Picosecond acoustic response of a laser-heated gold-film studied with time-resolved x-ray diffraction

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We apply time-resolved x-ray diffraction using ultrashort x-ray pulses from a laser-produced plasma to probe the picosecond acoustic response of a thin laser-heated gold film. Measurements of the temporal changes in the angular distribution of diffracted x-rays provide direct quantitative information on the transient evolution of lattice strain. This allows to disentangle electronic and thermal pressure contributions driving lattice expansion after impulsive laser excitation. The electron-lattice energy equilibration time $\tau_E=(5\pm0.3)$ ps as well as the electronic Grüneisen parameter $\gamma_e=(1.48\pm0.3)$ have been determined. © *2011 American Institute of Physics*. [doi:10.1063/1.3584864]

When a solid material is irradiated with an ultrashort laser pulse the optical energy is initially deposited in the electronic subsystem. Within in a few picoseconds the excess energy is transferred to the ionic degrees of freedom. Since this time is usually too short to allow for expansion of the material, the heating induced by femtosecond laser pulses occurs quasi-isochorically. This as well as the electronic excitation itself lead to a nearly instantaneous increase in pressure. Relaxation of the pressure triggers strain waves which can be regarded as a coherent superposition of longitudinal acoustic phonons in the subterahertz range.[1]

Because of the technological potential as a noninvasive probe of materials as well as from a fundamental physics viewpoint, short-pulse laser generated acoustic waves have been extensively studied in the past with time-resolved optical techniques,[2] and, more recently, using time-resolved x-ray[3] and electron[4] diffraction. Nie *et al.*[5] have recently used time-resolved electron diffraction to investigate the structural response of a laser-heated polycrystalline aluminum film and to determine the electron-lattice equilibration time as well as the electronic Grüneisen parameter.

This letter discusses time-resolved x-ray diffraction experiments on an epitaxial gold film to study its acoustic response upon femtosecond optical excitation with the view to disentangle the electronic and thermal driving forces.

Ultrashort x-ray pulses at 4.51 keV (titanium K_α) are generated by focusing 110 mJ, 120 fs pulses at 800 nm from a 10 Hz chirped-pulse-amplified Ti:sapphire laser system onto the surface of a moving titanium wire. The K_α radiation from the plasma is collected and monochromatized with a toroidally bent germanium crystal which produces a 1:1 image of the plasma source[6] on the surface of a 90 nm (111)-oriented gold film grown on mica.[7] A small fraction of the 800 nm laser radiation is split off from the main beam, frequency doubled to 400 nm and used for sample excitation. In an optical pump-x-ray probe configuration the transient changes in the angular distribution (rocking curve) of the symmetric (111)-reflection of the thin gold film are monitored with sup-picosecond temporal and 0.4 mrad angular resolution. The simultaneously recorded (400)-reflection of a nonexcited bulk gallium-arsenide crystal is used for normalization of the gold diffraction signals.

Typical experimental data are depicted in Fig. 1 which shows measured rocking curves (black solid curves) for a number of selected delay times between the optical pump and the x-ray probe pulse. The data measured at negative delay time (the x-ray probe pulse arrives before the optical pump pulse) are identical to the angular diffraction profile obtained for the unexcited sample. The measured rocking curve width is 0.37°, much wider than the expected width of 0.1° for a perfect crystalline film with 90 nm thickness, which is attributed to its mosaic structure. As compared to the rocking curve of the unpumped sample (black dashed curves in Fig. 1) a shift of the diffraction peak toward smaller diffraction angles and a slight broadening (accompanied by a reduction in the peak height) is observed for posi-

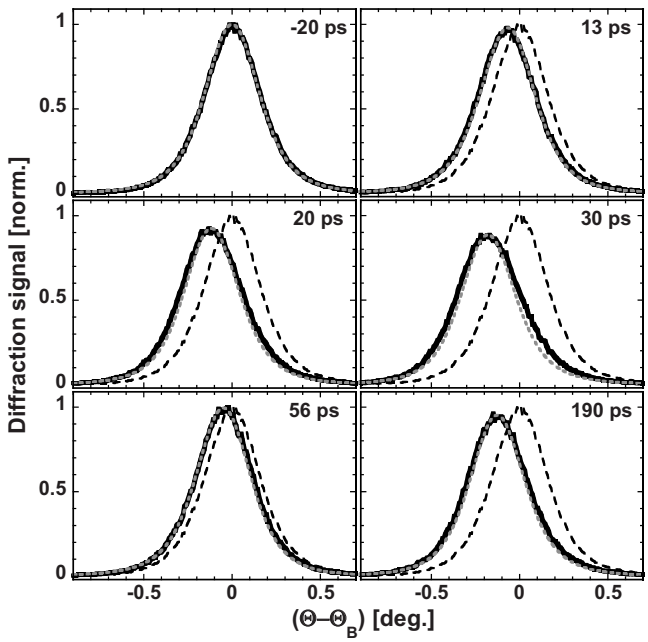

FIG. 1. Rocking curves of the (111) Bragg reflection of a 90 nm gold film on mica for different pump-probe time delays. Black solid curves: experimental data; black dashed curves: rocking curve measured at $\Delta t=-20$ ps as reference; gray dashed curves: results of model calculations with *time-dependent* pressure/stress [Eq. (2) with $\tau_E=5$ ps and $\gamma_e=0.5\gamma_L$].

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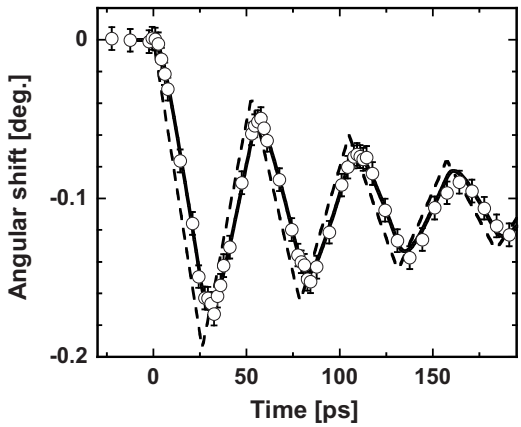

FIG. 2. Shift of the (111) Bragg peak (center of gravity) of a 90 nm gold film on mica as a function of pump-probe time delay. Open circles: experimental data; black dashed curves: result of model calculations with *time-independent* pressure; black solid curve: result of model calculations with *time-dependent* pressure/stress [Eq. (2) with $\tau_E=5$ ps and $\gamma_e=0.5\gamma_L$].

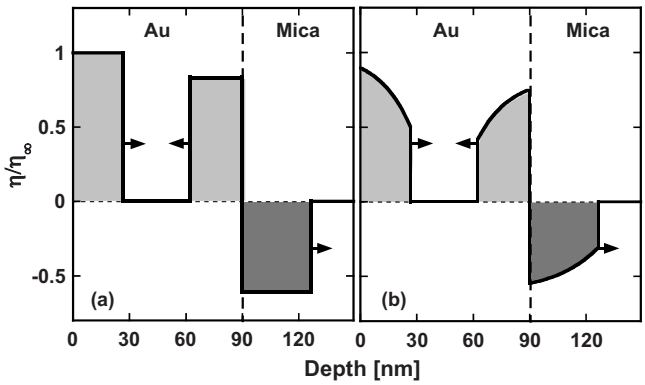

FIG. 3. Calculated strain distribution (normalized) in the film-substrate system derived from a solution of the acoustic wave equations with (a) *time-independent* pressure/stress and (b) *time-dependent* pressure/stress [Eq. (2) with $\tau_E=5$ ps and $\gamma_e=0.5\gamma_L$] at a time $t=0.3\cdot\tau_{ac}=8$ ps.

tive delay times. A shift to smaller diffraction angles indicates lattice expansion. However, the expansion dynamics is nonmonotonous, as is evident by comparing for example the rocking curves measured at $\Delta t=30$, 56, and 190 ps. Concerning the broadening and reduction in peak height we note that the angularly integrated x-ray reflectivity remains constant for all delay times within the experimental error of about $\pm 1.5\%$.

To quantitatively characterize the expansion dynamics we determined the center of gravity of all measured rocking curves. Figure 2 (open circles) shows its dependence on delay time.The rocking curve shifts initially toward smaller diffraction angles due to lattice expansion. The maximum shift/expansion is reached after 31 ps and followed by damped oscillations with a period of (26.4 ± 0.2) ps. As will be discussed below this oscillatory behavior directly reflects the propagation of acoustic waves in the film. The average shift measured at long delay times is $\Delta\Theta_\infty=(0.11\pm 0.008)°$, which corresponds to a strain $\eta_\infty=(0.27\pm 0.02)\%$. If this strain is interpreted as thermal expansion and taking into account the one-dimensional (1D) nature of the expansion process[8] a laser-induced temperature rise of $\Delta T_\infty=(64\pm 5)$ K is derived. For such a temperature rise the estimated reduction in the angularly integrated strength of the (111)-reflection due to the Debye-Waller effect is only 1% in agreement with the experimental observation.

To interpret our experimental data we model the strain evolution in terms of laser-induced acoustic waves. It should be mentioned that using a thin film as sample simplifies the analysis. Since the 90 nm film thickness is larger than the optical penetration depth at 400 nm (16 nm) there is no direct excitation of the substrate. Nevertheless, very fast electronic transport[9] ensures distribution of the deposited energy over the whole film thickness within a few hundred femtoseconds. Moreover, electronic as well as thermal energy loss into the substrate are negligible because of the large band gap of mica and the low thermal boundary conductance,[10] respectively. Thus the initial laser-generated stress/pressure driving the acoustic waves is spatially homogeneous in the film but negligible in the substrate. We apply the phenomenological description of Thomsen *et al.*,[1] who separate the stress into an electronic and a thermal contribution,

$$\sigma=\sum_k \delta n_e(k)\frac{\partial E_k}{\partial \eta}+\sum_q \delta n_p(q)\frac{\partial \hbar\omega_q}{\partial \eta}. \quad (1)$$

Herein $\delta n_e(k)$ and $\delta n_p(q)$ denote changes in the distribution function of electrons and phonons, respectively, and $\partial E_k/\partial\eta$ and $\partial\hbar\omega_q/\partial\eta$ the strain-induced variation in the electron and phonon energies. In general both the total pressure and the individual electronic and thermal contributions, change with time. The increase in the electronic pressure can be regarded as instantaneous since it directly follows the optical excitation. Relaxation of the excited electrons leads to a decay of the electronic contribution while the thermal pressure builds up as a consequence of the energy transfer from the hot electrons to the lattice. After the initial rise the thermal contribution remains essentially constant on the time scale of interest ($\approx$100 ps). By assuming thermal distributions for electrons and phonons with (initially different) temperatures T_e and T_L, and an electron-lattice energy exchange with an exponential time dependence with time constant τ_E Eq. (1) can be put into the following form for metals[12,13] [$H(t)$: Heavyside-function]:

$$\sigma(t)=\sigma_\infty\cdot H(t)\cdot\left[1+\left(\frac{\gamma_e}{\gamma_L}-1\right)\cdot e^{-t/\tau_E}\right]. \quad (2)$$

With $\sigma_\infty=c_S^2\rho\cdot\eta_\infty$ (Ref. 1) (c_S: sound velocity and ρ: density) the time dependence of the pressure is determined by only two independent parameters, namely, the electron-lattice equilibration time τ_E and the ratio γ_e/γ_L of the electronic and lattice Grüneisen parameters, respectively. With a stress/pressure according to Eq. (2) as an input we solved the acoustic wave equations for the film-substrate system to obtain the time evolution of the lattice strain. We will discuss the characteristic features of the acoustic response first for the simplified case of a steplike increasing, nondecaying pressure (i.e., $\gamma_e=\gamma_L$ or $\tau_E\to 0$); we call this the *time-independent* case. For these conditions the acoustic waves exhibit a steplike shape, as sketched in Fig. 3(a), which shows the normalized (to η_∞) strain distribution in the film-substrate system for a time $t=8$ ps after the instantaneous increase in pressure.

Two rarefaction waves are launched from the film-vacuum and film-substrate interfaces, respectively, into the pressurized film while the nonexcited substrate gets compressed due to the film expansion. The strain waves travel back and forth through the film because of reflection at the

film interfaces. Eventually the acoustic waves are damped out due to the finite acoustic transmission into the substrate (determined by the acoustic impedances). The characteristic acoustic time scale is given by the time $\tau_{ac}=d/c_S$ an acoustic wave needs to traverse the film thickness d. With $d=(90\pm1)$ nm and $c_S=3.39$ km/s along the (111)-direction[14] $\tau_{ac}=(26.5\pm0.3)$ ps, in agreement with the experimentally observed periodicity of the Bragg-peak shift (see Fig. 2).

For an explicit time-dependent pressure $\sigma(t)$ the shape of the acoustic pulses will change and directly reflect the (exponential) time dependence of the pressure: The time constant τ_E of the pressure evolution is transformed into a characteristic scale length l of the strain profile via the relation $l=c_S\cdot\tau_E$. Figure 3(b) shows as an example the strain distribution at $t=8$ ps$=0.3\cdot\tau_{ac}$ assuming a time-dependent pressure with $\gamma_e=0.5\gamma_L$ and $\tau_E=5$ ps (see below). It should be noted that the effects of a time-dependent pressure are strongest when τ_E is comparable to τ_{ac}, but the general features of the strain evolution, namely, the damped oscillatory behavior discussed above for the time-independent case are preserved.

The results of the acoustic modeling served as input to calculate the transient changes in the rocking curves using dynamic diffraction theory for the 1D strained crystal.[15] With a time-independent pressure the shift of the rocking curve (center of gravity) follows the black dashed curve shown in Fig. 2. While there is general qualitative agreement between the calculated and the measured time dependencies, there are important quantitative differences. (i) The time-independent model predicts a slightly larger amplitude of the oscillations of the Bragg-peak shift. (ii) The experimental time trace is displaced by 5 ps with respect to the calculated curve.

By using a time-dependent pressure the best fit of the measured Bragg-peak shift was obtained for $\tau_E=(5\pm0.3)$ ps and a ratio $\gamma_e/\gamma_L=(0.5\pm0.1)$, as indicated by the black solid curve in Fig. 2. This set of parameters leads to a pressure that increases with time which accounts for the experimentally observed delay in the shift as well as the reduced amplitude of the oscillations. In Fig. 1 the gray dashed curves represent the calculated rocking curves for the same parameter set $\tau_E=5$ ps and $\gamma_e/\gamma_L=0.5$ after convolution with a broadening function to account for the mosaicity of the film (determined by fitting the rocking curve of the unexcited sample). Beside a slightly larger width of the measured rocking curves at delay times when the peak shift is large (i.e., $\Delta t=30$ ps),[16] a good agreement between the calculations and measured data is obtained. This gives clear indication that the applied model provides an accurate description of the acoustic response of the laser-excited gold film.

Moreover, the derived values of the parameters that determine the time dependence of the pressure compare very well with previously reported results obtained by other methods. From measurements of the transient Debye-Waller effect the electron-lattice energy exchange time in gold has been determined to $\tau_E=(4.7\pm0.6)$ ps by Ligges *et al.*[17] using time-resolved electron diffraction. For the electronic Grüneisen parameter a value of $\gamma_e=(1.6\pm0.5)$ has been measured at cryogenic temperatures.[18] Using the known value for $\gamma_L=(2.96\pm0.04)$ from the same reference[18] we obtain $\gamma_e=(1.48\pm0.3)$, which agrees within the experimental error with the low-temperature measurement of γ_e.

In summary we have used ultrafast time-resolved x-ray diffraction to study the acoustic response of a thin gold film after femtosecond laser excitation. Comparison of the measured data with model calculations allowed us to separate the electronic and thermal driving forces, and to obtain the electron-lattice equilibration time as well as the electronic Grüneisen parameter. Our results provide further evidence that time-resolved diffraction represents an interesting possibility to determine γ_e at noncryogenic temperatures.

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