Atomic View of the Photoinduced Collapse of Gold and Bismuth

R. Ernstorfer[1], M. Harb[1], C.T. Hebeisen[1], G. Sciaini[1], T. Dartigalongue[1], I. Rajkovic[2], M. Ligges[2], D. von der Linde[2], Th. Payer[3], M. Horn-von-Hoegen[3], F.-J. Meyer zu Heringdorf[3], S. Kruglik[1], R.J.D. Miller[1]

[1] Institute for Optical Sciences and Departments of Chemistry and Physics, University of Toronto, 80 St. George St., Toronto, Ontario M5S 3H6, Canada
E-mail: dmiller@lphys.chem.utoronto.ca
[2] Fachbereich Physik, Universität Duisburg-Essen, 47057 Duisburg, Germany
[3] Fachbereich Physik and Center for Nanointegration, Universität Duisburg-Essen (CeNIDE), 47057 Duisburg, Germany

Abstract. Two different mechanisms of photoinduced melting were studied by femtosecond electron diffraction. The structural response of gold indicates an electronically-induced increase of the melting temperature. Bismuth was found to disorder within one vibrational period.

Introduction

In recent years, time-resolved diffraction techniques (electrons and X-rays) have become available to study the dynamics of photoinduced phase transitions. Intense optical excitation initially creates a strong non-equilibrium between the electrons and the lattice. The structural response of crystalline systems under this condition strongly depends on the effect of electronic excitation on the interatomic potential energy landscape. In free-electron metals like aluminum, the lattice stability appears to be mostly unaffected by electronic excitation. Subsequent to the optical excitation, electron-phonon scattering heats the lattice and results in thermal melting on the picosecond timescale [1]. In contrast, the excitation of semiconductors weakens the covalent bonding, softens the lattice and, at an excitation level of approximately 10% of the valence electrons, leads to the collapse of the transverse acoustic phonon bands, resulting in electronically-driven non-thermal melting [2]. We used femtosecond electron diffraction (FED) to study the photoinduced melting of two other classes of systems, namely gold, a noble metal, and bismuth, a semimetal with a Peierls-distorted crystal structure. In the case of gold, it has been theoretically predicted that strong electronic excitation induces an increase in the interatomic forces resulting in an increase of its melting point [3]. On the other hand, impulsive electronic excitation of bismuth shifts the minimum of its potential energy surface and launches coherent, large-amplitude optical phonons, equivalent to excited-state wave packet motion in a molecular system. For excitation below the melting threshold, a softening of the interatomic potential with increasing carrier density has been observed [4].

Experimental Methods

An essential requirement for any FED experiment is the ability to generate high density electron pulses with sub-picosecond durations. As the photoinduced melting of the samples is irreversible and the available sample area is limited, the number of electrons per pulse must be high enough to obtain data with a sufficient signal-to-noise ratio

in few shots. In order to limit space-charge broadening of the electron pulse during propagation, we employ a compact design comprising of a 55 kV DC electron gun and a magnetic lens. The photocathode-to-sample distance is < 30 mm. Approximately 10 individual acquisitions are averaged per given time delay. The electron pulse durations have been characterized using ponderomotive scattering of the electron pulse by an optical pulse [5]. The samples, free-standing, 111-oriented gold and bismuth films of 20 and 30 nm thickness, respectively, are excited with the second harmonic of a Ti:sapphire laser system. The instrument response function (given by electron and pump pulse durations as well as the shift of the sample position during the raster scan) is ≤ 450 fs, sufficient to resolve the dynamics of interest. The fastest dynamics of Bi were further verified with 200 fs electron pulses and an instrument response function of < 300 fs.
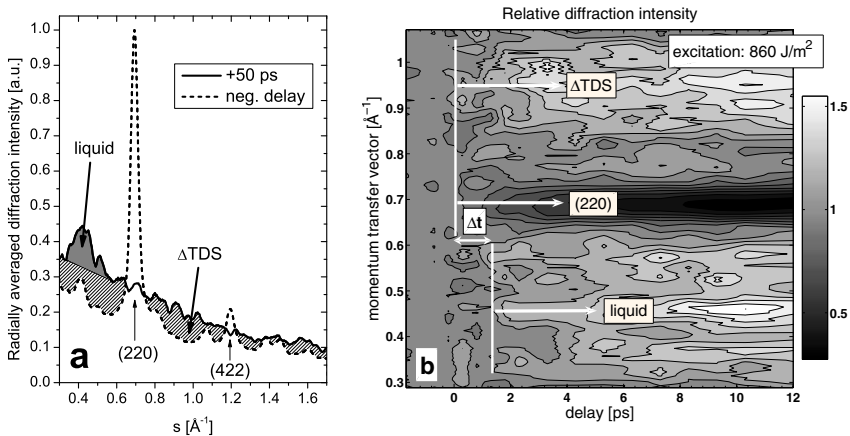

Fig. 1. (a) Diffraction pattern of 111-oriented (neg. delay) and hot liquid (+50 ps) gold. Excitation conditions: 860 J/m^2. (b) Temporal evolution of the diffraction pattern shown as relative diffraction intensity I(s,t)/I(s,t<0), where I(s,t<0) denotes the diffraction signal averaged over all negative delay points.

Results and discussion

Fig. 1a shows the radially averaged diffraction pattern of the gold film before and 50 ps after optical excitation with an incident fluence of 860 J/m^2. The temporal evolution of the diffraction signal (Fig. 1b) shows three distinct features in the scattering range 0.3 to 1.1 Å^{-1}: an overall rise of the scattering background, the rise of a broad peak (liquid structure factor) characteristic for the liquid product state, and the decay of the (220) Bragg peak. The temporal evolutions of these three features differ significantly. Quantifying the dynamics by fitting with monoexponential functions reveals that the increase of the diffuse scattering shows the fastest dynamics ($\tau = 3.5\pm0.6$ ps). In comparison, the decay of the Bragg peak, being a probe for lattice heating as well as disordering, is slightly slower ($\tau = 4.1\pm0.3$ ps). The rise of the liquid signature is delayed by 1.4$\pm$0.3 ps compared to onset of the diffuse scattering and (220) dynamics and shows the slowest dynamics ($\tau = 7.3\pm0.5$ ps). The retardation of the formation of the liquid signature reflects the time required to heat the lattice above the melting temperature, which is an indication of a thermal melting process. A study of the excita-

tion intensity dependence was conducted up to 2000 J/m^2, at which point the absorbed energy corresponds to fourteen times the heat required to melt the sample; the overall dynamics accelerate while the different time constants remain in their relative order. For the highest excitation conditions employed, we estimate that the lattice temperature reaches the melting point about 250 fs after the optical excitation, while we observe a time constant of 2.2±0.4 ps for the rise of the liquid signature. This indicates that the lattice remains in its fcc structure for an extended period of time. This observation is consistent with the theoretically predicted effect of electronic bond hardening in gold [3]. The highest excitation conditions employed in this work correspond to an initial electron temperature of approximately 4 eV, which instantaneously increases the melting temperature from 1340 K to 2400 K according to the ab initio calculations.

In contrast to gold, the structural response of bismuth indicates an electronically-driven, non-thermal melting mechanism. Fig. 2 shows the diffraction intensity of the Bragg spots of a bismuth film, which decays with a time constant of 470 ± 70 fs. Optical excitation of Bi launches optical phonons with a frequency of 2.9 THz (in the low-excitation limit). Increasing electronic excitation flattens the interatomic potential resulting in a red-shift of the phonon frequency [4]. The lowest phonon frequency that has been observed under reversible excitation conditions corresponds to a vibrational period of 470 fs. This indicates that the disordering of the Bi lattice occurs roughly on the time scale of one vibrational period.
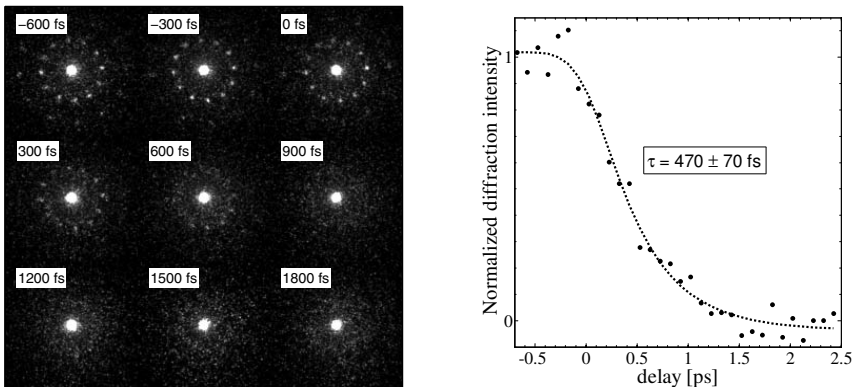

Fig. 2. Left panel: Raw diffraction data of the Bragg spots of a 30 nm thick 111-oriented Bi film at selected time points. Right panel: Normalized diffraction intensity above background as a function of time delay (dots). The data is fitted with a monoexponential function convoluted with the instrument response function (dashed line). Excitation conditions: incident fluence 220 J/m^2.

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