the ablation rates, and the velocity distributions of Ga atoms from the solid and liquid phase for irradiation with 0.5 ps and 15 ns pulses are determined. The threshold fluence for 0.5 ps laser ablation is found to be 7 times lower than that for 15 ns laser ablation and is identical for the solid and liquid samples of gallium. For ns pulses, the threshold fluence is 1.5 times higher for the solid compared to the liquid phase. This difference between the sub-picosecond and nanosecond laser ablation behaviour can be explained by the longer and deeper heat diffusion during the longer laser pulses. The time-of-flight measurements show the thermal behaviour of the removed Ga atoms in both 0.5 ps and 15 ns laser ablation and are fitted to Maxwell–Boltzmann distributions giving translational temperatures of several thousand Kelvin. An increase in the temperature as a function of the ablation laser fluence is observed.

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Pulsed UV laser ablation [1–3] has been successfully applied as an effective tool in the surface processing for mechanical and microelectronics applications. The interaction of laser light with matter and, in particular, the laser ablation of metals [4–6], semiconductors [7], oxides [8,9], and polymers [10,11] is extensively investigated. Ablation depends on both the materials properties and the laser beam characteristics. The use of short laser pulses simplifies the laser–matter interaction mechanism, enabling precisely ablated features [12,13] for materials processing. During short laser pulses, heat diffusion into the material can be neglected. A good approximation of the thermal diffusion length  $L$  is given by  $L \propto (Dt_p)^{1/2}$ , where  $D$  is the thermal diffusivity and

$t_p$  the pulse duration [14]. For metals and ns pulses,  $L$  is on the order of  $\mu\text{m}$ , whereas for fs pulses  $L$  is decreased to the nm scale. The use of fs laser pulses minimises the thermal diffusion length to within the optical absorption depth [15,16], and thus the energy is accumulated into a small volume of the material resulting in more efficient laser ablation and a decrease of the ablation threshold.

The aim of this work is to understand [17] the ablation of metals from the solid and liquid phase in more detail and to examine the influence of the thermal heat diffusion on the ablation process. The ablation threshold of metals with different thermal properties, such as thermal conductivity and heat capacity was measured with two different UV laser pulse durations (15 ns and 0.5 ps). This work is related to our previous studies [1,15] on short-pulse UV laser ablation of metals, where the ablation of solid nickel and solid and liquid indium by using ns and fs pulses were reported. A strong reduction of the ablation threshold was observed when the pulse duration was reduced from 15 ns to 0.5 ps. The measurements on solid and liquid indium show the influence of the thermal diffusion on the ablation process, whereas the time-of-flight measurements show that ablation is a thermal process. In the work presented here, aiming at understanding the ablation behaviour of metals, we have studied the ablation of neutral Ga atoms from the liquid and solid phase by using UV laser pulse durations of 15 ns and 0.5 ps. The ablated Ga atoms were ionised by resonant multiphoton ( $2 + 1$ ) ionization and were detected by time-of-flight mass spectroscopy.

In order to obtain information about the basic mechanism of laser ablation of metals it is necessary to perform experiments at low fluences. This way we avoid the interaction between the ablating species via collisions and stay below plasma formation in order to measure the initial stages of the ablation process.

## 1 Experimental

The experimental setup is schematically shown in Fig. 1. High-purity gallium (99.99%), was placed in a heatable ro-

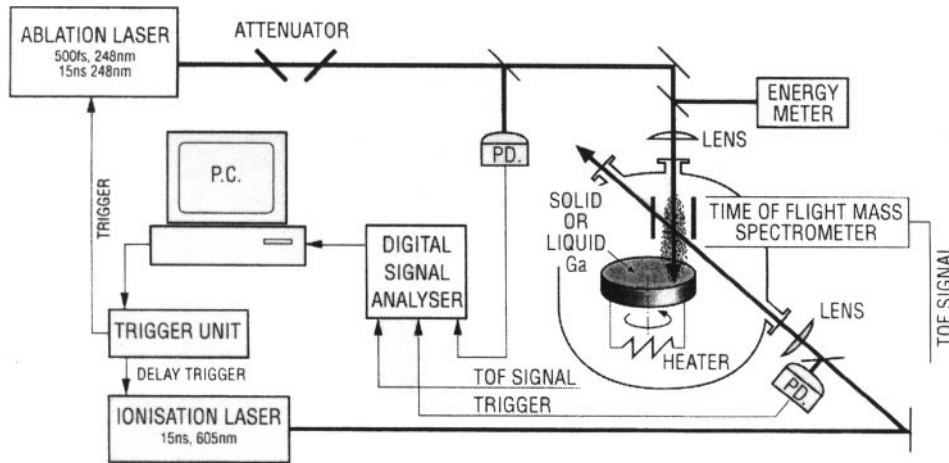


Fig. 1. Experimental setup

tating holder whose temperature was measured by a thermocouple. The experiments were performed in a high-vacuum chamber ( $10^{-7}$  mbar). The sample was heated up to 330 K. The time-of-flight apparatus [18] as well as the ablation lasers [1, 15] have been already described elsewhere. The ionization laser was a dye laser (605 nm, 15 ns) pumped by a pulsed excimer laser (308 nm). A homogeneous part of the ablation laser beam was focused ( $f = 300$  mm) onto the sample surface. A 50% dielectric mirror was used to reflect part of the beam onto an energy meter and the fluence could be changed by a variable attenuator.

The  $\text{Ga}^0$  atoms were ionised at 605 nm by resonant multiphoton ( $2+1$ ) ionization via the  $5p^2P^0$  state. The ionization occurs after a flight distance of 28 mm above the sample surface between the grids of the time-of-flight mass spectrometer.

The ablation thresholds of solid- and liquid-phase gallium and the dependence of the ablation signal on the laser fluence were measured and analysed. A constant delay time between the ablation and the ionization lasers was selected and the fluence of the ablation laser was varied by varying the pulse energy by means of the attenuator. The fixed delay time between the ablation (248 nm) and the ionization (605 nm) lasers was set to  $24 \mu\text{s}$  for the ns ablation case, whereas for the fs ablation laser it was set to  $20 \mu\text{s}$ . The laser fluence range was chosen in the desorption regime, where collision-free conditions predominate. The ablation signal versus delay time between the ablation and the ionization lasers was also measured.

## 2 Results

The Ga atom signal (with the proper isotope abundances) was measured as a function of the ablation laser fluence for solid- and liquid-phase gallium by using 15 ns and 0.5 ps laser pulses at 248 nm.

Figure 2 depicts the gallium atom signal from the solid and liquid phase ablated by a 248 nm, 15 ns excimer laser, as a function of the ablation laser fluence. The ablation for the gallium solid phase starts at  $17 \text{ mJ/cm}^2$  (threshold); for the liquid phase it is lowered to  $12 \text{ mJ/cm}^2$ . The atom signal for the solid increases slowly just above the threshold fluence and then, above  $25 \text{ mJ/cm}^2$ , shows a linear dependence for the in-

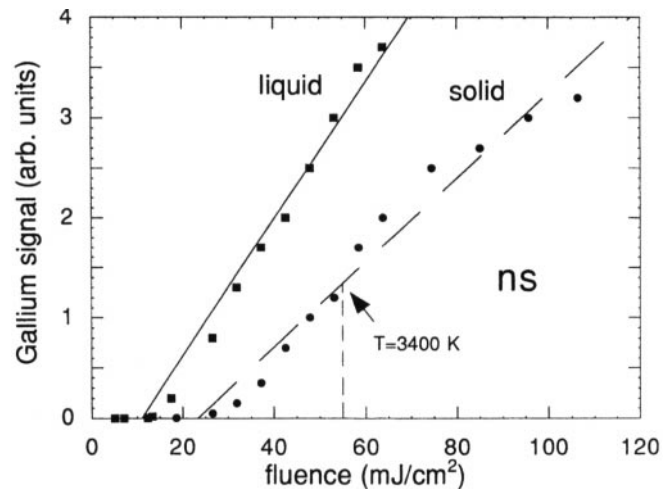
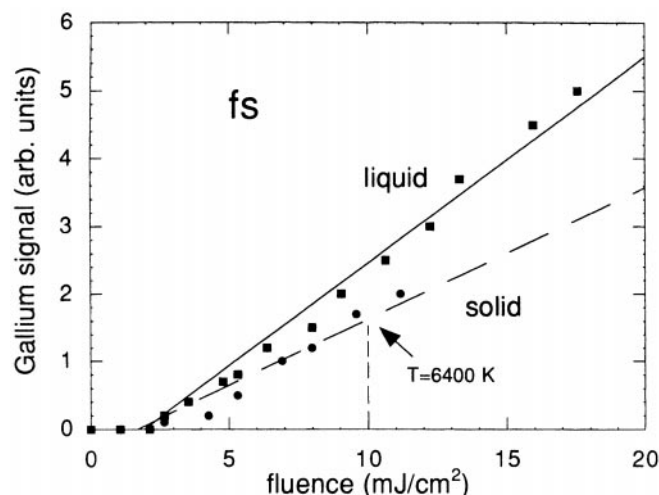


Fig. 2. Signal of the ablated neutral gallium atoms from the solid and liquid phases as a function of the laser fluence with 15 ns pulses at 248 nm. The ablation threshold of the liquid phase is lower than that of the solid phase. The arrow indicates the laser fluence at which the kinetic energy distribution was determined (see Fig. 4)

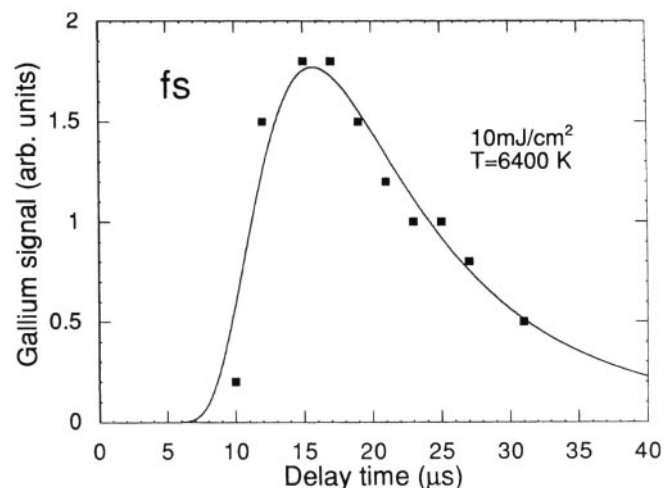
vestigated higher fluences. The slope of the ablation signal for the liquid phase is a factor of 1.6 higher than that of the solid phase.

For fs ablation, the threshold fluence of the gallium atoms from the solid phase is identical to that from the liquid phase at  $2.5 \text{ mJ/cm}^2$  (Fig. 3). The slope of the ablation signal for the liquid phase is a factor of 1.6 higher than that of the solid phase, which indicates a higher ablation efficiency. The threshold fluence is a factor of 7 smaller than the ns ablation threshold for the solid phase and by a factor of 5 smaller for the liquid phase.

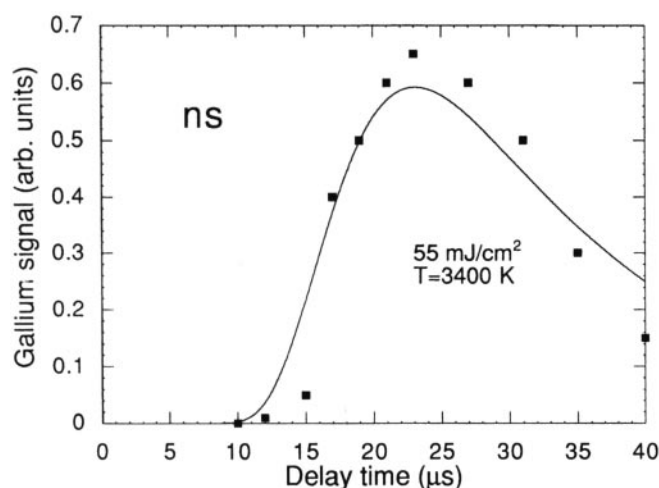
In order to obtain information about the dynamics of the ablation process, the ablation signal was measured, at constant ablation energy fluence, as a function of the delay time between the ablation and the ionization lasers. Figure 4 shows the time-of-flight distribution of the gallium atoms originating from the solid surface as a result of ns laser ablation at  $55 \text{ mJ/cm}^2$  (see arrow in Fig. 2). The experimental data can be approximated by a Maxwell-Boltzmann velocity dis-



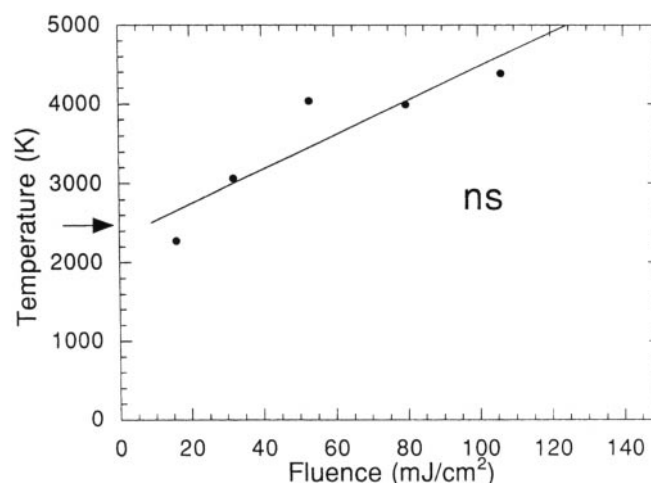
**Fig. 3.** Signal of the ablated neutral gallium atoms from the solid and liquid phases as a function of the laser fluence with 0.5 ps pulses at 248 nm. The ablation threshold was found to be equal for both the solid and the liquid phases of gallium. The ablation efficiency is 60% higher in the case of liquid gallium. The arrow indicates the laser fluence at which the kinetic energy was determined (see Fig. 5)



**Fig. 5.** Time-of-flight distribution of the gallium atoms from the solid surface at 10 mJ/cm<sup>2</sup> and 0.5 ps (see arrow in Fig. 3). The signal is fitted by a Maxwell-Boltzmann distribution corresponding to the temperature of 6400 K



**Fig. 4.** Time-of-flight distribution of the gallium atoms from the solid surface at 55 mJ/cm<sup>2</sup> and 15 ns (see arrow in Fig. 2). The signal is fitted by a Maxwell-Boltzmann distribution corresponding to the translational temperature of 3400 K



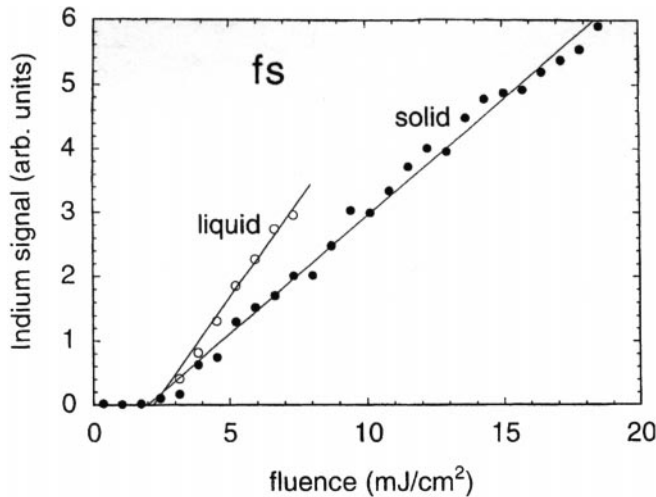
**Fig. 6.** The translational temperature of gallium atoms from the liquid surface as a function of the ns ablation laser fluence. The arrow on the vertical axes indicates the boiling point of gallium (at 1 atm)

tribution [19] corresponding to the translational temperature of 3400 K. Figure 5 depicts the time-of-flight distribution of the gallium atoms originating from the solid surface as a result of fs laser ablation at 10 mJ/cm<sup>2</sup> (see arrow in Fig. 3). A Maxwell-Boltzmann velocity distribution is shown with the translational temperature of 6400 K. Therefore, the translational temperature for the fs ablation (at a fluence 4 times above threshold) is about two times higher than that for the ns ablation (at a fluence three times above threshold). Additionally, for ns and fs ablation, systematic measurements of the time-of-flight distributions show that the translational temperature of the ablated gallium atoms increases with increasing laser fluence, which is shown in Fig. 6 for liquid gallium and ns pulses.

### 3 Discussion

The comparison of Figs. 2 and 3 shows that the threshold for removal of gallium atoms is strongly reduced when the laser pulse duration is reduced from 15 ns to 0.5 ps. In addition, the efficiency (slope of the ablation curve) is increased when gallium atoms are removed from the liquid phase rather than from the solid phase for both 15 ns and 0.5 ps laser pulses. Also, we notice that the efficiency for the ns laser ablation increases gradually just above threshold, whereas for the fs laser ablation it is constant at all the fluences studied.

The most prominent difference between the fs and ns ablation of gallium from the solid and liquid surfaces is that the ablation threshold for short pulses is *independent* of the metal phase. These results are in very good agreement with our previous work on indium. Figure 7 shows the ablation signal of the neutral indium [1] atoms from the liquid and solid



**Fig. 7.** The signal of the ablated neutral indium atoms from the solid and liquid phases as a function of the laser fluence with 0.5 ps pulses at 248 nm. The ablation threshold was found [1] to be equal for both the solid and the liquid phases of indium. The ablation efficiency is higher in the case of liquid indium

phase by 0.5 ps laser pulses at 248 nm. The ablation threshold is  $2.5 \text{ mJ/cm}^2$ , identical for the liquid and solid phases of both indium and gallium metals, apparently independent of the thermal properties of these materials (compare Figs. 3 and 7).

We suggest the following mechanism to explain this behaviour. For the 0.5 ps pulses, the thermal diffusion length during the laser pulse is about 5 nm only. The ablation threshold in the case of the 0.5 ps laser is small because the energy is accumulated within the optical penetration depth (about 20 nm) in the material. In contrast, in the case of the ns pulses, an energy dissipation occurs within the thermal diffusion depth of the material resulting in an increase of the threshold.

The thermal diffusivity changes at the melting point of Ga from  $40.6 \text{ W/mK}$  for the solid to  $33.1 \text{ W/mK}$  for the liquid at 330 K [20, 21]. Since the thermal diffusion length in the case of liquid gallium decreases, the energy is accumulated closer to the surface resulting in the decrease of the ablation threshold. The experimental data are in very good agreement with this concept, since the ablation threshold of gallium from the liquid phase is a factor of 1.5 lower than that of the solid (see Fig. 2). For the ns irradiation of liquid In, a reduction (by a factor of 3) in the threshold fluence was observed compared to the solid phase; this is also due to the (twofold) lower thermal diffusivity of the liquid compared to the solid.

The time-of-flight velocity distributions for ns and fs pulses are fitted to Maxwell–Boltzmann distributions; this supports the thermal mechanism model for the UV laser ablation of metals. We do notice that the temperature of the Ga atoms from liquid gallium at approximately the ablation threshold fluence ( $15 \text{ mJ/cm}^2$ ) is determined to be 2280 K, which is very close to the boiling point of gallium at 2477 K (at 1 atm) [21]; see arrow in Fig. 6.

The increase in the translational temperature of the ablated gallium atoms (Fig. 6) versus fluence is fitted to the equation  $(1 - R)\Delta Q = mc_p\Delta T$ , where  $\Delta Q$  is the laser pulse energy,  $R$  the reflectivity of the surface at 248 nm,  $c_p$  the heat

capacity, and  $\Delta T$  the induced temperature rise. The slope of this line gives a value for  $c_p$  of  $0.42 \text{ J/gK}$ , if we assume that the reflectivity of liquid gallium is 0.85 [23] and the energy is absorbed within the volume defined by the laser spot area and the penetration depth of 30 nm. This is in agreement with the tabulated value of  $c_p$ , which is  $0.45 \text{ J/gK}$  (obtained by extrapolation [21]).

Finally, the different slopes of the ablation rates for liquid- and solid-phase Ga for both fs and ns laser ablation may partly be due to the different surface properties of the liquid and solid surfaces. The slight difference of the reflectivities *cannot* explain the difference of the ablation efficiency between the liquid and solid phase since the reflectivity of Ga at 248 nm changes from 0.8 for solid Ga [22] to 0.85 for the liquid Ga [23] and this should rather lead to a higher efficiency for solid gallium. On the other hand, it was observed that during the laser ablation of the solid material, when the same surface area was illuminated, the ablation rate decreased with an increase in the applied number of laser pulses. This was also observed previously [1, 24] and is attributed to the removal of all weakly bound species near surface defects. This leads to a higher ablation efficiency from the liquid phase since that surface can rapidly change due to diffusing atoms and molecules.

## 4 Conclusions

A detailed study of the ablation of solid- and liquid-phase gallium with short UV laser pulses is reported. The fs ablation behaviour is independent of the metal phase. The ablation threshold is reduced to identical values for both the solid and the liquid phase when fs pulses are used instead of ns pulses. This decrease is explained by the reduced heat diffusion during the short pulse. In contrast, for the ns pulses, the ablation threshold of the liquid is lower than that of the solid, and this is due to the lower thermal diffusivity of the liquid, which allows a better accumulation of the pulse energy close to the surface. The time-of-flight measurements show a Maxwell–Boltzmann distribution, which indicates thermal behaviour of the ablated Ga atoms for both fs and ns laser ablation. The corresponding translational temperature of several thousand Kelvin increases linearly with the laser fluence. The efficiency for ablation of gallium atoms from the liquid phase is 60% higher than that from the solid.

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