Dynamics of Laser Desorption and Ablation of Metals at the Threshold on the Femtosecond Time Scale

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The dynamics of the laser-ablation (-desorption) process of metals (Al, Ag, Fe, and Ni) initiated by 30 fs laser pulses has been investigated by interferometric time-resolved pump-probe measurements. It is postulated that a sufficiently high density of hot electrons is essential for achieving desorption of metal ions. In addition, we have observed a new and unexpected behavior characterized by delayed ablation for a pump-probe beam delay in the range of several ps for Al, Ni, and Fe. This second peak is attributed to the development of a liquid surface layer developing after a few ps. Molecular dynamics simulations support this assumption.

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Advantages of using ultrashort laser pulses on the fs time scale as compared to longer pulses in the ps or ns range for laser ablation have been established recently, in particular for surface microprocessing, micromachining, and surgical application, where controlled removal of material is essential [1–3]. It is the general perception that the first step in the chain of processes responsible for ultrashort laser ablation of metals is the coupling of the laser field to the electrons of the metal and, as a consequence, the development of a nonthermalized electron gas [4–6]. The two-temperature model commonly describes the temporal evolution of the system and treats electrons and lattice as individual subsystems which may attain different temperatures and which are linked by a finite electron-phonon (e-ph) coupling constant [2,6–10]. Nonequilibrium electron heating and thermalization has been observed through transient reflectivity changes [11], optical damage [12], desorption of adsorbates from a surface [13], or time-resolved photoemission spectroscopy [14]. Such measurements on metals, usually applying pump and probe techniques, revealed that thermalization of electrons occurs between hundreds of femtoseconds and a few picoseconds and strongly depends on the laser fluence and the density of states of the metal near the Fermi energy [11,14–17]. The subsequent heating of the lattice has been measured to take place on the ps time scale [7,8].

In this paper we report the first measurements of the yield of emitted ions (singly charged) from a metal surface as a function of the pump-probe delay of two subthreshold laser pulses of duration below 30 fs. Only very few time-resolved measurements of that kind have been reported thus far [18], and none for metals and laser pulses below 100 fs. The experiments have been performed using a two-pulse autocorrelation setup in which the differential yield of emitted metal ions is measured as a function of the temporal separation between a pair of excitation pulses with a reflectron-type time-of-flight (TOF) spectrometer. We have chosen the interferometric method, which automatically yields information about the laser pulse length. Furthermore, a noninterferometric method would have required rotating the polarization of one of the beams. This can also introduce changes of the pulse shape, which we wanted to avoid. The intensity of each pulse is kept below the ablation threshold. In particular, we present the results of measurements on Al, Ag, Fe, and Ni targets. All targets were polycrystalline. The surface was mechanically polished. Each set of measurements has been performed on the same spot on the target. This method has been chosen, instead of using a virgin spot after each laser shot, because it was verified that the signals did not change with increasing shot number. The experiments have been performed in an UHV chamber equipped with a reflectron-type time-of-flight mass spectrometer. Details of the apparatus have been published previously [19]. In the present setup, the laser system consists of a mode locked Ti:sapphire oscillator (Laser Source Pro HP) and a multipass Ti:sapphire amplifier (Omega Pro). The system, operating at a repetition rate of 1 kHz, provides laser pulses at a center wavelength around 800 nm (1.5 eV photons) with a typical duration of 30 fs measured at the sample. The laser fluence could be varied between 10–150 mJ/cm^2. The beam was incident on the surface at an angle of 45 degrees measured from the surface normal and was focused to a spot of $\sim$500 μm diameter. This rather large spot size was chosen in order to minimize unpredictable influences on the ion signal due to a slight lateral drift and, hence, decreasing spatial overlap of the spots. The TOF axis was normal to the target surface and the distance between target and TOF entrance about 1 cm. The length of the TOF was about 2 m. We have detected only singly charged metal ions. The TOF mass spectrum showed no evidence of multiple charged ions. The base pressure in the UHV chamber was below 10^{-9} torr. In order to probe the relaxation dynamics of the first excitation — crucial for the ablation — with fs time resolution, the measurements were performed using a Michelson interferometer setup for splitting the laser pulse into a pair of equally polarized pulses of approximately the same intensity. One pulse was delayed with respect to the

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other by changing the length of one interferometer arm. For this purpose, one of the mirrors was mounted on a stepper-motor driven translation stage with a spatial resolution of 0.1 μm which corresponds to a time delay of approximately 0.7 fs. It must be pointed out that the time information obtained in this way concerns only the initial excitation responsible for ablation, but does not yield information about the dynamics of how this excitation is eventually transferred into kinetic energy of the ablated particles [13].

In Fig. 1 the signal for ablated (desorbed) Al and Ag ions is plotted as a function of the delay time between the two 30 fs subthreshold pulses. Different scales on the x axis visualize the two time domains. A major ablation feature is found, when the two pulses overlap in the time domain. With decreasing overlap, the amount of emitted ions decreases. The coherent region of the pulse overlap can be clearly identified by the interference pattern of the ablation signal as is shown in the inset graphs in Fig. 1. A slight asymmetry for the silver signal with respect to zero pump-probe delay (inset in Fig. 1) can be observed. Depending on the scan direction of probe vs pump beam, we always observe slightly enhanced ablation persisting for several seconds after the desorption maximum has been reached. This has to be attributed to a surface modification.

When the two beams are separated by more than 40 fs, Al and Ag behave differently: For Al the ion signal drops below the detection limit to essentially zero, while for Ag an exponentially decaying signal is observed. The small graphs in Fig. 1 show the signal with a high time resolution in the fs domain. For Ag two contributions can be clearly identified, one resulting from the combined action of the interfering laser pulses, the second one for pulse delays up to 200 fs.

An additional unexpected feature is observed when the two pulses are separated by more than 5 ps. While Ag behaves as expected, Al (and also Ni and Fe) shows a second peak of emitted ions. This implies that several ps after the pump pulse the probe laser pulse encounters the system in a state, in which it can further excite the surface to cause ablation. The astonishing fact is that the system is less receptive to a second laser pulse immediately after the end of the first pulse (up to a few ps). As can be seen in Figs. 2 and 3, a similar behavior is also found for Ni and Fe. In Fig. 2 the envelope of the measured interferometric signal from zero pulse delay up to 300 fs as well as the ps-delayed signals are compared for different metals. The signals in Fig. 2 are normalized to the maximum at zero delay. The dominant feature around zero pump-probe delay is a fast decaying ion signal that drops to zero for Al, Fe, and Ni when the two pulses are totally separated in time. Contrary to Al, Fe, and Ni, Ag exhibits an extended signal up to approximately 200 fs which can be fitted with an exponential decay with $\tau = 75$ fs. The right part of Fig. 2 shows, after the scale change of the x axis, the behavior of the targets for delays between pump and probe pulse in the ps range. The curves shown are best fits to the measured data. Error

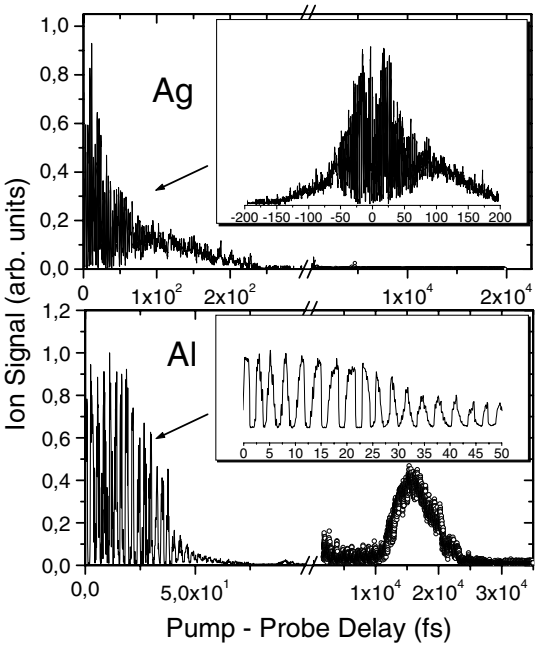

FIG. 1. Time profile of the Ag- and Al-ion signal emitted from a polycrystalline metal target surface under irradiation by two delayed 30 fs laser pulses. The intensity of a single pulse was below the ablation threshold of the respective target material. The x axis represents the delay of one pulse with respect to the other starting at the temporal overlap. On the x axis, two different scales have been used to better visualize the two time domains. The small graphs show the signal with a higher resolution in the fs domain.

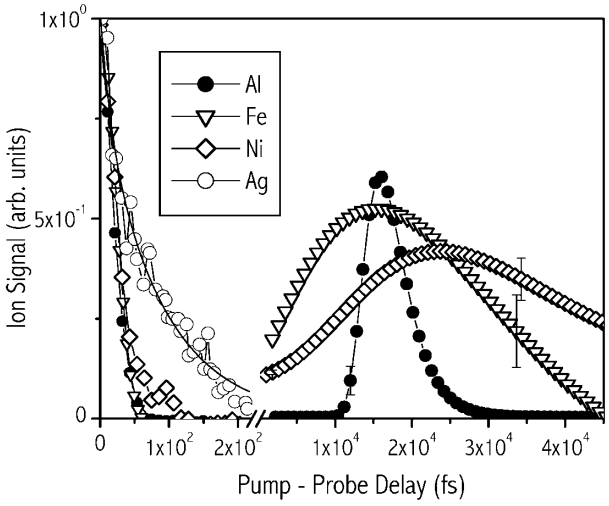

FIG. 2. Signal of emitted Ag, Al, Fe, and Ni ions as a function of the time separation near the pulse overlap of two subthreshold 30 fs laser pulses. Only the envelope of the measured interferometric signal is shown. On the x axis, two different scales have been used to better visualize the two time domains. In the ps range the best fit to the measured data for Al, Fe, and Ni is shown. Error bars are given to indicate the actual fluctuations of the measured data. The spectra are normalized to 1 at zero pump-probe delay.

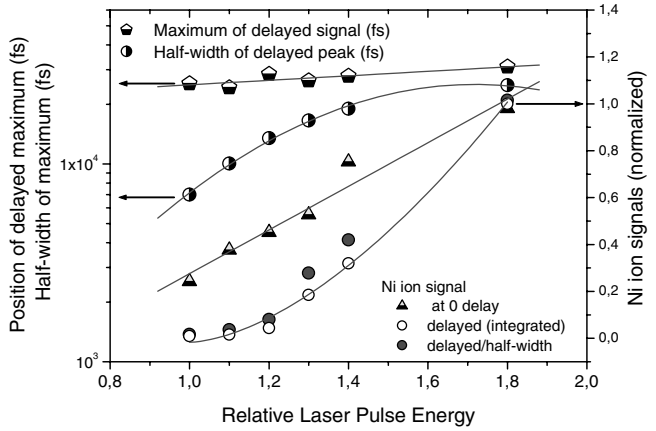

FIG. 3. Dependence of the measured Ni ion ablation data on laser intensity. Relevant measured parameters are shown as a function of the relative laser intensity arbitrarily set 1 for the lowest value. The absolute values were around 10^{12} W/cm^2, but in any case lower than the ablation threshold for one pulse. (For further details see the text.)

bars indicate that the fluctuations of the measured signals increase from Al to Fe. In all cases it was assured by blocking each of the two beams individually and adjusting the laser intensity that no emitted ions were detected. For Al, Fe, and Ni the absolute laser fluence was similar, while in the case of Ag the threshold was higher by a factor of 5 to 10. The signal for Ag in the ps range is not shown since it is essentially zero. For Al the delayed peak is located between 10–25 ps. The slope is rather steep and its width is small compared to Ni and Fe. In addition, the Ni peak is shifted to longer pump-probe delays as compared to Al and Fe. The position of the maximum is not influenced by the laser intensity.

The intensity range, which can be investigated, is rather limited, since each individual pulse has to be kept below the threshold. In Fig. 3 this question has been addressed for Ni. It shows the relevant parameters obtained from the measured spectra as a function of the relative laser intensity arbitrarily set 1 for the lowest value. The absolute values were around 10^{12} W/cm^2. While the maximum stays practically constant, the width more than doubles. While the peak at zero delay grows approximately with I to I^2 (I laser intensity), the total delayed yield (and yield divided by half-width) increases with I^3 to I^4. When pump and probe beam, each with intensity $I_{\text{pump}} = I_{\text{probe}} = I_{1,\text{metal}}$ overlap in time, all metals we have investigated show substantial emission of metal ions. Since the laser intensity $I_{1,\text{metal}}$ is below the threshold for detectable ion emission, we can conclude that the combined laser intensity $4I_{1,\text{metal}}$ of the interfering laser beams heats the electrons sufficiently to cause ablation. [6,7].

In order to explain the ablation behavior, we can assume that the photons of a fs pulse create an electron energy distribution with a high amount of ballistic electrons [20]. The time scale on which such a distribution thermalizes to a Fermi Dirac distribution of typically several thousand degrees kelvin strongly depends on the laser fluence, the electron energy above the Fermi energy and the density of states at the Fermi energy [6,14,17,20]. According to the Fermi-liquid theory, the lifetime of nonthermal electrons as created by the laser pulse scales with the inverse square of the energy above the Fermi energy. For Au the lifetimes have been measured for a laser fluence of 300 μJ/cm^2 and 0.4 eV electrons to be around 650 fs [14]. In the experiments presented here, a typical laser fluence of 10–50 mJ/cm^2 for the subthreshold pulses has been used. Therefore, we can expect Ag lifetimes for nonthermal 0.4 eV electrons of 200 fs or less. For Al, Fe, and Ni, the lifetimes should be even shorter, due to the higher density of states at the Fermi energy. For Ag the density of states near the Fermi energy is low and at least three 1.5 eV photons are needed to excite electrons from the d bands just above the Fermi energy. For Al, Ni, and Fe, the density of states favors the excitation of electrons with higher energy. For our considerations, the e-ph coupling of the ballistic electrons plays the essential part for ablation. We postulate that the ablation behavior around zero pulse can be explained in the following way: Essential for achieving ablation of metal ions is a sufficient density of ballistic electrons and the resulting energy transfer to phonons before the electrons thermalize, which happens for Ag within 200 fs and for the other metals within less than 30 fs, or before they move out of the excitation zone due to their high velocity of approximately 10^6 m/s. The threshold density can be achieved only if both laser pulses overlap in time or if the probe pulse can further increase the density of hot electrons. Other mechanisms for particle and, in particular, ion ablation, as, i.e., Coulomb explosion due to charging caused by electron emission and image charges, can be excluded for metals due to effective screening by the metal electrons. Field ion emission from developing asperities could also play some role, but would add only minor desorption of ions from the top surface layer.

We have now to address the question, how it can be possible to ablate particles, if the two laser pulses are delayed by a few ps but not between 30 fs (Fe, Ni, Al) or 200 fs (Ag). Here we claim that the energy transferred to the electrons by the pump and probe beam separately is not sufficient for ablation. Interactions of the second pulse with a plasma plume generated by the first pulse, as reported in [21], can be excluded since each pulse is below the ablation threshold and therefore does not lead to particle emission. In order to explain this phenomenon, we have performed molecular dynamics simulations of the laser interaction process with Al. Details of these calculations will be presented in a detailed paper together with the earlier mentioned calculations of the electron system. At this stage we can offer a qualitative picture of the process leading to the delayed emission. If a limited amount of energy is transferred to the crystal on a time scale comparable to the e-ph relaxation times (typically between 1 and 30 ps [7]), which still does not cause desorption, we

can observe that the crystal develops a liquidlike structure at the surface. This is observed for a few ps after the heating and relaxes for 20–30 ps to the original crystal structure. We postulate that the "surface liquid" absorbs the laser photons much more efficiently, i.e., the original electronic configuration of the solid is not valid in the surface region between 5–15 ps after the pump beam. As long as this modified electronic structure persists, the probe beam sufficiently further heats these regions of the surface (creates hot electrons) and causes desorption (ablation). It has been shown experimentally [7] that, due to the lower e-ph coupling of Au as compared to Ni, the deposited energy is much less localized in noble metals. The lattice heating takes longer times and is less effective for noble metals. This can explain why we do not observe melting and, as a consequence, the delayed peak for Ag. A similar observation has been made for fragmentation of gold nanorods [22]. The time scale of the development of the liquid surface phase is reflected in the shape of the delayed signal for Fe, Ni, and Al.

In summary, we have performed direct time-resolved measurements of the yield of ions due to ablation induced by 30 fs laser pulses. The yield of emitted ions is substantial, if the pump and probe beam coherently overlap in time. In some cases, it is also for pump-probe delays of 10–30 ps. Between these time regions the yield of emitted ions is essentially zero. The first contribution can be qualitatively understood by the lifetime of the hot, ballistic electrons between 20 fs (Ni, Fe, Al) and 200 fs for Ag. In addition, the phonon energy can also be raised above the desorption threshold by a second (probe-)laser pulse after the e-ph coupling has transferred enough energy from the electrons heated by the pump beam to the lattice and, consequently, has modified the surface into a liquidlike structure characterized by an increased laser absorption. As a next step, we will measure the emission of neutral atoms. Preliminary results indicate clearly that the delayed peak presented here is the result of an intrinsic emission of ions and not the consequence of neutrals ionized by the probe pulse.

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