X-ray diffraction experiments with femtosecond time resolution

D. VON DER LINDE and K. SOKOLOWSKI-TINTEN
Institut für Laser- und Plasmaphysik, Universität Essen, D-45117
Essen, Germany; e-mail: phy600@uni-essen.de

(Received 4 March 2002)

Abstract. Intense ultrashort laser pulses enable the generation of subpicosecond X-ray pulses in the multi-kilovolt range of photon energies. These X-ray pulses have opened the door to ultrafast time-resolved X-ray spectroscopy. Here, we report on the use of time-resolved X-ray diffraction to study ultrafast laser-induced order-to-disorder transitions and large amplitude picosecond acoustic transients that accompany the phase transitions.

1. Introduction

X-rays have always played an important role in science. One of the greatest scientific achievements made possible by X-rays is the huge amount of information they have provided on the atomic structure of matter and which is at our disposal today. Until recently, X-ray analysis provided only a static picture of the structure, because the time resolution of X-ray measurements was rather limited. However, during recent years new pulsed X-ray sources have emerged whose key property is extremely short pulse duration, in some cases as short as a few tens of femtoseconds. Femtosecond X-ray pulses enable atomic spatial resolution and high enough temporal resolution to observe the evolution of atomic configurations directly in time, thus providing a direct dynamic structural picture.

To date, a variety of approaches have been used to generate femtosecond X-ray pulses, among them schemes based on the interaction of very intense femtosecond laser pulses with solid materials. During the interaction of the laser pulse with the material, electrons are accelerated to very high kinetic energy. Electron–atom interaction processes, including familiar processes such as bremsstrahlung and characteristic line emission, create X-ray photons. The duration of the X-ray burst can be comparable to the laser pulse width. Available photon energies range from tens of electron volts to several MeV.

In pulsed laser-driven X-ray sources the X-ray pulses are automatically synchronized with the laser pulses. Thus, time-resolved experiments can be performed using excite-and-probe schemes similar to those commonly used in optical ultrafast spectroscopy. Femtosecond time-resolved variants for many common X-ray spectroscopies are feasible in which the laser pulse excites some process, say a structural change, and the X-ray pulse is used to probe its evolution.
This article describes the use of time-resolved X-ray diffraction to study ultrafast laser-induced structural phase transitions and various types of femtosecond laser-induced lattice distortions in semiconductors and metals.

2. Ultrashort X-ray pulses from laser-produced plasmas

The success of lasers in the production of X-rays is basically due to the strong electromagnetic field associated with intense laser pulses. During the interaction with the laser field, electrons pick up a kinetic energy of many tens of thousands of electron volts or even more, depending on the field strength. The electronic energy can be converted into high-energy photons, that is, short wavelength electromagnetic radiation, by a variety of electron–photon interaction processes.

A convenient way of generating X-rays is to focus an intense femtosecond laser onto the surface of solid material in order to produce a short-lived microplasma of high density and high electronic kinetic energy. The microplasma emits a short burst of incoherent X-rays consisting of bremsstrahlung radiation and characteristic line emission, in particular Kα lines [1, 2]. The latter type of narrow line emission is particularly useful in the X-ray diffraction experiments described in this article.

Typically, the spatial dimensions of the microplasma are several microns in diameter and a few tens of nanometres in depth. Thus, we have a nearly point-like source of X-ray pulses.

The duration of the X-ray bursts is limited by the duration of the laser pulses, and also to some extent by the duration of plasma expansion and electron cooling. Under suitable conditions, subpicosecond X-ray pulses can be expected [3]. However, measurement of the width of the X-ray pulses is quite difficult. With a few exceptions precise data are still lacking.

The widely accepted explanation of the origin of the Kα emission [1, 4] assumes that the energetic electrons escape from the primary hot, highly ionized plasma and penetrate into underlying colder material. Here they knock out electrons from inner electronic shells of the atoms, producing core holes. Recombination of the holes with electrons from outer shells leads to characteristic line emission, a mechanism very much like that in an ordinary X-ray tube.

A common implementation of a laser-plasma X-ray source uses laser pulses focused onto a thin metallic wire as a target [5]. To avoid the target erosion caused by the intense laser radiation, the wire is continuously pulled across the focal plain, thereby providing a fresh wire surface for each laser pulse. An advantage of this type of X-ray source is that it can be continuously operated over hours, simply by supplying a sufficiently large spool of wire.

Titanium is very suitable as a target material for an X-ray source to be used in diffraction experiments. The photon energy of the Ti Kα line emission is 4.51 keV which corresponds to a wavelength of 0.274 nm. A low-resolution X-ray spectrum of the Ti-wire source is shown in figure 1. The spectrum was obtained by analysing the distribution of the electrical charge on the individual photosensitive elements (pixels) of a CCD (charge-coupled device) chip after exposure to the X-rays from the titanium target. One can clearly distinguish the dominant Ti Kα line at 4.5 keV and the much weaker Kβ line at 4.9 keV. The doublet structure of the Kα line due to spin–orbit splitting is not resolved.
A disadvantage of the microplasma source is that the X-rays are emitted incoherently over the full solid angle. To be used as a probe in an experiment, the X-rays must be collected and focused onto the sample to be studied. Thus X-ray mirrors with high reflectivity and large acceptance angle are required. Bent crystals are excellent candidates as they allow one to make use of the strong Bragg reflection of X-rays from the lattice planes of crystals [6].

3. Time-resolved X-ray diffraction

To perform ultrafast time-resolved measurements in the X-ray regime one can use suitable variants of pump–probe techniques that are well established in optical time-resolved spectroscopy. Figure 2 illustrates an optical pump–X-ray probe scheme for measuring ultrafast time-resolved X-ray diffraction, say from a single crystal.

To generate multi-keV X-rays from microplasmas moderately high laser intensity is needed, typically about $10^{17}$ W cm$^{-2}$. We work with near-infrared laser pulses of 50–100 mJ laser energy obtained from a titatium:sapphire oscillator–amplifier laser system working in the chirped pulse amplification (CPA) mode.

The basic laser pulses are divided to form an optical pump beam and a probe beam with an adjustable time delay. The actual X-ray probe pulses are obtained from the microplasma generated by one of the beams. The X-rays are collected and focused onto the specimen under study by means of a suitable X-ray mirror. The optical pump pulse and the X-ray probe pulse must spatially overlap on the sample surface. The incident X-ray probe beam typically covers an angular range much larger than the angular width of the reflection characteristic of the crystal (‘rocking curve’). The diffracted X-rays are detected by a CCD camera with a detector area large enough to enable complete rocking curves to be recorded.

Changes in the crystalline structure induced by the optical excitation can be measured by recording the resulting changes of the rocking curve as a function of the delay time. The time resolution is determined by the duration of the X-ray pulses, which can be as short as a few hundred femtoseconds.
4. Ultrafast structural phase transitions

There is extensive evidence to show that transition from the solid to the liquid phase takes place on a time scale of a few hundred femtoseconds, when a semiconductor material such as Si or GaAs is very strongly photo-excited by an ultrashort laser [7]. The process was discovered in the early eighties [8, 9] and attracted a lot of attention because the speed of the apparent phase transition could not be explained by a normal thermal melting process. Theory indicates that such an ultrafast structural transformation occurs in covalent semiconductors when an electron–hole concentration of approximately \(10^{22} \text{ cm}^{-3}\) is achieved, that is, when more than 10% of the covalent bonds are broken [10–12]. Until very recently, the only indication of such ultrafast solid-to-liquid transitions came from optical data [7, 13]. However, because optical radiation cannot resolve the actual atomic configuration it was not possible to obtain direct evidence of a structural change.

The time-resolved reflectivity spectra of Si depicted in figure 3 represent a typical example of the type of information obtained from optical ultrafast spectro-

![Figure 2](image1.png)

**Figure 2.** Schematic of an optical pump–X-ray probe experiment.

![Figure 3](image2.png)

**Figure 3.** Spectra of the optical reflectivity of silicon. Full line: liquid silicon. Dashed line: crystalline silicon. Data points: measured transient reflectivity spectra of laser-excited silicon for different delay times between pump and probe.
scopy. These data show the evolution of the reflectivity of crystalline Si after photo-excitation by an intense femtosecond pulse. They indicate that a change from crystalline to metallic liquid reflectivity occurs within a few hundred femtoseconds.

Similar structural transformations can be observed in compound semiconductors such as gallium arsenide. Unlike centro-symmetric silicon, GaAs lacks a centre of inversion in the crystalline phase and possesses large second-order nonlinear susceptibility $\chi_2$, which gives rise to optical second harmonic generation. On the other hand, molten GaAs is an isotropic metallic liquid and hence $\chi_2$ vanishes. Figure 4 depicts the result of femtosecond optical pump–optical probe measurements of the reflected second harmonic from photo-excited GaAs. The data show that after the arrival of the pump pulse the second harmonic disappears within about 100 fs. The vanishing of the second harmonic is accompanied by a rise of the optical reflectivity from the solid to the liquid value. Both the second harmonic and the reflectivity measurements indicate that a transition from the solid to the liquid phase has occurred on a time scale of $\approx 100$ fs.

Obviously, this type of extremely fast structural phase transition represents an ideal case to be studied by ultrafast X-ray diffraction.

5. **Penetration depth of X-rays**

Observation of the lattice structure by X-ray diffraction requires wavelengths shorter than the lattice constants, i.e. a few Angstroms or photon energies of several kilovolts. Generally speaking, X-rays of this wavelength penetrate deeply into the crystal, typically much farther than the thickness of the molten surface layer that is produced by a laser-induced solid–liquid transition. This thickness is typically less than 100 nm. Under these conditions X-ray diffraction would be strongly dominated by the bulk crystal. It would essentially ignore the very thin molten surface layer, unless special precautions were taken to ensure that the X-rays probe a very thin surface layer only.
To avoid the problem one can use certain types of semiconductor heterostructures. For example, extremely thin crystalline layers of germanium can be grown by surfactant-mediated heteroepitaxy on standard Si (111) wafers [14]. The key point is that one obtains a heterostructure with a highly perfect crystal layer whose lattice constant does not match the lattice constant of the substrate. In fact, the lattice mismatch is quite large in the Ge–Si (111) system, and the Bragg reflections from bulk Si and from the Ge surface layer are clearly separated (difference of the diffraction angles \(\Delta \theta \approx 1^\circ\)). This is demonstrated by figure 5, which shows the CCD camera read-out of the (111) reflections from a 390 nm Ge–Si heterostructure. These data represent a one-minute recording with the X-ray pulses from our Ti K\(_\alpha\) source. The strong sharp line is due to the Si substrate, whereas the broader and weaker peak represents the diffraction from the 390 nm Ge layer.

![Diagram of Ge–Si heterostructure and X-ray diffraction](image)

Figure 5. Top: Ge–Si heterostructure. Bottom: (111) X-ray diffraction from the Ge–Si heterostructure using the laser-driven Ti K\(_\alpha\) X-ray source. Insert: image recorded on the CCD camera. \(\theta_{B,Ge}\) is the angle of the (111) Bragg diffraction of Germanium.

6. Time-resolved X-ray diffraction measurements of ultrafast solid–liquid transitions

These Ge–Si heterostructures proved to be very useful in the time-resolved X-ray diffraction experiments of Siders et al. [15] who studied non-thermal melting in Ge. This work has provided, for the first time, direct structural evidence that intense femtosecond optical excitation of covalent semiconductors can indeed trigger a solid-to-liquid phase transition, as suggested by the earlier optical investigations. These results were confirmed and extended in more recent measurements [16].
In these experiments the basic scheme in figure 2 was employed. Briefly, the 4.51 keV probe beam from the Ti Kα source was focused on the laser-excited surface area of a Ge–Si heterostructure wafer. The Bragg angle for diffraction from the (111) lattice planes of Ge at 4.51 keV was about 25°, corresponding to an angle of incidence of 65° of the X-ray probe beam. The Ge film was photo-excited using a small fraction of the fundamental laser pulses at 800 nm. This wavelength corresponds to a secondary direct band gap of Ge. Thus, Ge is strongly absorbing at 800 nm, while the optical absorption of the Si substrate is negligible. In the optical pump–X-ray probe experiment the Bragg reflection from the Ge film (thickness 170 nm) was measured as a function of the time delay between the X-ray pulse and the 800 nm excitation pulse.

Results of the experiments are shown in figure 6. The measured X-ray diffraction signal, integrated with respect to the diffraction angle ('integrated reflectivity'), is plotted versus delay time for two different energy fluences of the excitation pulses. The remarkable feature of the data is the initial fast drop of the X-ray diffraction within a few hundred femtoseconds after the pump pulse, followed by a more gradual further decrease over several picoseconds. The two data points to the right of the time axis represent the diffraction signal from the laser-excited spot measured a few minutes later (delay time ‘infinity’).

From the observed decrease of the X-ray diffraction it can be concluded that a portion of the Ge crystal underwent structural disordering within a few hundred femtoseconds. For example, the 25% decrease in the diffraction efficiency indicates a loss of crystalline order in a 40 nm layer in the first 300 fs, that is, the formation of a disordered or molten layer. A Debye–Waller effect due to lattice heating can be ruled out as an explanation because temperatures in excess of 5500 K would be required to produce the observed decrease in the (111) diffraction. An angular shift resulting from a possible laser-induced lattice distortion can also be excluded because in the experiment a sufficiently large angular range was simultaneously recorded (see rocking curves in figure 9, section 8).
The observed structural change is much too fast to be explained by an ordinary thermal melting process, even if strongly superheated conditions were assumed. If the sound velocity were used for an estimate of the ultimate upper limit of the propagation speed of the melt front, it would take at least 8 ps to melt a 40 nm layer.

On the other hand, it was observed that after the initial rapid drop, the diffraction efficiency continued to decrease over several tens of picoseconds. In fact, extensive measurements on the picosecond time scale (data not shown here) indicated that the electronically driven non-thermal ultrafast phase transition is followed by a rapid thermal melting process, presumably under highly superheated conditions. This subsequent thermal melting could be driven both by heat transfer from the hot liquid and heat directly deposited in the solid phase behind the molten layer. From the observed rate of the decrease in the X-ray diffraction efficiency one can estimate the propagation velocity of the melt front to be 850 m s$^{-1}$. This value is in good agreement with earlier measurements of the melt-front velocity during picosecond laser melting experiments [17, 18].

The diffraction measurements on the laser-exposed spot at delay time ‘infinity’ show that the molten layer has recrystallized. However, we observed only a partial recovery of the diffraction. Examination of the final surface morphology by interference microscopy indicated that weak laser ablation had taken place causing the removal of a 10 to 20 nm thick surface layer.

7. **X-ray pulse duration**

The time resolution in optical pump–X-ray probe experiments is ultimately limited by the duration of the X-ray pulses. At the present time, satisfactory methods for the measurement of ultrashort multi-keV X-ray pulses are not yet available. Great progress has been made in X-ray streak cameras, but time resolution significantly less than one picosecond is still difficult to achieve [19]. On the other hand, our X-ray diffraction experiments and those of others [20–22] have furnished clear evidence of an X-ray time response as short as a few hundred femtoseconds. The apparent time response is the result of a convolution of the X-ray pulse width and the actual material response (in our case the speed of the structural disordering of the semiconductor crystal).

An estimate of the upper limit of the X-ray pulse duration can be obtained by assuming an instantaneous, step-like material response in the X-ray diffraction experiments, that is, we assume that the laser-induced change from the crystalline to the liquid state occurs instantaneously. Figure 7 shows fits of the measured X-ray diffraction data using calculated convolutions of a step-like material response with Gaussian-shaped X-ray probe pulses. It can be seen that good fits of the data are obtained with X-ray pulse widths between 250 and 350 fs. We conclude that for the Ti K$_\alpha$ source an upper limit of the X-ray pulse duration of 300 fs with an uncertainty of $\pm 50$ fs can be given.

So far, no effort whatsoever has been made to minimize the X-ray pulse duration by optimizing the parameters under which the X-ray source is operated. Models that can serve as a basis for the optimization have been discussed in the literature [3]. We are quite confident that it will be possible to substantially reduce the X-ray pulse width in the future.
8. Picosecond acoustic transients

The electronically induced ultrafast solid-to-liquid transition is completed within less than a picosecond, leaving behind a hot, pressurized layer of liquid Ge on top of some non-molten crystalline Ge (see figure 8(a)). The optical energy deposited in the material relaxes within a few picoseconds to some partial thermal equilibrium, and, as a result, thermally induced mechanical stress is set up in the Ge crystal. Release of pressure and stress in the various strata of the material gives rise to interesting acoustic perturbations, which develop on a picosecond time scale. These acoustic waves can be observed in X-ray diffraction through the accompanying lattice distortions, which lead to changes in the Bragg angle.

Figure 8(b) shows a qualitative picture of the physical situation after thermalization of the optical energy. The solid line shows the initial pressure–stress profiles, which are taken to be flat top, for the sake of simplicity. The essential point is that there is a substantial pressure discontinuity at the liquid–solid interface. The initial stress in the Si substrate is negligible, because at 800 nm the optical absorption in Si is much less than in Ge.

Several acoustic perturbations start from the three interfaces: (1) a compression wave propagates from the liquid–solid interface into solid Ge and a rarefaction wave back into the liquid; (2) a rarefaction wave develops at the liquid–vacuum boundary and travels into the liquid; (3) compressive and expansive waves similar to, but weaker than (1), are launched from the Ge–Si interface. We believe that (1) is the dominant acoustic perturbation because pressure is expected to have a maximum in a 40 to 50 nm surface layer where the largest portion of the optical energy is deposited. In addition to the acoustic perturbations, the liquid–solid interface (melt front) moves forward into solid Ge. The liquid layer grows at the expense of the solid layer, resulting in a continuous overall reduction in the diffraction efficiency. As mentioned above, the melt-front velocity can be estimated from the observed long term, picosecond time scale rate of decrease in the diffraction.

The different acoustic perturbations (1), (2) and (3) do not overlap for times shorter than the travel time between the interfaces. Later on, however, reflections occur at the various interfaces because of the mismatch of the acoustic impedance.
The situation becomes quite complicated until the acoustic transients have finally damped out.

Figure 9 presents examples of measured time-dependent rocking curves, which illustrate some of the effects discussed in the foregoing paragraph. The dashed lines in figures 9(a)–(d) represent the rocking curves of the unperturbed Ge layer and Si substrate. The solid line in figure 9(a) shows that at 0.8ps after laser excitation the shape and the position of the rocking curve has not changed, but there is a reduction in the diffraction of Ge to somewhat less than 70%. This is the signature of the order–disorder phase transition as discussed above in more detail.

According to the discussion in the context of figure 8, the first acoustic effects to be noticed should be compression in Ge and, to a lesser extent, also in Si. The rocking curve for 13ps, figure 9(b), shows that this is indeed observed. There is a clear shift of the Ge line towards larger diffraction angles and a weak shoulder of the Si curve in the same direction.

The rarefaction wave approaching from the liquid surface is expected to affect the crystalline layer after times $t > L_{\text{liq}}/c_{\text{liq}} \approx 15\text{ps}$, where $c_{\text{liq}} = 2660\text{ m s}^{-1}$ is the sound velocity of liquid Ge. In fact, the Ge rocking curve at 27ps, figure 9(c), shows a new side band at lower diffraction angles and exhibits a doubly peaked structure. This shape indicates that at this time both compressed and expanded strata are present in Ge.

Finally, the data for 123ps, figure 9(d), reveal further points of interest. At this late stage the acoustic perturbations of the Ge layer have damped out leaving the
relaxed, thermally expanded material, as indicated by a shift of the diffraction profile to smaller angles. The observed shift represents a thermal strain of $\varepsilon = 0.008$. This thermal expansion corresponds to a temperature of approximately 1100 to 1200 K. This value is close to the melting temperature of Ge, suggesting that liquid and solid Ge have reached equilibrium near the melting point.

Concerning the Si rocking curve at 123 ps, the main feature is a pronounced side band at lower angles, presumably attributable to the thermal expansion of Si caused by heat transfer from the hot surface layers. However, the rocking curve of Si at 123 ps has a rather complex structure, and both expansive and compressive strain can be recognized.

9. Conclusion

Laser-driven short pulse X-ray sources have matured to the point where time-resolved X-ray spectroscopy with picosecond and femtosecond resolution is possible. We have shown that the new time-resolved X-ray techniques can reveal extremely fast structural changes and the dynamics of lattice distortions associated with acoustic perturbations.

An attractive feature of laser-driven X-ray sources is that they enable relatively small-scale, almost tabletop-type experiments. On the other hand, large-scale facilities for the generation of very powerful ultrashort X-ray pulses will be available in the future, for example free electron lasers or other schemes that make use of high-energy electron beams.

At the present time, two highly developed disciplines of science are about to be tied together, namely X-ray science and ultrafast time-resolved spectroscopy. The combination of high time-resolution with atomic-scale spatial resolution should eventually enable researchers to record detailed, quasi-instantaneous pictures of complex atomic structures.

Figure 9. Examples of rocking curves for different delay times. Dashed lines: measured rocking curves in the absence of laser excitation. Full lines: rocking curves measured with the laser excitation.
Acknowledgments

The authors are indebted to Ch. Blome, A. Tarasevitch, J. Blums, C. Dietrich and A. Cavalleri for their contributions to this work. We are also indebted to I. Uschmann and E. Förster for providing the X-ray mirror, and to M. Horn-von Hoegen and M. Kammler for growing the heterostructure samples used in the experiments. Financial support by the Deutsche Forschungsgemeinschaft and the European Union XPOSE network is gratefully acknowledged.

References