EPJ Web of Conferences **41**, 04013 (2013)
DOI: 10.1051/epjconf/20134104013

Ultrafast laser-induced melting and ablation studied by time-resolved diffuse X-ray scattering

M. Nicoul[1], F. Quirin[1], A. M. Lindenberg[2], A. Barty[3], D. M. Fritz[4], D. Zhu[4], H. Lemke[4], M. Chollet[4], D. A. Reis[2], J. Chen[2], S. Ghimire[2], M. Trigo[2], M. Fuchs[2], K. J. Gaffney[2], J. Larsson[5], T. Becker[1], S. Meyer[1], T. Payer[1], F. Meyer zu Heringdorf[1], M. Horn von Hoegen[1], M. Jerman[1], K. Sokolowski-Tinten[1]

[1]Faculty of Physics and Center for Nanointegration Duisburg-Essen (CENIDE), University Duisburg-Essen, Lotharstr. 1, 47048 Duisburg, Germany.
[2]Stanford PULSE Institute, SLAC National Accelerator Laboratory, 2575 Sand Hill Rd., CA 94025 Menlo Park, USA.
[3]Centre for Free Electron Laser Science (CFEL) Notkestrasse 85, 22607 Hamburg, Germany.
[4]SLAC National Accelerator Laboratory, 2575 Sand Hill Rd., CA 94025 Menlo Park, USA.
[5]Department of Physics, Lund University, 22100 Lund, Sweden.

Abstract. Time-resolved diffuse X-ray scattering with 50 fs, 9.5 keV X-ray pulses from the *Linear Coherent Light Source* was used to study the structural dynamics in materials undergoing rapid melting and ablation after fs laser excitation.

1 Introduction

Ultrafast pulsed excitation of solids allows to create states of strong electronic excitation and high temperature and pressure. Subsequent to the initial deposition of energy a complex chain of secondary relaxation processes can lead to disordering/melting on very rapid time-scales, and often along unusual, non-equilibrium pathways. Here we report about experiments carried out at the *Linear Coherent Light Source* (LCLS), the world's first hard X-ray free electron laser, where we applied time-resolved diffuse X-ray scattering to study the structural response of materials undergoing rapid melting and ablation after excitation with intense fs laser pulses.

2 Time-resolved X-ray scattering at the LCLS

Thin films (25 - 100 nm thickness) of solid materials deposited onto free standing Si_3N_4-membranes, have been irradiated by 50 fs, 800 nm optical laser pulses at fluences sufficient to melt and ablate the material. Subsequently the scattering of a time-delayed 50 fs, 9.5 keV X-ray pulse from the LCLS has been observed in normal-incidence transmission geometry. The measurements covered a large range of scattering angles corresponding to a momentum transfer $q = 4\pi/\lambda \cdot \sin(\theta/2)$ from 0.04 Å-1 < q < 5 Å-1. Although the analysis presented in this paper is still preliminary, the scattering data provide information about the transient structural changes on different length scales. Laser-induced melting as well as the structural dynamics after disordering have been investigated for different classes of materials over wide time- and fluence ranges.

3 Laser-induced melting and liquid phase dynamics

Fast fs laser-induced melting has attracted continuing interest for nearly three decades, both from a fundamental physics viewpoint as well as with respect to technological applications such as laser-processing. Today there is experimental as well as theoretical evidence that under such extreme conditions some materials can melt (disorder) on sub-picosecond time scales along a non-thermal pathway, while others melt only thermally on a ps time-scale.

As an example we discuss here the melting dynamics in laser-excited Bi. Fig. 1a (left) shows in a false color representation the measured diffraction pattern I(q) as a function of pump-probe time-delay of a 25 nm Bi-film undergoing melting after excitation at a fluence of 25 mJ/cm^2 (note the logarithmic time-axis and the zero delay offset by 0.7 ps).

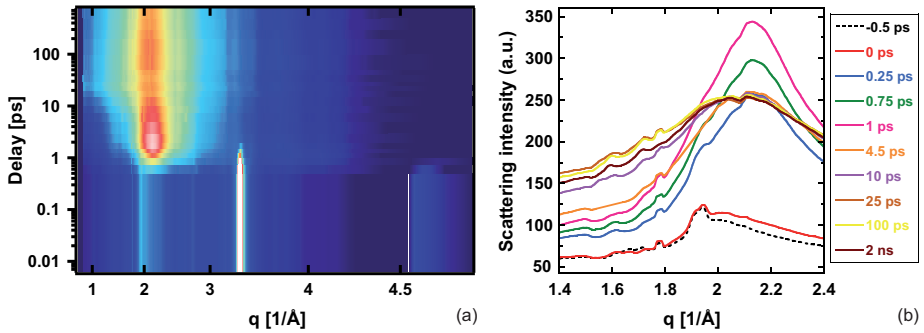

Fig. 1. Left: False-color representation of the tansient diffraction pattern I(q,Δt) of laser-excited Bi; Right: Line-outs in the vicinity of liquid structure factor peak around 2.1 Å-1 for selected delay times.

At these high fluences well above the melting threshold the material melts non-thermally within a few hundred fs as indicated by the rapid decay of the two diffraction peaks of the solid phase at 3.3 Å^{-1} and 4.6 Å^{-1}. On the same time-scale a broad diffraction feature appears at 2.1 Å^{-1}, indicative of the formation of the disordered liquid state. Moreover, as can be clearly seen in Fig. 1b (right) the position as well as the shape of the liquid structure factor peak changes with time.

4 Femtosecond laser-induced ablation

Laser ablation describes the permanent removal of macroscopic amounts of material from a laser-irradiated surface. For ablation induced by ultrashort laser pulses it is believed that subsequent to the initial fast heating and disordering rapid adiabatic expansion can push the material into metastable or even unstable regions of the state diagram leading to its disintegration and transition into a volatile state. However, the underlying processes are still not well understood and different ablation mechanisms like spallation, phase explosion and fragmentation have been invoked (i. e. [1-5]).

We used time-resolved X-ray scattering at small scattering angles (0.04 Å^{-1} < q < 0.6 Å^{-1}) to follow the formation of nm length scale inhomogeneities expected to occur during the ablation process. In agreement with these expectations and with our earlier experiments performed with much lower X-ray flux at the SPPS [6] we observe a strong transient small-angle scattering signal. Fig. 2 shows as an example data obtained on a 100 nm thick, laser-excited Au-film (Left side: Fluence-dependencies for different delay times; Right: Time-dependencies for two different fluences).

The data presented in Fig. 2 exhibit two remarkable features: (1) The scattering signal at small scattering angles is only observed for fluences above a threshold value of F_{th} = 0.5 J/cm^2. This fluence coincides exactly with the ablation threshold (i.e. threshold for crater formation) as determined by a *post-mortem* analysis of the final structural modifications of the irradiated film. (2) The scattering signal is delayed with respect to the excitation and occurs *after* melting of the material. Moreover, the delay depends on excitation fluence, as evidenced by the time-dependent data presented in the right graph. For 2 J/cm^2 (well above threshold) the scattering signal can be

observed only for delay times larger than 100 ps. For 0.75 J/cm^2 (close to threshold) it sets in much earlier (≈ 20 ps). In line with this we find that for early delay times (Δt = 100 ps) the small angle scattering is only observed for fluences in a limited range above threshold, while for later delays (Δt = 500 ps) it increases continuously with fluence.

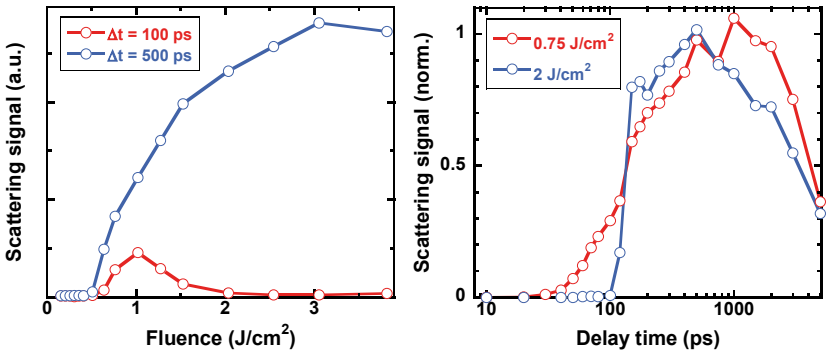

Fig. 2. X-ray scattering at small angles (0.04 Å^{-1} < q < 0.6 Å^{-1}) of a 100 nm thick laser-excited Au-film. Left: Scattering signal as a function of fluence for pump-probe time delays of 100 ps (red) and 500 ps (blue). Right: Normalized scattering signal as a function of delay time for laser fluences of 0.75 J/cm^2 (red) and 2 J/cm^2 (blue).

These observations give clear evidence that ablation is responsible for the appearance of the small angle scattering signal. However, the pronounced differences for low and high fluences indicate different ablation mechanisms in the different fluence regimes. To interpret our experimental data at lower fluences we refer to the results of recent molecular dynamics simulations [3-5] which have given evidence that close to the threshold the rapid adiabatic expansion puts the material under strong tensile stresses (negative pressure). When the tensile strength is exceeded the material simply tears apart. Therefore, ablation can be described as a spallation process and is of mechanical nature.

Within this picture a very simple prediction can be made for the case of a homogeneously heated film (as in our experiment): Spallation will start when the two rarefaction waves propagating from the film boundaries into the film meet in its center, that is $t_{spall} = d/2c_S$ (d: film thickness, c_S: sound velocity). Using the known film thickness d = 100 nm and the published value of the sound velocity of liquid Au c_S = 2.567 km/s [7] we calculate t_{spall} = 19.5 ps, exactly what we measure in the experiment for the onset of the small angle scattering in the fluence regime close to the threshold.

Acknowledgements

Financial support by the German Research Foundation (SFB 616 *Energy dissipation at surfaces* and grant So 408/8-1) is gratefully acknowledged. Portions of this research were carried out at the *Linac Coherent Light Source* (LCLS) at the SLAC National Accelerator Laboratory. LCLS is an Office of Science User Facility operated for the U.S. Department of Energy Office of Science by Stanford University.

References

1. K. Sokolowski-Tinten et al., Phys. Rev. Lett. **81**, 224 (1998).
2. D. von der Linde et al., Appl. Surf. Science **154**, 1 (2000).
3. D. Perez et al., Phys. Rev. B **67**, 184102 (2003).
4. P. Lorazo, et al., Phys. Rev. B **73**, 134108 (2006).
5. A. K. Upadhyay et al., Phys. Rev. B **78**, 045437 (2008).
6. A. M. Lindenberg et al., Phys. Rev. Lett. **100**, 135502 (2008).
7. S. Blairs et al., J. Inorg. Nucl. Chem. 42, 1555 (1980).