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Femtosecond reflectivity study of photoacoustic responses in bismuth thin films

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ABSTRACT

We report on generation and observation of photoacoustic pulses in bismuth thin films using femtosecond reflectivity spectroscopy. Upon photoexcitation of bismuth thin films with a femtosecond laser pulse, hot carriers are created in the optical penetration depth and diffuse into the interior. They scatter off the interface effectively and raise the lattice temperature generating a picosecond acoustic phonon pulse which propagates towards the free surface and modulates the reflectivity. By monitoring the reflectivity change at the surface in real time, we investigate photoacoustic responses as a function of excitation fluence and film thickness.

1. Introduction

Bismuth has been a prototypical material for examining coherent optic phonons, electron-phonon coupling, electronic bond softening and phase transitions using ultrafast laser spectroscopy and ultrafast diffraction methods [1–19]. The generation mechanism of coherent optic phonons is known as displacive excitation of coherent phonons (DECP) and observed commonly not only in bismuth but also in other semi-metallic materials such as telluride and antimony [5,6]. In DECP, photoexcited carriers are created upon impulsive optical excitation and they alter the potential energy surface (PES). As a consequence, atoms are located suddenly in a repulsive region and driven to move coherently back and forth along the diagonal direction on the new PES. This is the totally symmetric A_{1g} optic phonon mode in bismuth. The A_{1g} phonon oscillations undergo a redshift with increasing carrier density or pump fluence due to electronic bond softening but return back to the equilibrium frequency as carriers recombine [9]. The A_{1g} optic phonons relax as the PES returns to the equilibrium one with electron-hole recombination and can also couple to acoustic phonons via anharmonic coupling and generate them at high pump fluences [2,14].

Photoacoustic responses also provide valuable information on the dynamics of lattices and hot carriers such as transport, relaxation and coupling with lattices [20–24]. However, contrary to extensive studies of the optic phonon generation and the relevant electronic and structural dynamics, there has been little work on photoacoustic responses in bismuth. Here, we report on generation and observation of photoacoustic pulses in bismuth thin films using femtosecond reflectivity spectroscopy. Upon photoexcitation of very thin bismuth films with a femtosecond laser pulse, hot carriers are created in the penetration depth and then they reach the interface between bismuth and substrates via diffusion or ballistic transport. They raise the lattice temperature through electron-lattice coupling and cause a sudden volume expansion and thus an acoustic pulse at the interface. It propagates towards the bismuth surface and influences the transient reflectivity change. By monitoring the reflectivity change, we investigate photoacoustic responses as well as the ultrafast dynamics of hot carriers as a function of excitation fluence and film thickness.

2. Experimental

Femtosecond transient reflectivity was measured using a 1 kHz Ti:sapphire laser system which produces 70 fs long pulses with a center wavelength of 800 nm. Every laser pulse was divided into a pump and a probe beam by a beam splitter. The pump-probe delay time was varied up to 100 ps by an automated delay stage. Pump fluence was controlled by an attenuator composed of a half wave plate and a polarizer and subsequent neutral density filters. The pump beam was chopped at 500 Hz and the pump-induced reflectivity change of bismuth was measured by the probe pulse using a lock-in amplifier. Both pump and probe were *p*-polarized. A (111)-oriented single crystal and thin films with different thickness were used. The films were grown by sputtering deposition on silica glass or oxidized silicon substrates. The substrates were sonicated in acetone and then plasma-cleaned before deposition. They were kept at 440 K during sputtering deposition (RF mode) and the deposition rate was controlled to 0.04 nm/s. The film thickness was determined from spectroscopic ellipsometry measurements using dielectric functions. Podwer X-ray diffraction was used to examine the

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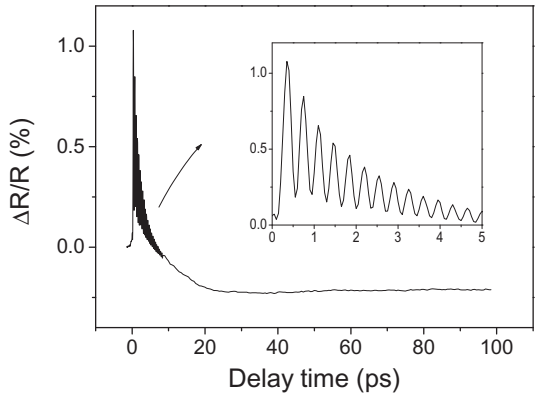

Fig. 1. Transient reflectivity change of a bismuth single crystal after photoexcitation with a fluence of 3.1 mJ/cm^2 at $t = 0$. The inset zooms in the reflectivity from 0 to 5 ps to show the coherent A_{1g} phonon oscillations clearly.

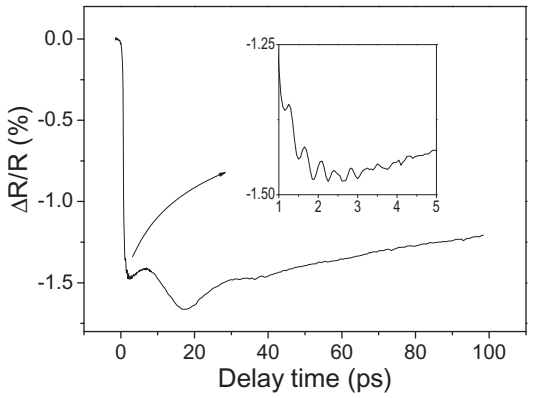

Fig. 2. Transient reflectivity change of a bismuth thin film (25 nm) after photoexcitation with a fluence of 2.6 mJ/cm^2 at t = 0. The coherent A_{1g} phonon oscillations are shown at early delay times from 0 ps to 5 ps in the inset.

crystallinity of the films and showed that the films are all polycrystalline with a preferential (113) surface orientation and no evidence of amorphous bismuth.

3. Results and discussion

Fig. 1 shows the time-resolved reflectivity signal of a bulk single crystal after photoexcitation with a fluence of 3.1 mJ/cm^2 at $t = 0$. The signal features are consistent with the previous works [16,18]. The reflectivity rises sharply at t = 0 and decays fast for the first 10 ps due to electron-phonon coupling and non-radiative carrier recombination. The reflectivity continuously decreases until around 30 ps and then increases very slowly towards the undisturbed value. The minimum reflectivity coincides with the maximum lattice temperature around the same delay time obtained from our earlier thermal analysis [25]. The subsequent slow increase is due to slow cooling of the lattice driven by thermal conduction. The reflectivity signal at early delay times displays strong oscillations clearly as shown in Fig. 1 inset. The oscillatory signal is attributed to coherent phonon oscillations of the A_{1g} optic mode launched by the DECP mechanism [5,6].

The photoinduced reflectivity change of bulk bismuth can be generally fitted to the sum of two exponential functions as follows:

$$\frac{\Delta R}{R} = A_e \exp\left(-\frac{t}{\tau_e}\right) + A_p \exp\left(-\frac{t}{\tau_p}\right)\cos(2\pi f t + \phi_0), \tag{1}$$

$$f = \beta t + f_0 \tag{2}$$

Here, A_e and τ_e are the amplitude and the decay time for the background electronic signal and A_p, τ_p, and ϕ_0 are the phonon amplitude, dephasing time, and initial phase at time origin [7,14,18]. f is the instantaneous phonon frequency which assumes to change linearly with time. β and f_0 represent the linear chirp rate and initial phonon frequency, respectively. For bulk bismuth under a fluence of 3.1 mJ/cm^2, the chirp rate and initial phonon frequency are measured as 0.01 THz/ps and 2.8 THz, respectively. The phonon frequency is redshifted from the equilibrium frequency of 2.93 THz revealing bond softening as observed in previous works [9,13,18].

Fig. 2 shows the time-resolved reflectivity change of a 25 nm thin film on silica glass after photoexcitation with a fluence of 2.6 mJ/cm^2. Unlike bulk bismuth, it is always negative. It falls sharply at $t = 0$ and decreases until 3 ps. After this decrease, the reflectivity then increases towards the unperturbed value, but again decreases soon and reaches a minimum value around 17 ps forming a distinct dip. The dip indicates an acoustic phonon pulse generated by ultrafast photoexcitation. This will be discussed shortly. The reflectivity background signal of thin films is different from that of bulk bismuth. The difference is because film thickness affects electronic structures. More details on the thickness dependence can be found in our previous work [18]. As shown in the inset of Fig. 2, the film also shows oscillations but the amplitude is much smaller compared to that of bulk bismuth. The initial phonon frequency and dephasing time are measured as 2.5 THz and 1 ps, respectively. These are also smaller compared to those of bulk bismuth in Fig. 1 despite the lower fluence. This is attributed to carrier confinement effects in thin films [18].

The narrow dip around 17 ps is observed only in thin films and not in bulk as shown in Figs. 1 and 2. The dip is commonly observed in the same film for several pump fluences and its depth grows with increasing fluence as shown in Fig.3. The origin of the dips is acoustic phonon pulses photogenerated in thin films. Upon photoexcitation by a femtosecond laser pulse, hot carriers are created and the lattice temperature increases quickly due to fast electron-phonon coupling. In a simplest macroscopic limit where transport of nonequilibrium carriers is ignored, the lattice temperature change (ΔT) decays exponentially with increasing depth (z) from the surface as given by

$$\Delta T(z) = \frac{F(1-R)}{C\delta}\exp\left(-\frac{z}{\delta}\right), \tag{3}$$

where F, R, C and δ are the fluence of laser pulse (J/m^2), the reflectivity, the specific heat capacity, and the optical penetration depth of bismuth, respectively [21]. For 800 nm wavelength, $\delta \cong 16$ nm. A fast rise in the lattice temperature ($\Delta T > 0$) causes a sudden volume expansion and accordingly generates an acoustic pulse. It propagates into the interior of bismuth and is reflected from or transmitted through the

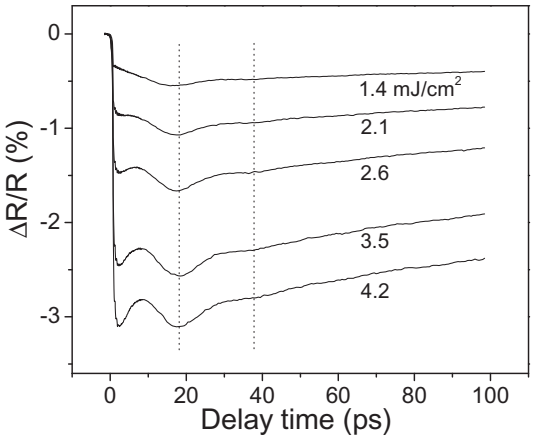

Fig. 3. Transient reflectivity change of a 25-nm thin film as a function of pump fluence from 1.4 mJ/cm^2 to 4.2 mJ/cm^2. The dashed lines assign the location of the acoustic pulses approximately as 17 ps for the first and 38 ps for the second dip, respectively.