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Observation of a transient insulating phase of metals and semiconductors during short-pulse laser ablation

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Abstract

We have investigated the dynamics of femtosecond laser-induced ablation from the surface of various materials. Combining pump–probe techniques with optical microscopy we have monitored the structural modifications of the irradiated surfaces both in space *and* time. In the fluence regime below the threshold for plasma formation ablation is caused by the hydrodynamic expansion of laser-heated material. Upon expansion into vacuum each of the investigated materials (Si, GaAs, Al, Au, Mg, Hg) evolves from the initial metallic state into an optically transparent phase with high index of refraction.

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1. Introduction

During the last few years the potential of ultrashort (subpicosecond) laser pulses for material processing applications has attracted increasing interest. In a number of cases advantages over nanosecond and picosecond pulses have been demonstrated [1]. However, the various physical processes ultimately leading to the removal of material are not fully understood as yet [2]. In this paper we present results of time-resolved experiments concerning the dynamics of femtosecond laser-induced ablation of semiconductors and metals on a time-scale of 10^{-13}–10^{-9} s. Our studies focus on a fluence regime in the vicinity of the ablation threshold, between the extensively explored regime of ultrafast laser melting [3], and the regime of plasma formation [4]. The data show that the ablation mechanism is of thermal nature and corresponds to the hydrodynamic expansion of a hot, most likely supercritical metallic fluid. The measured time dependence of the reflectivity indicates that the ablated material undergoes a transformation from a metallic state to a highly refractive, insulating phase.

2. Experimental results

Time-resolved microscopy [5,2] is a powerful tool which combines ultrafast pump–probe techniques

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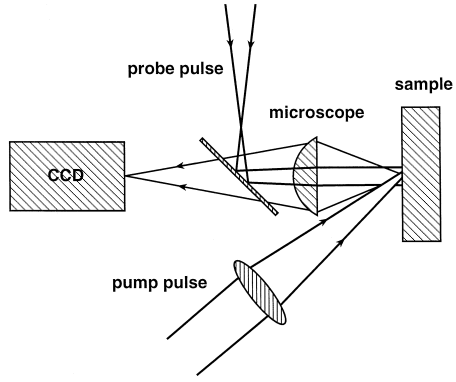

Fig. 1. Experimental setup for femtosecond time-resolved microscopy.

with optical microscopy. Using this technique the evolution of the surface morphology after laser excitation can be monitored with femtosecond temporal and micrometer spatial resolution. Fig. 1 shows a schematic of the experimental setup. The standard illumination of an optical microscope is replaced by a femtosecond probe pulse which can be delayed with respect to the excitation pulse using suitable optical delay lines. The optical micrographs of the surface are recorded with the help of a CCD camera. This scheme permits snapshot pictures of the surface to be taken over an almost arbitrary range of delay times. In our experiments we used laser pulse of 100 fs duration at a wavelength of 620 nm both for pump and probe.

Fig. 2 shows a series of micrographs of a silicon crystalline wafer at various time delays for a laser fluence of 0.5 J/cm^2. The fluence corresponds to approximately three times the melting threshold [3]. During the first picosecond the optical reflectivity of the material increases from the value of the crystalline phase to that of the metallic liquid. This rapid change of the reflectivity indicates the well-known ultrafast non-thermal structural phase transition [3].

In Fig. 2 the pump pulse is incident from the left at an angle of 45°. Therefore, as the laser pulse sweeps across the surface from left to right, the surface area on the left side is molten first. Between 2 and 150 ps we observe the formation of some *dark cloud*, i. e. a drastic decrease of the reflectivity in the central zone of the excited surface area. During the subsequent 200–300 ps a series of dark and bright rings develops in the central zone. The number of rings increases and their spacing decreases with time. This striking spatial modulation of the reflectivity disappears after a few nanoseconds. Using a variety of techniques we have verified that the surface area covered by the dark cloud and the ring structure is identical to the area on which ablation has occurred. In particular, the laser fluence must exceed a well-defined threshold value in order to observe the formation of a dark cloud, a ring structure and an ablation crater. For silicon the threshold fluence was measured to be 0.32 J/cm^2, about twice the threshold of ultrafast melting.

The ring structure vanishes after about $\Delta t > 5$ ns, and the liquid surface behind the ablated volume reappears. The diameter of the molten area decreases as more time elapses, indicating progressive resolidification of the liquid material. Subsequently, several low contrast rings appear on the surface. These features can be attributed to the formation of amorphous and crystalline modifications of silicon. These structures are also visible in pictures taken effectively at time infinity, i.e. several minutes after excitation. They represent the permanent changes of the irradiated surface. It is interesting to note that the boundary of the ablated area is marked by a sharp dark ring.

Fig. 3 shows a series of pictures taken on the surface of a 100 nm thick polycrystalline aluminum film excited with 1.2 J/cm^2 (ablation threshold: 0.52 J/cm^2). Detailed comparison with silicon indicates that the qualitative behavior of the two different materials is very similar. A distinct ring structure is observed, and the number and the spacing of the rings changes as in the case of silicon. As a matter of fact, this type of behavior has been observed in all the materials investigated so far. Typical examples from measurements on Si, GaAs, Al, Au, Mg, Hg, are shown in Fig. 4. The evolution of the surface reflectivity into the ring structure appears to be a universal phenomenon associated with ablation.

In order to clarify the physical nature of the ring structure frequency-tunable probe pulses were produced using femtosecond white light continuum generation [6], and pictures were taken at different probe wavelengths. Fig. 5 shows the measured fringe spacing as a function of wavelength for silicon. The

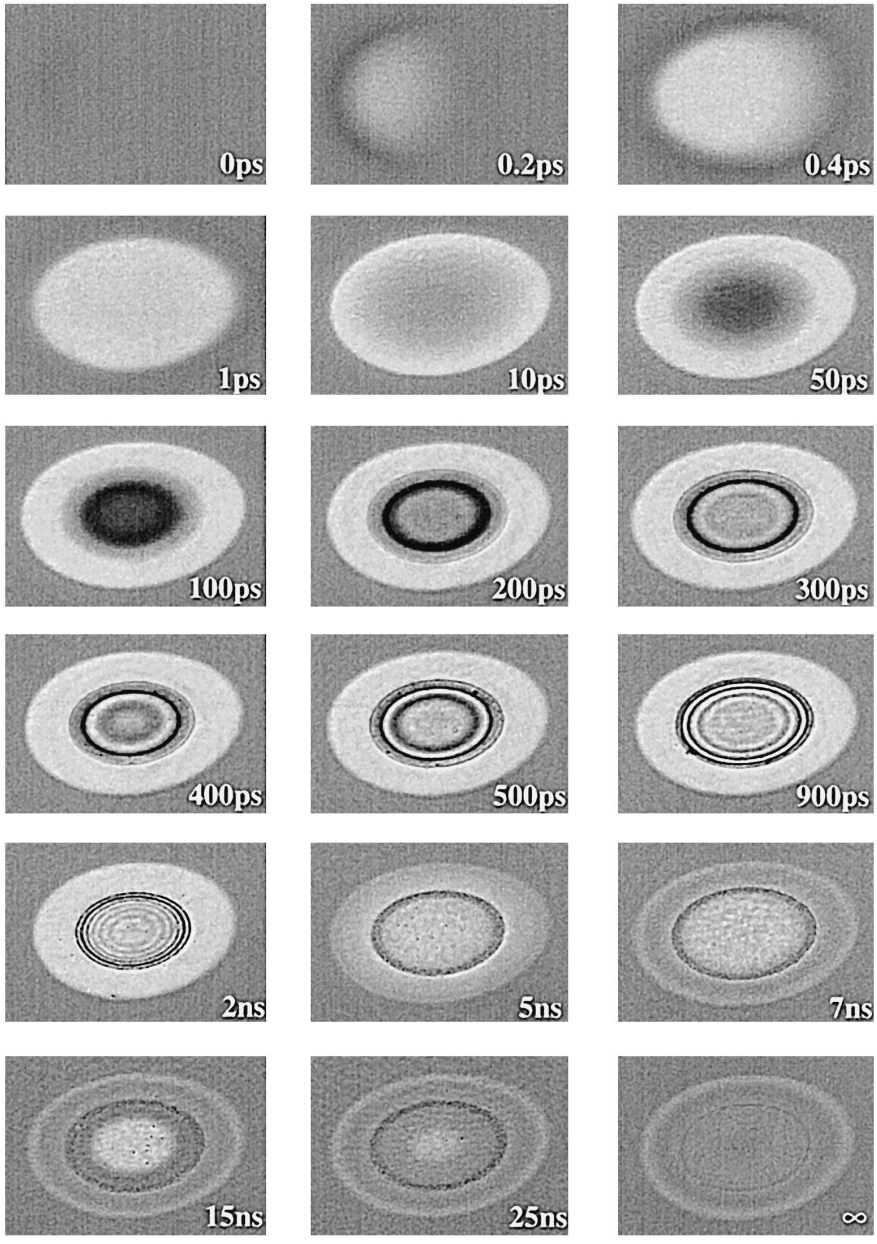

Fig. 2. Pictures of a Si(111) surface at different times after exposure to the pump pulse (pump fluence 0.47 J/cm^2). Frame size: 300 μm $\times$ 220 μm.

pump energy and the delay time were 0.5 J/cm^2 and 0.9 ns, respectively. The dots (squares) correspond to horizontal (vertical) cuts through the elliptical excitation spot. The variation of the spatial period with wavelength rules out the possibility that the observed rings represent an undulatory deformation of the surface. Instead, the linear dependence of the fringe spacing on wavelength is a clear indication that the

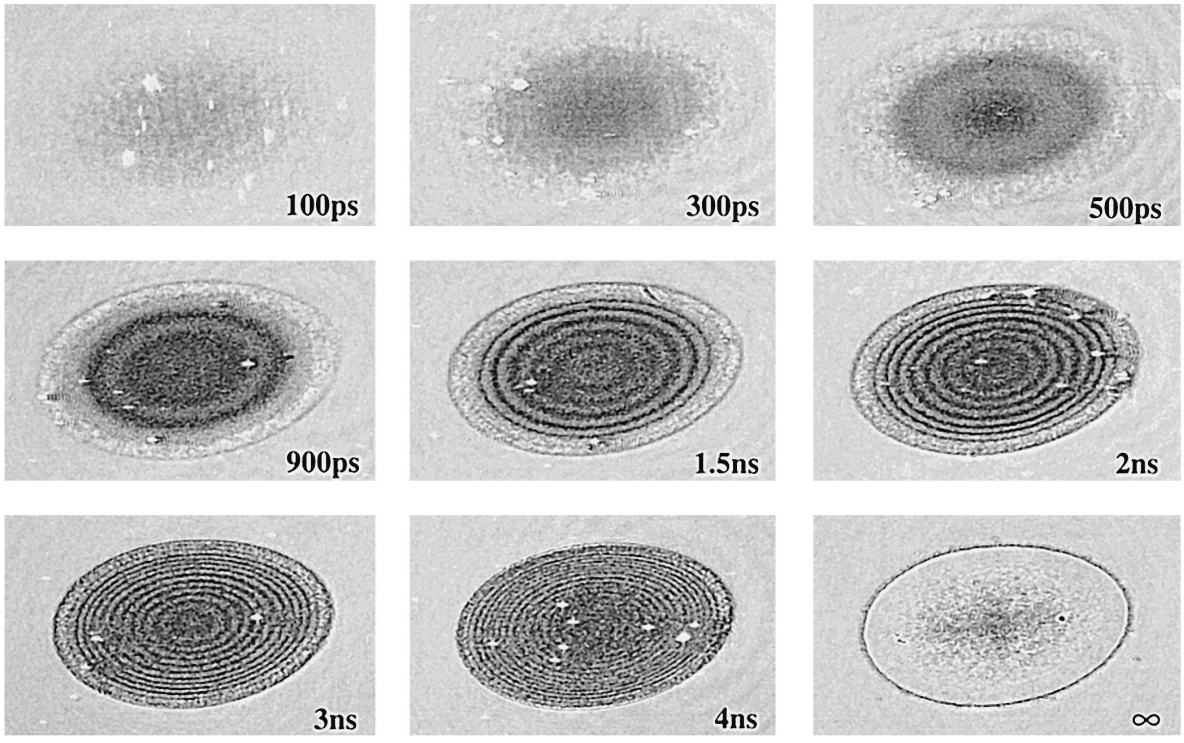

Fig. 3. Pictures of a 100 nm aluminum film excited at 1.2 J/cm^2. Frame size: 280 μm $\times$ 160 μm.

apparent ring structure represents Newton-fringes [1] caused by optical interference of light reflected from two optically smooth interfaces. From the change of the fringe spacing it must be concluded that the distance between the two interfaces increases with time.

3. Discussion

The precise congruence of the area of the fringe pattern with the ablation crater suggests that interference is caused by the expansion of the layer of ablated material. We propose an explanation of the interference phenomena along the following lines. The laser energy deposited in the material is thermalized in about a picosecond. Hence it can be assumed that after a few picoseconds the irradiated material can be described as a pressurized hot, possibly supercritical, fluid metal. The pressure gradient drives a hydrodynamic expansion of a layer of fluid material towards the vacuum. The dilution of the expanding material should be accompanied by drastic changes of the optical properties. A possible explanation of the fringe patterns could be that the interference is caused by the two boundaries confining the expanding layer of ablated material. A quantitative analysis of the change of the fringe spacing would then provide the optical thickness of the layer and the expansion velocity.

The measured fringe contrast puts some limits on the magnitude and characteristic distance of the change of the refractive index across the boundaries and on the optical absorption coefficient of the ablating material. In brief, from a detailed analysis the conclusions given below were drawn.

(i) On the vacuum side there should be a sharp ablation front in which the optical density drops on a characteristic distance much shorter than the optical

[1] Careful Fourier-analysis of the pictures shows that the fringes are not a *diffraction artifact* caused by the limited resolution of the microscope objective.

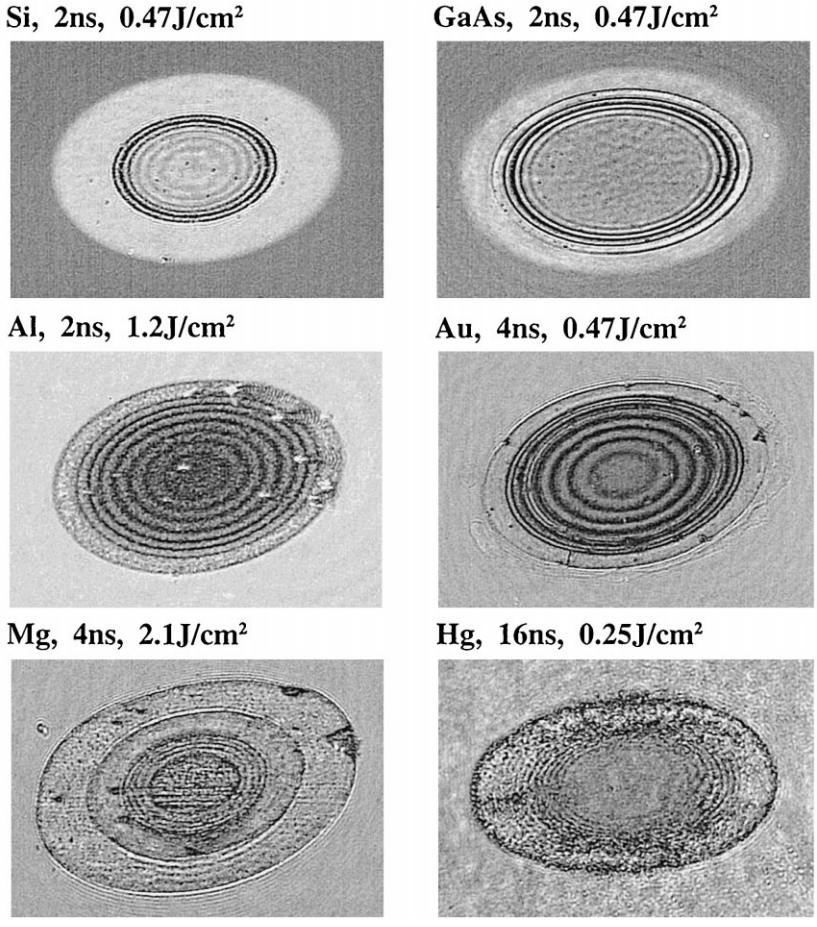

Fig. 4. Pictures of the *ring-like structure* on six different materials (silicon, gallium arsenide, aluminum, gold, magnesium, mercury).

wavelength. Smoother density profiles would lead to fringes with much lower contrast.

(ii) The initially metallic material must become highly transparent during expansion. More specifically, the imaginary part of the dielectric function should drop below $\epsilon_2 < 0.2$. With stronger optical absorption the number of observable fringes and their contrast would be much lower than what was observed in the experiments.

(iii) The real part of the dielectric function should be greater than $\epsilon_1 > 5$, i.e. the ablating material should have a high refractive index.

Neither a Drude-model of a diluting metal nor a Clausius–Mosotti description of a dense atomic gas are capable of accounting for these anomalous optical properties. One might invoke the occurrence of a metal–insulator transition [7] in order to explain the existence of a highly refractive, transparent phase. However, this hypothesis seems unlikely because in our experiments the interference patterns were observed over a wide range of parameters and in many different materials. Metal–insulator transitions have been observed in mercury and a few other metals, but only in a very narrow range of pressure and density near the critical point.

4. Conclusion

In conclusion we have presented experimental results concerning the dynamics of femtosecond

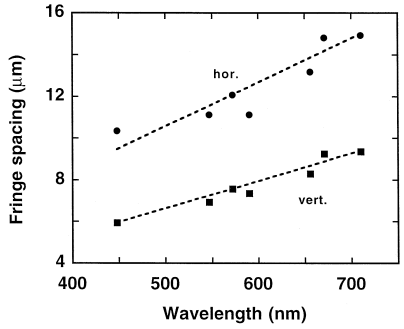

Fig. 5. Fringe spacing measured on silicon for fixed delay ($\Delta t =$ 1.2 ns) and fixed pump fluence (0.43 J/cm^2) as a function of the wavelength of the probe pulse. The dots (squares) correspond to horizontal (vertical) cuts through the elliptical excitation spot.

laser-induced ablation from semiconductor and metal surfaces. The data are interpreted in terms of hydrodynamic expansion of a hot, possibly supercritical fluid. Our data give compelling evidence that during the ablation process the material undergoes a transition from the initial metallic state into a highly refractive, insulating phase. Further studies are clearly required in order to understand the formation of a steep ablation front as well as the anomalous optical properties.

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