Laser–solid interaction in the femtosecond time regime

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

Institut für Laser und Plasmaphysik, Universität Essen, D-45117 Essen, Germany

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Abstract

Modification of the surface structure of solid materials by laser radiation involves a complex chain of processes. The first step is the deposition of a certain amount of optical energy in the material. The character of the material excitation is strongly dependent on the laser pulse duration. With the use of ultrashort laser pulses non-equilibrium energy distributions with large excess population in the excited states can be produced. The distinct physical processes which come into play in laser–solid interaction on the ultrafast time scale open new routes of modifying the structure and the morphology of materials and offer interesting perspectives in laser materials processing.

1. Introduction

Laser technology began to move into the subpicosecond time regime in the early seventies [1]. In the following years subpicosecond and femtosecond laser pulses were primarily applied for the study of a broad variety of ultrafast processes in different scientific fields [2,3], including time-resolved spectroscopy of solids. More recently, femtosecond laser pulses have been considered for use in laser processing of materials. While laser treatment of materials with laser sources operating in CW or long pulse modes has matured over many years, femtosecond laser processing is still in its infancy. Advantages of using ultrashort laser pulses over longer nano- and picosecond laser pulses have been demonstrated in a number of cases. Although it is too early for a sound general assessment of the potential of femtosecond laser processing, it appears time to take a look at some fundamental aspects of femtosecond laser–solid interaction with a view of trying to identify the specific potential advantages of the use of ultrashort laser pulses in laser materials processing.

2. Fundamental physical processes

The first step in any structural modification of a material by laser radiation is the deposition of a certain amount of laser energy. The total laser energy and the spatial and temporal energy distribution determine what kind of final modification will be obtained.

The primary laser–solid interaction process is the excitation of electrons from their equilibrium states to some excited states by absorption of photons. For example, in semiconductors electrons can be excited from the valence band to the conduction band by
absorption of single photons, as shown schematically in Fig. 1. Other possible excitation mechanisms are two-photon or higher order multiphoton electronic transitions. It is clear that for a given laser fluence a shorter pulse duration favors multiphoton excitation processes, because the probability of nonlinear absorption increases strongly with laser intensity.

The initial electronic excitation is followed by a complex hierarchy of secondary processes, which eventually end in the final structural modification of the material. The time scales of this chain of events can be crudely classified as shown in Fig. 2.

The primary electronic excitation is associated with a very short-lived coherent polarization of the material. Dephasing processes destroy the polarization roughly on a time scale of about $10^{-14}$ s [4]. One can think of pure dephasing as a process which changes the phase of the excited states without affecting the electronic energy distribution. The notion of dephasing is related to the spin–spin relaxation processes and the corresponding relaxation time $T_2$, familiar from magnetic resonance [5].

The initial distribution of excited electronic states corresponds to the set of states coupled by the optical transitions. The occupation of these primary states is rapidly changed by carrier–carrier interaction processes, and a quasi-equilibrium situation is established among the electrons on a time scale of about $10^{-13}$ s. The energy distribution of the carriers over the available states is described by the Fermi–Dirac distribution with an electron temperature $T_e$, greater than the lattice temperature. The experiments of Knox et al. [6] on GaAs/GaAlAs quantum well structures represent a fine example of electron thermalization.

The quasi-equilibrium electrons cool down on a time scale of $10^{-13}$ to $10^{-12}$ s by emission of phonons. A recent experimental demonstration of the relaxation of a thermal distribution of very hot electrons in photoexcited silicon can be found in Ref. [7].

Electron cooling by phonon emission leads to the population of certain phonon modes. These phonons relax predominantly by inharmonic interaction with other phonon modes. An example of this type of process is the built-up of a non-equilibrium population of zone center LO-phonons during the relaxation of photoexcited carriers in GaAs, and the subsequent relaxation of the LO-phonons by emission of acoustic phonons [8].

The final stage of the thermalization process is the redistribution of the phonons over the entire Brillouin zone according to a Bose–Einstein distribution. At this point the temperature of the laser-excited material can be defined, and the energy distribution is characterized by the temperature. There is almost general agreement now that a few picoseconds after
the deposition of the laser energy the energy distribution is close enough to thermal equilibrium that for most practical purposes it is justified to describe the further evolution in terms of thermal processes. This point of view does not exclude that the establishment of rigorous thermal equilibrium including all modes of material excitation may take longer.

After the thermalization the spatial distribution of the energy can be characterized by the temperature profile. For a sufficiently short laser pulse it is determined by the profile of the optical absorption. Thus very steep temperature gradients can be produced in strongly absorbing materials. Under these conditions thermal diffusion can take place on a time scale of the order of 10^{-11} s. The details depend on the thermal transport coefficients and the optical properties of the material.

When a sufficient amount of energy is deposited in the material, the melting temperature is eventually reached, and a transition from the solid to the liquid state takes place. Normal thermal melting occurs heterogeneously by nucleation and growth of the liquid phase. The boundary separating the phases moves from the liquid into the solid. The times to melt a layer of solid material are relatively long, because the upper limit of the velocity of the solid–liquid interface should be of the order of the speed of sound. For example, it takes typically 50 to 100 ps to melt a 20 nm surface layer of silicon using picosecond laser pulses [9]. Detailed measurements showed that in silicon melt front velocities of several 100 m/s can be reached [10].

An important conclusion to be drawn from the consideration of the time scale of energy thermalization is the following. There is a distinct dividing line at about 10^{-12} s separating the regime of non-thermal processes and thermal processes. From the point of view of femtosecond laser processing the time necessary to bring about a desired modification is of key importance. If a certain structural modification takes much longer than 10^{-12} s, it must be concluded that thermal mechanisms are operative. Under these conditions it is unlikely that the pulse duration in the initial energy deposition plays an important role. On the other hand, there are specific ultrafast physical mechanisms which may lead to new applications in laser materials processing.

3. Ultrafast phase transformations

Laser-induced solid-to-liquid transitions in semiconductors such as silicon, gallium arsenide and alike, provide excellent examples for the illustration of thermal and ultrafast, non-thermal physical mechanisms. Blombergen [11] has pointed out that for laser pulse durations down to about 10^{-11} s the laser essentially acts as a very fast heat source. As a matter of fact, heating rates of the order of 10^{14} K/s are readily attainable with picosecond laser pulses. These extremely high heating rates can lead to remarkable physical effects such as dynamical superheating of solid material by many hundreds of degrees beyond the equilibrium melting point [12] and unprecedented high values of the melt front velocity [10]. These rapid thermal processes could provide interesting new opportunities in laser processing of materials.

It was shown by Sokolowski-Tinten et al. [13] that under certain circumstances femtosecond laser pulses produce the very same thermal melting phenomena on semiconductors as picosecond pulses. In particular, the time for melting of a given thickness of a surface layer is the same as in the case of picosecond laser pulses (tens of picoseconds) for laser energy fluences close to the threshold fluence. However, at higher fluences there is a distinct change of the character of the solid-to-liquid transformation. This change manifests itself primarily in a drastic increase of its speed. In the high fluence regime the transition to the metallic liquid state occurs in less than 1 ps. This effect was observed for the first time by Shank et al. [14].

Fig. 3 shows an example of femtosecond laser-induced ultrafast structural changes of crystalline gallium arsenide [13]. The crystal was irradiated with 100 fs laser pulses at a fluence of 0.75 J/cm², approximately five times the melting threshold. The changes of the reflected second harmonic and of the optical reflectivity were measured using a pump-probe scheme. The diamonds and the circles represent, respectively, the second harmonic and the reflectivity. Time zero marks the arrival of the peak of the pump pulse. For negative delay times the probe pulse arrives before the pump pulse and therefore interacts with the intact crystalline surface. The crys-
The crystalline phase of the material is non-centrosymmetric and possesses a large nonlinear optical susceptibility $\chi^{(2)}$. The strong second harmonic signal detected for negative delay times is therefore indicative of the crystalline state. Also, the measured optical reflectivity is in agreement with the known reflectivity of crystalline gallium arsenide.

The interaction with the pump pulse causes drastic changes of both the second harmonic and the optical reflectivity. There is a sharp drop of the second harmonic to a very low level, and, during the same time, a rise of the optical reflectivity.

Liquid gallium arsenide is metallic. Only very weak second harmonic generation is expected in the liquid state because the dipolar nonlinear optical susceptibility $\chi^{(2)}$ vanishes. On the other hand, the reflectivity of the metallic liquid is much greater than that of the crystal. In fact, the reflectivity plateau for long times agrees well with the optical reflectivity of liquid gallium arsenide. Thus both the observed decrease of the second harmonic and the increase of the optical reflectivity indicate a transition from the crystalline state to the metallic liquid state. The decay times of the second harmonic and the rise times of the optical reflectivity reveal that the transition is accomplished in approximately 100 fs.

From the ultrashort transition time it must be concluded that a non-thermal physical mechanism is operative, because such a short melting time cannot be explained by classical thermal melting. Recent theoretical work by Stampfli and Bennemann [15] showed that for a high concentration of carriers the crystal lattice becomes unstable. Under these conditions structural transformations on a time scale of less than one picosecond are possible. A similar melting mechanism in which the presence of an electron-hole plasma played a key role has been proposed earlier by Van Vechten et al. [16].

Theory predicted that electronic melting would require a carrier density in the order of $10^{22}$ cm$^{-3}$. Such a high carrier concentration can be readily achieved with femtosecond photoexcitation of semiconductors. In fact, for the laser fluences necessary to produce the ultrafast solid–liquid transitions the carrier concentrations estimated for electronic melting are reached. Fig. 4 shows the measured concentration of femtosecond photoexcited electron–hole pairs as a function of laser fluence for silicon, obtained from an analysis of optical reflectivity data. It can be seen that an electron-hole density of $10^{22}$ cm$^{-3}$ is reached at a laser fluence of about 0.2 J/cm$^2$.

4. Femtosecond time-resolved microscopy

The combination of time-resolved pump–probe techniques with optical microscopy places at one’s disposal an extremely powerful tool for monitoring
ultrafast laser-induced structural modifications both in time and space [17]. One can directly observe the evolution of the changes of the surface morphology, e.g., the onset of melting and material ablation, the formation of a hole and the like. In particular, the method provides the time delay between deposition of the laser energy and formation of the structure. This is crucial information for establishing the thermal or non-thermal character of the process.

Fig. 5 shows the experimental arrangement for femtosecond time-resolved microscopy. One uses an optical microscope in which the standard illumination is replaced by a femtosecond laser pulse. Pictures of the surface can be taken at arbitrary times after the pump pulse by controlling the delay time of the illumination pulse. In this way the evolution of laser-induced structural changes can be recorded in a sequence of optical micrographs. The temporal resolution is given by the duration of the illumination pulse, while the spatial resolution is determined by the properties of the microscope (typically a few micrometers).

As a first example a series of pictures representing the evolution of a silicon (111) surface after exposure to a 130 fs laser pulse at 620 nm is shown in Fig. 6. The energy fluence was 0.47 J/cm², about three times melting threshold. This series covers the entire period from the deposition of the laser energy \( t = 0 \) to the appearance of the final structure \( t = 75 \) ns. It should be noted that the physical phenomena observed during this large time span have not been fully analyzed as yet. Here, only a few important features will be pointed out.

During the first picosecond one observes the development of an elliptical bright area which signifies the increase of the reflectivity on the irradiated surface area due to the photoexcited electron–hole plasma and the formation of a metallic liquid, as discussed in the previous section. The appearance of a dark cloud after about \( \approx 20 \) ps marks the onset of material ablation. There is a distinct ablation threshold \( 0.32 \) J/cm², higher than the melting threshold \( 0.15 \) J/cm². For fluences less than 0.32 J/cm² the molten surface resolidifies without ablation, leaving behind a flat, undisturbed surface. It can be shown that the periphery of the dark cloud coincides the boundary of the final ablated area.

The dark cloud transforms into a system of interference fringes over a period of a few nanoseconds. For example, a distinct fringe pattern can be recognized in the frame recorded at 2 ns. From the observed temporal evolution of the fringe system it follows that the interfering interface moves at a velocity in the order of \( 10^3 \) m/s.

The bright surface area turns dark after about 5 ns, indicating that resolidification is occurring. Note the distinct dark ring which persists until the end of the series at 75 ns. The inspection of the surface after the exposure shows that this feature surrounds the area where ablation has occurred. On the time scale of tens of nanoseconds the formation of several low contrast dark and bright rings can be recognized. These features are attributable to crystalline and amorphous modifications of silicon.

Fig. 7 shows a similar series of pictures recorded on a 200 nm aluminum film on a glass substrate at an energy fluence of 1.2 J/cm². In this example the evolution of the interference pattern associated with the ablation front can be followed very clearly. The persistent outermost dark ring makes its first appearance in the 0.9 ns frame. Again, it can be shown that this feature outlines the ablated area and that there is a well-defined fluence threshold for its formation \( 0.52 \) J/cm².

The final example in Fig. 8 is a series of pictures recorded on optical glass (BK 7). The energy fluence was 5.4 J/cm² which corresponds to a peak laser intensity of about \( 4 \times 10^{13} \) W/cm² and an optical electric field of \( 1.8 \times 10^8 \) V/cm. A large increase of
the reflectivity from 4% to more than 60% is observed. In this case the increase of the reflectivity is due to a highly reflective solid density plasma which is produced by optical breakdown and full ionization of the material [18]. The ionized material is ejected very rapidly with a velocity in the order of $10^7$ cm/s, which is the expansion velocity of the plasma.

Direct ionization of solid material leading to rapid ablation of the ionized material layer represents an ablation mechanism which is only possible when the laser pulses are so short that plasma expansion during the pulse is negligible. This is the case for pulses of 100 fs or less. On the other hand, longer pulse durations allow the plasma layer to expand to a thickness large enough to screen the solid from the laser light. The interaction with the laser pulse is

Fig. 6. Pictures of a Si(111) surface at different times after exposure to the pump pulse. Frame size: 300 μm × 220 μm.
Fig. 7. Pictures of a 200 nm aluminum film. Frame size: 280 μm × 160 μm.

Fig. 8. Pictures of a glass surface (BK7). Frame size: 150 μm × 80 μm.
then restricted to the vicinity of the critical density,
which is much less than solid density at optical
frequencies.

It was shown that there is a sharp intensity thresh-
old for the onset of direct plasma ablation [18]. The
existence of a well-defined ablation threshold is a
very useful feature for laser processing applications.
The threshold is probably related to the critical field
to produce optical breakdown. The threshold inten-
sity measured for a variety of transparent optical
materials was found to be a few times $10^{13}$ W/cm$^2$,
indicating a critical field for breakdown of about $10^8$
V/cm [18].

5. Femtosecond laser-induced changes of the sur-
face morphology

In this section examples of the final structural
modifications produced by exposure to a single fem-
tosecond laser pulses on semiconductors, metals and
insulators are presented.

Although the time-resolved measurements indi-
cate very similar behavior of silicon and gallium
arsenide at early times, the final surface topographies
of these materials are quite different. For example, it
was found that the exposed area on the silicon wafer
which was used to record the series of pictures of
Fig. 6 was warped upwards. On the other hand, pits
with steep walls and flat, uniform bottoms were
obtained on a gallium arsenide surface treated in a
similar way. An example is shown in Fig. 9. Phase
contrast microscopy (upper photograph) reveals a
sharp dark ring. Interference microscopy (lower pho-
tograph) indicates that the ring feature marks the
boundary of a surface area from which a uniform, 50
nm thick layer of material was removed by laser
ablation.

Fig. 10 depicts the results of similar measure-
ments on a metal surface. The example shows the
final topography of the aluminum film on which the
pictures of Fig. 7 were recorded. Comparing with the results of gallium arsenide the main difference is that in the case of the metal film the ablated layer is not uniform. Otherwise the results are quite similar.

The final pair of photographs in Fig. 11 illustrates the topography of the surface area of the glass sample corresponding to the picture sequence of Fig. 8. It can be seen that plasma ablation by a single laser pulse produces a rather deep crater. The distinct curvature of the interference fringes indicate that the depth of the ablation crater is less uniform. The measured depth in the center is 150 nm.

6. Summary and conclusions

A distinctive aspect of femtosecond laser–solid interaction is the fact that large amounts of optical energy can be deposited in solid material during a time much shorter than the time required for the thermalization of the energy. Femtosecond excitation can produce highly nonequilibrium states of excitation. Such high degrees of excitation can open up new channels for structural modifications, not accessible by other means. Ultrafast melting of highly excited semiconductors represent a well-known example of this type of processes.

In a large class of solid materials the thermalization of the optical energy requires only a few picoseconds. Therefore, if the time to bring about a certain structural modification is longer than a picosecond, thermal physical mechanisms should play the principal role. Laser-processing with picosecond laser pulses can be characterized as rapid thermal processing. Extremely high heating rates and steep temperature gradients are characteristic features of picosecond laser–solid interaction.

Many applications of laser processing require ablation of matter from solid surfaces. Because ablation involves transport of large numbers of heavy particles, these processes tend to be slow compared with the time scale of energy thermalization. Thermal mechanisms of ablation such as evaporation and boiling are likely to play an important role, even if the processing energy is delivered by a femtosecond laser pulse. Miotello and Kelly [19] have recently published an excellent critical assessment of possible thermal ablation processes.

A notable exception from the slow thermal ablation mechanisms is the fast material ablation following a direct, ultrafast solid-to-plasma transition. This process occurs when the optical electric field of the laser pulse exceeds the threshold of optical breakdown. This unique ablation mode is likely to dominate in laser treatment of materials with intense femtosecond laser pulses.

This article has emphasized aspects of ultrashort laser–solid interactions which are fundamentally different from the long pulse regime. As regards the application of ultrashort laser pulses in laser processing, there are, of course, other potentially useful features which were only briefly mentioned or not discussed here. These include, for example, prevalence of multiphoton excitation, suppression of the interaction of the laser pulse with ablated material, and reduction of undesired effects caused by heat conduction. Concerning the latter point, it appears that fast modes of material modification are of key importance, while a short pulse duration is only a necessary, but not sufficient condition.
References