Lattice dynamics of femtosecond laser-excited antimony

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ABSTRACT

Ultrafast electron diffraction is used to probe the lattice dynamics of femtosecond laser-excited antimony thin film. The temporal hierarchies of the intensity and position of diffraction orders are monitored. The femtosecond laser excitation of antimony film was found to lead to initial compression after the laser pulse, which gives way to tension vibrating at new equilibrium displacement. A damped harmonic oscillator model, in which the hot electron-blast force contributes to the driving force of oscillations in lattice spacing, is used to interpret the data. The electron-phonon energy-exchange rate and the electronic Grüneisen parameter were obtained.

Keywords: Keywords: Antimony; Femtosecond excitation; Lattice dynamics; Electronic Grüneisen parameter

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1. Introduction

Ultrafast electron diffraction (UED) allows for direct observation of the transient state of the crystal lattice excited by a femtosecond laser pulse [1,2]. UED has revealed subtle information on the dynamics of the transient state of the crystal lattice, including charge density waves [3], measurements of electronic Grüneisen parameter in Ni [4], studies of solid-liquid phase transition in Bi [5], anisotropy of electron-phonon energy exchange in Bi [6,7], and observation of hot electron-blast force in Bi nanoparticles [8], UED has been applied to study the dynamics of isolated chemical reactions, interfaces, surfaces, and nanocrystals [9].

In our UED experiments, the processing of temporal evolution of the electron diffraction pattern is focused on the simultaneous measurements of both the intensity and the position of the diffraction order. The lattice perturbations resulting from femtosecond pulse excitation affect both, and the temporal hierarchy between them is an important source of information on the relaxation of the energy stored in the electron subsystem. We discuss UED study of Sb thin film, taking into account electron-blast force, which significantly affects the lattice relaxation dynamics. Both the intensity and position of diffraction orders are measured.

2. Experimental

The Sb samples of 20 ± 2 nm thickness were prepared by thermal evaporation on carbon-coated transmission electron-diffraction 3-mm grids. Sb pellets (99.999% pure) were loaded into a tungsten boat. The base pressure of the evaporation chamber was in the low 10^{-6} Torr range. The evaporation rate was controlled by varying the current through the tungsten boat. A quartz crystal thickness monitor was used to measure the deposition rate and thickness. Evaporation was done at room temperature at a rate of $\sim 0.5 \text{ \AA s}^{-1}$. The film average thickness was determined during deposition by a crystal thickness monitor that was calibrated by post-deposition thickness

measurement by an ellipsometer. High-resolution field emission transmission electron microscope (TEM) (JEM-2100F, JEOL) was used to observe the morphology of the Sb film.

An electron gun [10,11], was used to produce electron pulses by photoemission from silver thin film photocathode excited by frequency-tripled femtosecond (110 fs duration, 800 nm fundamental wavelength, at 1 kHz repetition rate) laser pulses. The gun produced 35 keV electron pulses of ~1.4 ps duration at the photocathode excitation level used. The electron pulse width was measured using the response time of the diffraction intensity from an Al thin film.

The Sb film was exposed to the fundamental 800 nm wavelength at a pulse energy density of $5 - 7 \text{ mJ/cm}^2$, which is lower than the damage threshold of $\sim 12 \text{ mJ/cm}^2$ found in our measurements. A micro-channel plate proximity focused to a phosphorous screen is used for diffraction pattern detection. The UED pattern was captured by CCD camera PIXIS-1024 with exposure time 15 – 20 s at the repetition rate 1 kHz. The UED system is operated in an ultrahigh vacuum (low 10^{-9} Torr).

The diffraction pattern analysis included radial profile scanning (“ImageJ” software), background subtraction, and Lorentz function fitting (“Origin” software). To evaluate a lower limit of accuracy of our measurements the standard deviation of the diffraction order radius

$\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^N (R_i - \mu)^2}$ was determined of the diffraction peak positions R_i at the absence of excitation over measurements taken at different delay times (number of the delay time points $N = 32$). The standard deviation value was found to be 1.1×10^{-4} . This measurement provides the limits of our detection capability of changes in diffraction angle with excitation.

3. Results and discussion

Fig. 1(a) is a TEM image of the Sb film showing that it is made out of connected flat islands with irregular shapes and lengths of a few hundred nm. Some voids in the film are observed at the intersection of islands. Fig. 2(b) is a diffraction pattern obtained from the UED system, which shows a ring pattern with uniform radial intensity distribution that is characteristics of a polycrystalline film. The radial profile of the electron diffraction pattern from the Sb sample under study is presented in Fig. 1(c). We present results on three diffraction peaks, (01 11), (217), and (104), which cover a wide spread in diffraction angles. The results of our measurements of the intensity, $I(t)$, and radius (or Bragg peak position), $R(t)$, of diffraction orders as a function of the delay time are shown in Fig. 2 as a dependence $(\varphi(t) - \varphi_0)/\varphi_0$ where $\varphi(t) = I(t)$ or $R(t)$, and φ_0 is the unperturbed value of I or R . All the diffraction orders exhibit approximately the same temporal behavior showing lags of $R(t)$ relative to $I(t)$ and weak fast-decaying oscillations. The lag value for each diffraction order was determined as the time interval between two coordinates of the minima of the first derivatives of $R(t)$ and $I(t)$ for the diffraction order, and was found to vary within delay time of $2.7 - 4$ ps. A 1 ps lag was previously observed in X-ray diffraction of femtosecond laser-excited Ge and in UED of Al [12,13]. For the (217) and (104) diffraction orders, the dynamics of $R(t)$ dependence starts with positive changes (compression) shortly after zero-delay time, which transforms into a negative one (expansion) as the delay time increases. The time within which the change of $R(t)$ shows compression is $3 - 5$ ps. The amplitude of the positive peak in the diffraction order was found to be proportional to the pump energy and was dependent on the diffraction order with the compression showing clearly for the (217) and (104) diffraction orders. The (01 11) order of Sb

does not show a clear positive peak in the vicinity of zero-delay time, or at least its amplitude is small enough that it is within the instrumental limitations.

The temporal behavior of the intensity change, $I(t)$, is well studied and widely presented in numerous publications [1,2,7,8]. It is well established that the intensity drop of the diffraction order, hkl , is due to the Debye-Waller factor e^{-2M} and the scattering vector, $s_{hkl} = 2 \sin(\theta)/\lambda$. The value of M depends on the mean-square atomic displacement, which is material-dependent through the Debye temperature θ_D , and the atomic mass and increases with lattice temperature. The Debye temperature $\theta_D = 174 \pm 14$ K of the thin Sb film under study was obtained from the static diffraction intensity measurements taken at different temperatures (inset of Fig. 3), with the film heated on a hot stage. Knowing this value, the ratio of $I_{hkl}[T(t)]/I_{hkl}[T(t < 0)]$ can be converted to temperature change $\Delta T(t)$, as shown in Fig. 3. $I_{hkl}[T(t < 0)]$ is the diffraction intensity at room temperature. By fitting this temperature dependence with exponential function, we retrieve the time constant for lattice thermalization τ_{e-ph} . For all three diffraction orders, the time constant was found to be $\tau_{e-ph} = 1.08 - 1.36$ ps. We note that on a time scale of a few ps, the excited acoustic phonons are not in equilibrium with the phonon bath [6]. Therefore, T_L should be considered as an effective lattice temperature.

The temporal dependence of $R(t)$ for the (217) and (104) diffraction orders show clearly the stress dynamics of the excited lattice, which undergoes the initial compression (positive $\Delta R(t)$) giving way to the tension (negative $\Delta R(t)$) vibrating at new equilibrium displacement, as shown in Fig. 2. One can assume that the compressive peak is caused by impulsively generated thermal stress, which after its release results in the travelling compression/expansion strain wave into the film. This stress wave was observed in optical pump-probe experiments with rather thick samples (220 nm of α -As₂Te₃ and 280 nm Ge) [14], and in ultrafast X-ray studies of InSb crystal

[15]. Theoretically, the strain pulse is formed under conditions when the absorption length is smaller than the film thickness [14]. The dynamics of $\Delta R(t)$ should be considered as a competition between two forces, one of which is compressive and the other, tension. In previous analysis [22], three forces are caused by the ultrafast laser pulse interaction with the film were considered including the thermal force F^{th} (due to electrostatic interaction between excited electrons and the ions under the gradient of electronic pressure), the polarization force F^{pol} (as a dependence of polarizability on the atomic displacement), and the ponderomotive force F^{pond} . For Bismuth, which has a similar crystal structure as antimony, the contribution of the forces of these mechanisms relative to F^{th} was theoretically derived to be $1 > 0.355 > 0.034$ [22]. F^{pol} and F^{pond} are effective only during the laser pulse. An additional force arises in the ultrafast laser interaction due to the hot electron blast force when there is a gradient in electron temperature across the sample thickness. This hot electron blast force is directed perpendicular to the film surface and acts as a compression force [18]. Similar behavior of the diffraction peak position with time showing compression followed by expansion was observed in ultrafast X-ray diffraction experiments on 150-nm thick Au(111) crystal [22, 23]. In [22] the authors interpreted the compression peak as a hot electron blast-force. The maximum amplitude of compression peak was found to be 6%, which is significantly larger than that in our observations, which is limited to 0.04%. There are two reasons that could explain such a large difference in the observed amplitude. Firstly, it is the gradient of the effective electron temperature along the depth of sample, which is significantly higher in the 150-nm Au crystal than the 20-nm Sb film. Secondly, the different orientations of Sb grains can suppress the effect of the electron blast-force. We suppose that both of these mechanisms could be presented in our measurements. The contribution of electronic pulse pressure to acoustical phonons dynamics was evaluated in

several publications [1,12–14,16,17]. Because the laser spot size on samples is much larger than the laser skin depth in Sb, a one-dimensional approximation of hot electron-blast force is valid. For the one-dimensional case (z -axis directed toward laser pulse propagation inside sample) the excitation of the hot electron-blast force results in electron kinetic pressure

$$P(t, z) = \frac{2}{3} C_{e0} T_e^2(t, z), \quad (1)$$

where $C_{e0} = \pi^2 N k_B / 2 T_F$ is the electron heat capacity, k_B is the Boltzmann constant, N is the number density of atoms, T_F is the Fermi temperature, and T_e is the electron temperature [18].

The electron heat capacity, C_e , is assumed to be proportional to the electron temperature,

$C_e = C_{e0} T_e$. The absorption coefficient of the 800-nm laser in Sb is $\alpha_{sb} = 7.7 \cdot 10^5 \text{ cm}^{-1}$ [19].

Therefore, the initial distribution of the absorbed laser energy (and, consequently, the electron temperature and electron density) decreases exponentially in the film depth. This gradient in the electron temperature produces a gradient in pressure and creates a hot electron-blast force

$$F_z(t, z) = \frac{\partial}{\partial z} P(t, z) = \frac{\partial}{\partial z} \left(\frac{2}{3} C_{e0} T_e^2(t, z) \right),$$

which is directed perpendicular to the surface of the film [18]. For simplicity we consider the electron-blast force at the film surface $z = 0 \text{ nm}$, which allows one to use one-dimensional presentation $F(t, z = 0 \text{ nm}) = F(t)$. As a result, compressive stress σ_z arises normal to the surface of the film. In highly anisotropic materials like Sb, any one component of stress causes strain in all six components, $\varepsilon_{ij} = S_{ijkl} \cdot \sigma_{kl}$ (S_{ijkl} is fourth-ranked tensor compliance) [20]. Therefore, the hot electron-blast force directed along the z -axis causes strains in the x - y plane of the film as well. It is these components, σ_x and σ_y , which are responsible for radius change of the diffraction order of the excited film in the geometry of our experiment. In anisotropic media, the strain amplitude is determined by the stress values, which

differ from one diffraction order to another, providing different contributions to the driving force and the resulting lattice dynamics.

Due to electron transport, electron-phonon energy exchange, and recombination of excited carriers, the distribution of electron temperature and electron density become uniform across the film thickness and, therefore, the compressed state of the excited film decays in time. For acoustic phonon generation, the driving force, $\sigma(t)$, is represented by the combination of stress due to the hot electron blast force (compression) and transient thermal stresses consisting of electronic, σ_e , and lattice, σ_l , heating (tension) [13–15,21], which can be written as

$$\sigma(t) = \sigma_{\nabla T_e}(t) + \sigma_e(t) + \sigma_l(t) = AF(t) - \gamma_e C_e \delta(T_e) - \gamma_l C_l \delta(T_l) \quad (2)$$

where $\sigma_{\nabla T_e}$ is stress due to the hot electron-blast force, σ_e is electronic thermal stress, σ_l is lattice thermal stress, C_e and C_l are the electron and phonon heat capacities, γ_e and γ_l are the Grüneisen parameters for electrons and phonons, $\delta(T_e)$, $\delta(T_l)$ are the temperature variations of electron and phonons in equilibrium states, and A is a scaling factor used to match $F_z(t)$ to the driving force. Following the arguments of [13], we assume that the total energy (E_{total}) deposited into a unite volume of the film is conserved on ps time span, and hence we can write $C_e \delta(T_e) + C_l \delta(T_l) = E_{total} G(t)$, where $G(t)$ represents normalized temporal profile of femtosecond laser pulse. Since the hot electrons thermalize with other electrons within several femtoseconds [24], the gradient blast force and thermal pressure from hot electrons $\sigma_{\nabla T_e}(t) + \sigma_e(t)$ dominate over the electronic and lattice heating terms at the initial stage of excitation.

Under these conditions the sum $\sigma_e(t) + \sigma_l(t)$ can be expressed [13] by

$$\sigma_e(t) + \sigma_l(t) = -\gamma_e E_{total} (G(t) - 1 + e^{-t/\tau_{e-ph}}) - \gamma_l E_{total} (1 - e^{-t/\tau_{e-ph}}) \quad (3)$$

The phenomenological description of results in Fig. 1 can be given on the basis of a model of temporal evolution of coherent phonons [1]. In this model, the temporal evolution of lattice displacement, $X(t)$, is described as a driven harmonic oscillator

$$X'' + 2\beta X' + \omega_0^2 X = H\sigma(t) \quad (4)$$

where H is a scaling factor, β is the damping constant, and ω_0 is the phonon angular frequency. An exact calculation of the temporal shape of the electron-blast force requires the solution of coupled nonlinear Boltzmann and thermal-conductivity equations, which is a difficult procedure [18, 21]. Nevertheless, the temporal shape of $P(t, z = 20 \text{ nm})$ can be reconstructed on the basis of numerical calculations presented in Fig. 10 of Ref. [18], in which the distribution of the electronic kinetic pressure over the thickness of the sample is given within 0.2 to 3.0 ps temporal interval. These data provide four points, which allow one to plot the temporal dependence of $P(t, z = 0 \text{ nm})$. By fitting this dependence with different pulse functions, the best correspondence for stress due to the hot electron-blast force was found for extreme function

$$\sigma_{\text{Te}}(t) = \sigma_0(t) + C \exp\left[-\exp\left[-\left(\frac{t-t_0}{w}\right)\right] - \left(\frac{t-t_0}{w}\right) + 1\right] \quad (5)$$

Introducing the driving forces described by Eqs. (3) and (5) into the right part of Eq. (4), the expected temporal profile of the lattice spacing can then be fitted with the experimental results for diffraction ring radius changes shown in Fig. 2. The fitting of the numerical solution of Eq. (3) to experimental results are made for three diffraction orders, as shown in Fig. 4. This fit yielded the ratio γ_e/γ_l values 0.58, 0.75, 0.68 for the diffraction orders (01 11), (217), and (104), respectively). Thus, the average ratio of the Grüneisen parameters is found to be $\gamma_e/\gamma_l = 0.67 \pm_{0.09}^{0.08}$. To illustrate the influence of the electron-blast force on the dynamics, the numerical

fit for the (217) order is calculated from Eq. (3) when the driving force in Eq. (2) does not include the blast force (dashed line) and when it includes the blast force (solid line).

To determine the value of γ_e for Sb, measurements of the linear thermal expansion of a single-crystal Sb rod were used, in which the lattice Grüneisen parameters were found to be $\gamma_{\perp} = 1.2$, $\gamma_{\parallel} = 0.94$, where $\parallel$ and $\perp$ refer to directions parallel and perpendicular to the trigonal axis of the crystal [25]. Disregarding possible anisotropy of γ_e and accepting the average value of γ_l , the ratio γ_e/γ_l results in $\gamma_e = 0.71 \pm 0.09$. As far as we know, neither experimental data nor theoretical evaluations of electronic Grüneisen parameter γ_e of Sb were previously published.

4. Conclusion

In conclusion, the dynamics of coherent, acoustic phonons induced by femtosecond laser pulse in Sb thin polycrystalline film were studied using UED. Well-pronounced compressive peak was observed in lattice spacing dependence along with lag relative to intensity change. We used a damped, harmonic oscillator model in which the hot electron-blast force was taken into account as a part of the driving force. The temporal shape of the electron-blast force, its peak position, and decay time were identified. The electron-phonon energy exchange rate and electronic Grüneisen parameter for Sb were determined.

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Figure captions

Fig. 1. (a) Transmission electron microscopy image of the Sb film. (b) Diffraction pattern obtained in the UED system. (c) Radial profile of the diffraction pattern of the Sb film as a function of momentum transfer $= 2\pi/d$, where d is the distance between adjacent planes.

Fig. 2. Temporal dependence of radius $R(t) = ((R(t) - R_0)/R_0)$ change in % (dashed line, open circles) and intensity $I(t) = (I(t) - I_0)/I_0$ change (solid line, closed circles) of diffraction orders of the Sb thin film. Circles are the experimental data, and the lines are the results of smoothing by low-pass parabolic FFT filtering of the data.

Fig. 3. Temperature evolution of the (01 11) diffraction order intensity. The solid line is the numerical fit with exponential function. Inset: natural logarithm of the intensity ratio of antimony 20 ± 2 nm thin film as a function $(\sin \theta/\lambda)^2$.

Fig. 4. Numerical fitting of the solution of Eq. (4) to the results of experiments for the diffraction orders (01 11), (217), and (104). For illustration, the numerical fit of the electron-blast force contribution to lattice dynamics for the (217) order is presented without the electron-blast force (dashed line) and when this force is included in the right part of Eq. (4) (solid line).

Fig. 1

Fig. 2

Fig. 3

Fig. 4