Comparing ultrafast surface and bulk heating using time-resolved electron diffraction

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From measurements of the transient Debye-Waller effect in Bismuth, we determine the buildup time of the random atomic motion resulting from the electronic relaxation after short pulse laser excitation. The surface sensitive reflection high energy electron diffraction and transmission electron diffraction yield a time constant of about 12 ps and 3 ps, respectively. The different energy transfer rates indicate relatively weak coupling between bulk and surface vibrational modes.

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Time-resolved electron diffraction has become a valuable tool for studying structural dynamics on an ultrafast time scale. In particular, the buildup and the decay of lattice vibrations following short pulse laser excitation have attracted a great deal of interest. Using reflection high energy electron diffraction (RHEED) or transmission electron diffraction (TED), one can selectively study either surface or bulk atomic motion. The coupling between bulk and surface vibrational modes is an important issue in many research fields. For example, in catalytic chemical processes the substrate phonon heat bath supplies the energy for activating the sample at approximately 3

and 26 kV (RHEED). In RHEED, the electron beam strikes the backside of the sample with a fluence of approximately 2 mJ/cm² per pulse. The time resolution in the TED experiment is better than 1 ps. A detailed description of the experimental setup and of the sample preparation is given in Refs. 12 and 13, respectively.

The sample in the RHEED experiment is an 8 nm thick epitaxial Bi film grown on a Silicon (111)-(7 × 7) reconstructed substrate. Normal incidence of the optical beam with an incident excitation fluence of 2 mJ/cm² per pulse is used. In the RHEED geometry, the velocity mismatch between the electron pulses and the laser pulses leads to a large spread of the electron arrival times across the sample surface. This mismatch is compensated by passing the laser beam through a zero dispersion delay line. This device produces a suitably tilted pulse front such that the temporal overlap (or delay) with the laser pulse is maintained as the electron pulse sweeps across the surface. The time resolution of this setup has been determined in a separate experiment to be 2 ps (for an electron energy of 29 keV (Ref. 15)).

Electron diffraction patterns are recorded as a function of the delay time between the laser and the electron pulses, and the temporal evolution of the diffraction intensity of the sample.

In TED, we used a free standing Bi film of 22 nm thickness with (001) surface orientation (we use the hexagonal notation). The optical pump is s-polarized and incident on the backside of the sample at an angle of 50° with a fluence of about 2 mJ/cm² per pulse. The time resolution in the TED experiment is better than 1 ps. A detailed description of the experimental setup and of the sample preparation is given in Refs. 12 and 13, respectively.

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Schematics of the TED and the RHEED setup are shown in Fig. 1. In both experiments, the electron pulses are generated by illuminating a semi-transparent photocathode (Au) with the third harmonic (266 nm, 50 fs) of a Ti:Sapphire laser and accelerating the photoelectrons to 30 keV (TED) and 26 kV (RHEED). In RHEED, the electron beam strikes the sample at approximately 3°; in TED, we use normal incidence. The diffraction patterns are recorded by a MCP detector which is read out by a CCD camera. In our optical pump-electron probe schemes, the samples are excited by the laser fundamental (800 nm).

FIG. 1. Schematics of the experimental setup. (a) TED: Pump incident on the backside of the sample and (b) RHEED: pump with tilted pulse front, normal incidence.
individual diffraction spots is analyzed. Examples are shown in Figs. 2 and 3. All data are normalized to the diffraction intensity prior to excitation (before zero delay time).

The full circles in Fig. 2 show the temporal evolution of the (00)-spot of the Bi surface obtained in the RHEED measurement. The base temperature of the sample is 90 K. As expected, the diffraction intensity is constant until the arrival of the pump pulse (delay zero) and drops subsequently to a level of about 52%. In a separate temperature calibration experiment, it has been determined that the final level corresponds to a temperature rise of about 72 K.

Fitting the data by an exponential function (solid line), we obtain a time constant of (10.9 ± 0.3) ps for the intensity drop. The corresponding time constant of the atomic mean square displacement (see below) is \( \tau = 12 \) ps. The temporal resolution under the conditions of this experiment has been determined to be better than 3 ps by measuring the thermal response of a Pb (111) film on Si (111) (open squares and dashed line).

As an example for the results of TED experiments, we show in Fig. 3 the time evolution of the diffraction intensity averaged over the (300) type of equivalent diffraction spots (indicated by white circles in the TED diffraction pattern). At approximately zero delay time the drop of the diffraction intensity sets in, reaching a final constant level of approximately 94%. An exponential fit of the data (dashed line) yields a time constant of \( \tau = (3.2 ± 0.3) \) ps.

Both in the RHEED and the TED experiments, the observed decrease in the diffraction signals following the optical excitation can be interpreted in terms of the timedependent Debye-Waller effect. As the primary electronic excitation relaxes, energy is transferred to the lattice creating some random motion of the atoms. The decrease in diffraction signal is related to the Debye-Waller factor \( D \) which is usually written as \( D = e^{-2W} \), where \( W = \frac{1}{2} \langle (\Delta \mathbf{k} \cdot \mathbf{u})^2 \rangle \). Here, \( \mathbf{u} \) is the atomic displacement vector and \( \Delta \mathbf{k} \) is the momentum transfer, i.e., the difference between the wave vector of the incident and the scattered electrons. In the TED and the RHEED experiments, we have \( \Delta k = 4.8 \text{ Å}^{-1} \) directed parallel to the surface and \( \Delta k = 9.3 \text{ Å}^{-1} \) perpendicular to the surface, respectively. Thus, TED and RHEED probes the component of \( \mathbf{u} \) parallel and perpendicular to the surface, respectively.

The atomic displacements are composed of contributions from all possible vibrational modes of the system. In the bulk, \( \mathbf{u} \) is determined by bulk acoustic and optical phonons, whereas the motion of surface atoms is most likely dominated by surface vibrational modes. Applying the Debye model to calculate \( W \) for bulk acoustic modes one obtains

\[
W = \frac{3h^2 \mathbf{A}^2T}{2M_k \Theta_D^2},
\]

where \( \Theta_D \) is the Debye temperature (\( \approx 100 \) K for Bi), \( M \) is the mass of the unit cell, i.e., for diatomic Bi, \( M = 2M_B \).

The result of the TED experiment depicted in Fig. 3 shows that the motion of the bulk atoms builds up with a time constant of 3.2 ps and that an equilibrium situation is established in approximately 10 ps. Assuming thermal equilibrium and applying (1), the increase of the lattice temperature is calculated from the final level of the diffraction signal to be about \( \Delta T \approx 70 K \), similar to the temperature rise in the RHEED experiment.

Comparing the results of the TED and the RHEED experiments (Figs. 2 and 3), the following differences can be noticed: (i) The buildup time of the relevant atomic displacements in RHEED is almost four times longer than in the TED experiment, and it takes about 40 ps to establish the steady state situation and (ii) the decrease in the diffraction signal in RHEED is much greater than in TED, although the laser-induced temperature rises are very similar.

The difference in the buildup times in TED and RHEED results suggest the following interpretation. In a first step, the primary electronic energy is transferred to the bulk atoms.
within a few picoseconds by electron-phonon interaction processes. During this initial period, the surface atoms are hardly affected. Coupling between bulk and surface vibrational modes then leads to a transfer of vibrational energy from the bulk to the surface. According to this interpretation, the bulk-to-surface transfer of vibrational energy is relatively slow.

Finally, we note that the much larger decrease in the diffraction signal in RHEED cannot be accounted for only by the larger momentum transfer. If we take the bulk formula (1) to calculate the final level of the diffraction signal for the momentum transfer in RHEED, \( D_k = \frac{9.3 \text{Å}}{C_0} \), we obtain 81%, i.e., the expected decrease is much less than experimentally observed. This observation corroborates that in RHEED the transient Debye-Waller effect is dominated by surface vibrational modes and indicates that the corresponding displacements of the surface atoms are significantly larger (a factor of at least 1.5) than those of the bulk atoms.\(^{18}\)

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