Ultrafast critical dynamics of a ferroelectric phase transition in $Pb_{1-x}Ge_xTe$

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Transient responses of the electronic excitation and coherent soft phonon are investigated both above and below the ferroelectric phase transition temperature T_c in $Pb_{1-x}Ge_xTe$ by using an optical pump-probe technique. The coherent soft mode shows large redshift and heavily overdamped decay as the temperature approaching T_c from the low temperature side, and the soft mode disappears above T_c. The transient electronic response exhibits an abrupt change across T_c. The critical behaviors of both the phononic and electronic dynamics are interpreted by the ferroelectric phase transition.

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Until now optical rewritable memory media commonly used in commercial disks is $Ge_2Sb_2Te_3$ (GST) system,[1] in which the laser-induced phase change between crystalline and amorphous phases predominates the recording process. The rapid phase transition time in GST was found to be several nanoseconds range. On the other hand, utilizing the reversal of ferroelectric domains by ultrashort optical pulses, optical data storage or optical switching with time scale of less than 10 picoseconds has been proposed.[2] In this optical switch, one may switch the orientation of ferroelectric domains within a few phonon periods in time using femtosecond laser excitation, where the phonon displacement reaches a critical displacement of an order of 1% of the interatomic distance.[3,4]

Ferroelectric structural phase transition has been extensively investigated by monitoring the soft mode, i.e., the lowest frequency transverse optical (TO) phonon, whose zone center frequency ω_{TO} is drastically reduced toward zero near the critical point T_c.[5,6] By using frequency domain techniques, such as Raman and neutron scattering, temperature dependence of ω_{TO} has been examined,[6] although the observation of the soft mode near T_c is very difficult because of the extremely low frequency and broad linewidth of the soft mode.

Motivated by the observation of real-time dynamics of ferroelectric phase transitions, a few researches have examined femtosecond pump-probe measurements of the coherent soft modes in *order-disorder* type perovskites, such as $KNbO_3$ (Ref. 7) and $SrTiO_3$,[8] and in *displacive* type ferroelectric semiconductor GeTe.[9] The generation mechanism of the coherent soft mode in perovskites was considered to be *nonresonant* impulsive stimulated Raman scattering (NR-ISRS),[7] while in optically absorbing media, like GeTe, the coherent phonon can be generated by *resonant* impulsive stimulated Raman scattering (R-ISRS),[10] which is recognized to be the general case of the displacive excitation of coherent phonons (DECP) mechanism.[11] Note that those pump-probe measurements were not done at the higher temperature than T_c because the soft mode becomes Raman inactive due to the symmetry changes and thus it will disappear at $T > T_c$.

Femtosecond pump-probe reflectivity technique has also been applied to observing coherent phonon dynamics in GST film by Först *et al.*[12] They observed drastic changes of the coherent optical phonon properties across the phase transition temperatures, and concluded that there was a metastable phase between the crystalline and amorphous phases. Until now, however, the time-domain study of the soft mode and electronic transient responses associated with the ferroelectric phase transition at the temperatures both above and below T_c is still missing.

In this paper, we investigate both the coherent soft phonon and transient electronic response in $Pb_{1-x}Ge_xTe$ (PGT) utilizing a femtosecond optical pump-probe technique in a wide range of the lattice temperature. The ferroelectric material PGT is a narrow band-gap semiconductor ($E_g \sim 0.3$ eV) with a high carrier mobility and is useful for infrared laser and detectors.[13] It exhibits structural phase change from rhombohedrally distorted structure below T_c to cubic rocksalt structure above T_c, and T_c depends on the composition x, promising that one can control T_c by changing x.[14–16] The spectroscopic measurements revealed that the band-gap energy in PGT is very sensitive to the ferroelectric phase transition,[16] suggesting that ultrafast dynamics of photogenerated carriers exhibit significant changes across T_c.

The time-resolved reflectivity measurement was performed on a single crystal of $Pb_{1-x}Ge_xTe$ ($x=0.07$) obtained by Bridgman method. At this composition x, T_c is expected to be 160–170 K.[15] In PGT the TO phonons (A_1 and E symmetries) are soft modes, whose displacement is along the cubic (111) direction (A_1 mode) and is perpendicular to the cubic (111) direction (E mode), and those modes are responsible for the phase transition.[14] The light source used was a mode-locked Ti:sapphire laser amplified with a center wavelength of 800 nm (1.55 eV) and a pulse duration of ~150 fs. The pump and probe beams were focused on the sample to a diameter of ~70 μm and the pump fluence (F_p) was reduced

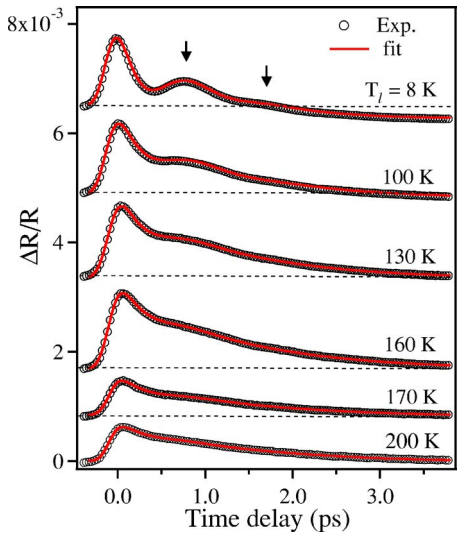

FIG. 1. (Color online) Transient reflectivity changes at the different T_l as a function of the delay time. Open circles represent experimental data, and solid curves are the fitting using Eq. (1).

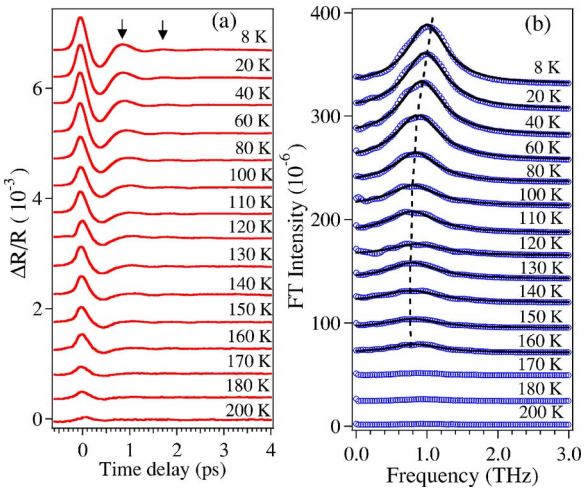

FIG. 2. (Color online) (a) Oscillatory part of the transient reflectivity at different T_l. The arrows indicate coherent soft mode. (b) The FT spectra obtained from the time-domain data in (a). Open circles represent experimental data, and solid curves are the fitting using Lorentz function. The dotted curve represents the peak frequency.

to below 0.1 mJ/cm^2 to prevent heating the sample. The probe fluence was fixed at 0.02 mJ/cm^2. The transient isotropic reflectivity change ($\Delta R/R$) was recorded to observe the coherent A_1 mode as a function of the time delay at the lattice temperature (T_l) from 8 to 200 K.

Figure 1 shows the $\Delta R/R$ signal observed at various T_l from 8 to 200 K at the constant fluence of F_p=0.1 mJ/cm^2. The fast transient signal arising from the negative time delay represents linear electronic response with a few picoseconds relaxation time,[17] whereas the adjacent dip and the following coherent oscillation (indicated by arrows in Fig. 1) is the contribution from the coherent lattice vibration. The frequency of the coherent lattice vibration is $\approx$1.0 THz (=33 cm^{-1}) at 8 K. The Raman measurements showed that the peak frequency of the A_1 mode in $Pb_{1-x}Ge_xTe$ with different composition of x=0.05 was $\approx$23 cm^{-1}.[14] The larger Ge composition of our sample (x=0.07) would result in higher frequency of the A_1 mode,[15] and in addition, we are using conventional isotropic reflectivity technique which dominates totally symmetric A_1 mode rather than the E mode.[18] Therefore, this coherent oscillation corresponds to the soft A_1 mode. It should be emphasized that the fast electronic transient drastically changes: the transient electronic amplitude suddenly decreases around 170 K as shown in Fig. 1. These features imply that the phase transition occurs between 160 and 170 K, and this value is quite close to the T_c value reported by Raman scattering at the same Ge composition.[15]

In order to subtract the transient electronic response from the time-domain data and to obtain only coherent soft phonon, we utilize the following function to fit the data:

$$\frac{\Delta R(t)}{R_0} = H(t)[Ae^{-t/\tau_A} + Be^{-t/\tau_B} + Ce^{-\gamma t}\cos(\omega t + \phi)], \quad (1)$$

where H(t) is the Heaviside function convoluted with Gaussian to account for the finite time resolution. A and B are the amplitudes, and τ_A and τ_B are the relaxation time of the fast and slow electronic responses, respectively.[19] C, γ, ω, and ϕ are, respectively, the amplitude, damping rate, frequency, and initial phase of the underdamped soft A_1 phonon. As shown in Fig. 1, Eq. (1) fits the data very well at all T_l.

Figure 2(a) shows the oscillatory part of the changes of the reflectivity, which is obtained by extracting the exponential decay term from the above fitting at various T_l from 8 to 200 K at the constant F_p=0.1 mJ/cm^2. With increasing T_l, the coherent A_1 oscillation becomes weaker and almost vanishes at $T_l \approx$ 170 K. This is explained by the fact that the A_1 mode is the soft mode, whose frequency reduces toward zero and damping becomes larger; we can detect only monocycle oscillation (the second cycle is rather weak) below T_c (=160–170 K). Figure 2(b) represents the Fourier transformed (FT) spectra obtained from the time-domain data in (a). In Fig. 2(b), at T_l=170 K, the A_1 mode almost disappears, supporting the idea that T_c is 160–170 K. The FT spectra show the decrease in the peak frequency ω and the broadening of the linewidth of the coherent A_1 mode (this corresponds to the damping rate γ) as T_l increases as shown in Fig. 3. The frequency ω gradually decreases with increasing T_l, while the damping γ increases until $T_l \sim$ 140 K. The broadening of the linewidth of the coherent phonon spectra with T_l is explained by the enhanced anharmonic phonon-phonon coupling between the soft optical phonon and acoustic phonons,[20] as observed in Bi.[21] The T_l dependence of ω just below T_c significantly deviates from the Landau's mean field theory;[22]

$$\omega = \alpha(T_c - T)^{\beta} \quad (2)$$

which describes the second-order phase transition, where, amplitude α and exponent β are the fitting parameters. As a result of the best fitting using the data at $T_l \leqslant$ 140 K, α =0.47, and β=0.14±0.02 are obtained for the fixed value of

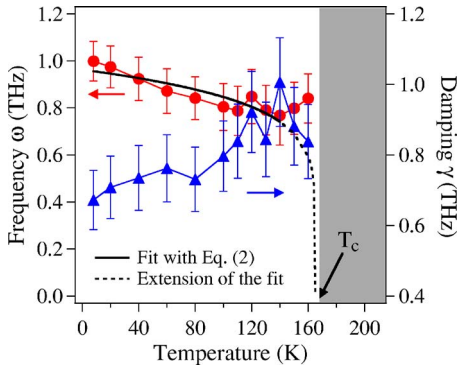

FIG. 3. (Color online) Temperature dependence of the frequency ω and the damping rate γ. The closed triangles and circles represent the experimental data. The solid curve is the fit of ω with Eq. (2) and the dotted curve represents extension of the fitting using Eq. (2) with the obtained parameters. The gray region at $T_l \geq 170$ K represents the region in which no soft mode is available.

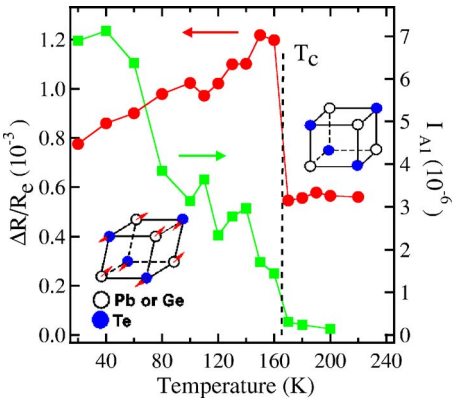

FIG. 4. (Color online) Temperature dependence of the amplitude of the electronic transient (closed circles) and that of the FT intensity of the coherent A_1 mode (closed squares) with solid guided lines. Below T_c, the arrows represent the displacement of the soft A_1 mode along (111) direction.

$T_c = 165$ K. The deviation of the experimental ω from the Landau theory near T_c suggests that the ferroelectric phase transition in PGT may be a mixture of the first-order and the second-order characters in the critical region due to the very large fluctuation amplitudes of the atoms.[23]

In Fig. 4, the amplitudes of the electronic transient and that of the coherent A_1 mode are plotted as a function of T_l in order to discuss more details of the drastic change of the electronic transient as observed in Fig. 1.[24] At $T_l \approx 165$ K the electronic amplitude $(\Delta R/R_e)$ decreases from 1.2×10^{-3} to 0.6×10^{-3}, which corresponds to $\sim 50\%$ huge relative change. Since this huge change in $\Delta R/R_e$ occurs at the same temperature of the expected T_c value, we interpret the drastic change in the fast electronic transient in terms of the result of ferroelectric phase transition. On the other hand, the A_1 mode amplitude (I_{A1}) gradually decreases with T_l, and becomes almost zero at $T_l = 170$ K, being consistent with the ferroelectric character that the intensity of the soft mode becomes weak due to strong damping below T_c and it vanishes due to the symmetry change at $T_l \geq T_c$.[6]

The structural phase transition from ferroelectric phase $(T_l < T_c)$ to paraelectric phase $(T_l > T_c)$ accompanies displacement of the ions in the unit cell and modifies the ionic polarization: the spontaneous polarization below T_c in the ferroelectric phase is large, while that above T_c in the paraelectric phase vanishes.[5] This ferroelectric phase transition then induces the changes in the electronic band structures,[16] including the position of the acceptor levels.[25] Based on the above considerations, possible origins for the drastic change in $\Delta R/R_e$ are considered as follows. First, the change in the electronic band structures would result in the change in the band gap via deformation potential (or more possibly piezoelectric effect due to spontaneous polarization) and also the change in the carrier mobility due to the electron-phonon interaction.[26] These effects would change the interband optical absorption coefficient, and thus may change the electronic response $\Delta R/R_e$. Second, the change in the position of the acceptor levels affects the free carrier concentration,[25] and this effect will result in the modification of the free carrier absorption, which contributes to the electronic response $\Delta R/R_e$. By using the huge change in the electronic transient $\Delta R/R_e$ across T_c, optical switching or optical memory using PGT can be proposed. In this case, photoinduced phase transition between ferroelectric and paraelectric phases is required. Such the photoinduced phase transition will be realized if one could precisely control both the amplitude[27,28] and the frequency[9] of the coherent soft phonon.

In summary, we have investigated ultrafast dynamics of both the coherent soft mode and the transient electronic polarization in ferroelectric semiconductor below and above T_c by using the pump-probe technique. Low frequency coherent soft mode in PGT was observed only below T_c, showing the redshift of the frequency and heavily overdamped behavior as the temperature approaches T_c. The drastic decrease in the transient electronic response was revealed across T_c, suggesting the change in the electronic band structure, including the position of the acceptor levels.

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