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Ultrafast carrier and phonon dynamics in Bi_2Se_3 crystals

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Ultrafast time-resolved differential reflectivity of Bi_2Se_3 crystals is studied using optical pump-probe spectroscopy. Three distinct relaxation processes are found to contribute to the initial transient reflectivity changes. The deduced relaxation timescale and the sign of the reflectivity change suggest that electron–phonon interactions and defect-induced charge trapping are the underlying mechanisms for the three processes. After the crystal is exposed to air, the relative strength of these processes is altered and becomes strongly dependent on the excitation photon energy. © *2010 American Institute of Physics*. [doi:10.1063/1.3513826]

Recently there has been an emerging interest in Bi-based compounds, such as $Bi_{1-x}Sb_x$, Bi_2Se_3, and Bi_2Te_3, as exemplars of a class of quantum matter known as a topological insulator.[1] Among these compound materials, Bi_2Se_3 stands out owing to its relatively simple topological surface states and its sizable bulk band gap of ~0.3 eV,[2,3] which hold promise for applications in future spintronic and quantum computational devices. Indeed, in the past year the electronic properties of Bi_2Se_3 have attracted considerable attention[4–7] as field effect transistor type devices have been demonstrated experimentally.[8–10] However, in order to implement room-temperature operation of Bi_2Se_3-based devices, it is essential to understand the dynamics of phonons and excited carriers in this material,[11] particularly the electron–electron, electron–phonon, and phonon–phonon interactions. In this letter, we report the ultrafast time-resolved optical spectroscopy study of Bi_2Se_3 crystals in both the time domain and the energy domain. Our measurements reveal three underlying relaxation processes in the transient response of Bi_2Se_3, each associated with different physical mechanisms. It is also shown that the relative strength of these processes is sensitive to air exposure of the samples. The observed charge trapping and air doping effects are likely due to the presence of Se vacancies, a major issue material scientists working to use the properties of Bi_2Se_3 will face in the near term.

The Bi_2Se_3 single crystals studied in this work were synthesized via the Bridgman method at Purdue University and Fudan University. During crystal growth, the mixture of high purity elements was first deoxidized and purified by multiple vacuum distillations, and then heated to 850–900 °C for 15 h, followed by a slow cool down under a controlled pressure of Se to compensate for possible Se vacancies. Afterwards, the samples were zone refined at a speed of 0.5–1.5 mm/hour with a linear temperature gradient set to 4–5 °C/cm, until a temperature of 670 °C was reached. The as-grown Bi_2Se_3 crystals from both groups are naturally n-doped due to remnant Se vacancies.[4] Hall measurements show typical carrier densities over 1×10^{18} cm^{-3} at ambient conditions.

In the pump-probe experiment, the transient reflectivity changes, $\Delta R/R$, are measured at room temperature by employing a Ti:sapphire laser with a repetition rate of 76 MHz. The laser is capable of producing ~150 fs-wide pulses in a wavelength range from ~720 nm (1.72 eV) to ~940 nm (1.32 eV). Cross-polarized (linear) pump and probe beams of the same wavelength are focused onto the sample in a spot ~100 μm in diameter. To avoid heating damage, the typical pump light fluence used in this work is 2.5 μJ/cm^2.

Figure 1 shows the measured $\Delta R/R$ with the pump-probe wavelength centered at 760 nm (1.63 eV) over long (main panel) and short (inset) timescales. As one can see, $\Delta R/R$ undergoes a sharp rise within ~1 ps, followed by a decay. In addition, two apparent oscillatory behaviors are superimposed on the $\Delta R/R$ profile. One appears within the initial ~15 ps with a higher frequency as evidenced in the small periodic "wiggles" in the inset to Fig. 1 while the other arrives after ~6 ps and decays in a few periods with a much lower frequency but a larger amplitude (see the main panel of Fig. 1). The low frequency oscillation has been widely

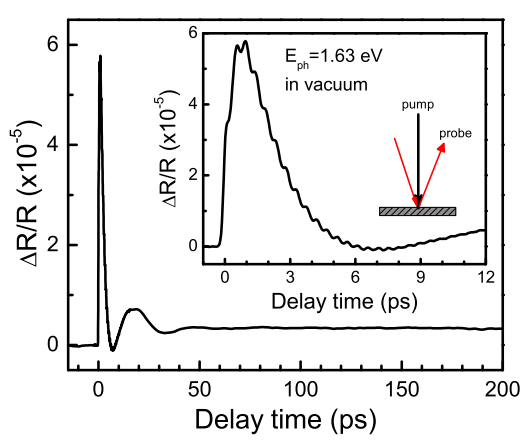

FIG. 1. (Color online) Time-resolved response of Bi_2Se_3 at room temperature for the pump-probe photon energy 1.63 eV over long (main panel) and short (inset) timescales. A schematic drawing of the measurement configuration is also shown in the inset.

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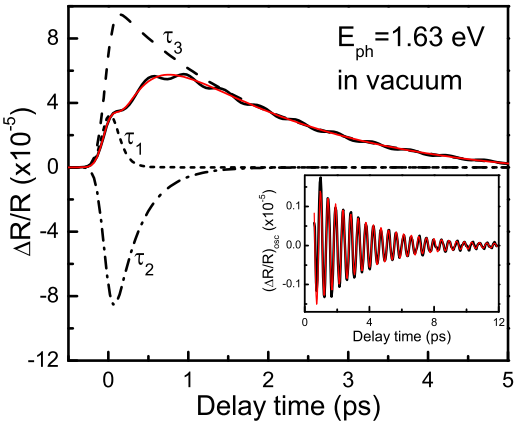

FIG. 2. (Color online) $\Delta R/R$ signal of Bi_2Se_3 as a function of delay time at E_{ph}=1.63 eV. The best fit to data (red solid line) is obtained by using a model consisting of three independent exponential relaxation processes with time constant τ_1 (short dashed line), τ_2 (dashed-dot line), and τ_3 (dashed line). Inset: Extracted oscillations from the measured $\Delta R/R$ and the best fit to data (red solid line) as an exponentially damped oscillation.

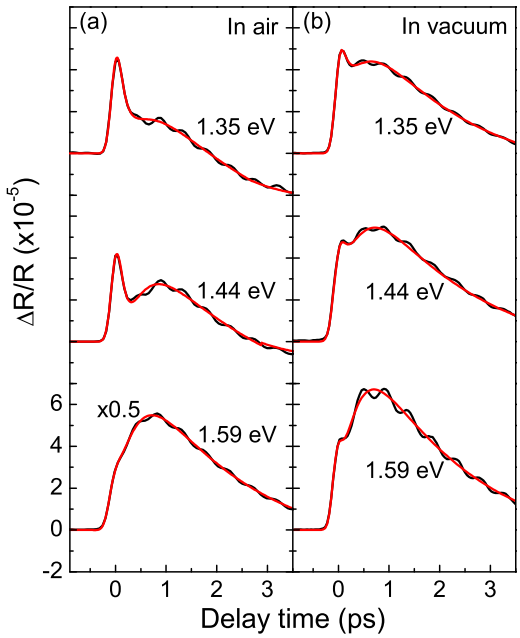

FIG. 3. (Color online) Side-by-side comparison of the $\Delta R/R$ signals of Bi_2Se_3 exposed to air and in vacuum at three different excitation photon energies. Traces are offset for clarity. The red solid lines are the best fits to data with three independent exponential relaxation processes.

observed in ultrafast time-resolved optical measurements of other systems[12] and has been attributed to coherent longitudinal acoustic phonons generated by the pump light. To study the high frequency oscillation, we first extract it by subtracting the nonoscillatory component from the differential reflectivity data, and then fit it as an exponentially damped oscillation.[13] As shown in the inset to Fig. 2, our data can be fit well by this method with a single frequency ν centered at 2.13 THz and a damping rate of $\Gamma \sim 0.33$ THz. Here the deduced ν value is consistent with the energy of the A_{1g}^1 longitudinal optical phonon in Bi_2Se_3 obtained by Raman spectroscopy[14] while the damping rate represents the timescale of the phonon–phonon interactions. Moreover, ν and Γ are found to be independent of the excitation photon energy E_{ph} within our experimental error.

Now let us discuss the non-oscillatory transient response of Bi_2Se_3 in the first few picoseconds after pumping. Figure 2 plots $\Delta R/R$ as a function of delay time measured at room temperature and E_{ph}=1.63 eV. We note that the reflectance rise time in Bi_2Se_3($\sim$1 ps) is much longer than that expected for typical semiconductors and metals ($\sim$300 fs).[15] This timescale corresponds to the delayed thermalization of the carriers via electron–electron interactions. Such a slow rise may indicate the presence of a relaxation process with a negative amplitude (A_2), as illustrated by the dashed-dot line in Fig. 2. In addition, as further evidenced in Fig. 3, two positive processes also contribute to the transient reflectivity changes, with distinctive time constant τ_1 and τ_3. Thus, to obtain the best fit to the data in Figs. 2 and 3 (the red solid lines), we employ a model consisting of three independent exponential relaxation processes.[16] The deduced time constants, $\tau_1=0.11\pm0.02$ ps, $\tau_2=0.32\pm0.03$ ps, and $\tau_3=2.3\pm0.2$ ps, are independent of the pump intensity and the excitation photon energy available with our experimental set-up.

What is the possible origin of the three relaxation processes? The first process is characterized by a fast relaxation (τ_1=110 fs), as the excited carriers lose their high excess energy rapidly through the electron–phonon (particularly electron–optical-phonon) interactions.[16–18] The third process, on the other hand, represents a relatively slow relaxation (τ_3=2.3 ps), which might be attributed to electron–acoustic-phonon interactions.[16,18] The coexistence of a subpicosecond and a few-picosecond electron–phonon relaxation processes due to different phonon modes has been reported previously, and quantitative agreement is achieved in the extracted relaxation timescales.[16,18] The second process with a negative amplitude A_2, however, is more subtle. Such a negative-amplitude process was previously observed in strongly correlated electron systems,[19] as well as in disordered low-temperature molecular-beam-epitaxy grown III–V semiconductors.[20,21] One possibility is that this process is associated with the ultrafast trapping of electrons by Se vacancies. This trapping mechanism could cause a negative change in reflectivity and limit the relaxation time to less than 1 ps,[21] in agreement with our observations.

An important material issue for Bi_2Se_3 crystals is unintentional charge doping from air, which could modify or even dominate its electronic properties.[7] To pursue this issue, we perform comparative studies of the time-resolved response of Bi_2Se_3 exposed to air and in vacuum at different excitation photon energies. To prepare an "in-vacuum" sample, we first rapidly cleave it to obtain a mirror-like surface and load it into a sealed measurement chamber within 20 s, the chamber is then pump down to $\sim 10^{-5}$ mbar in $\sim$20 mins. As shown in Fig. 3, a clear difference in $\Delta R/R$ is evident as a function of E_{ph}. Since $\tau_{1,2,3}$ exhibit almost no change when the samples are exposed to air, the observed differences are mainly from the relative changes in the amplitudes $A_{1,2,3}$. Figure 4 summarizes the E_{ph} dependence of $|A_2/A_1|$ and A_3/A_1 for the measurements in air and in vacuum. While the relative strength of the three relaxation processes in vacuum is only weakly dependent on E_{ph}, an abrupt change occurs for the samples exposed to air when $E_{ph}\sim 1.47$ eV. Air doping may raise the Fermi level in Bi_2Se_3 and affect the band bending near the crystal surface. This alters the spatial electron-hole distribution function,[22]

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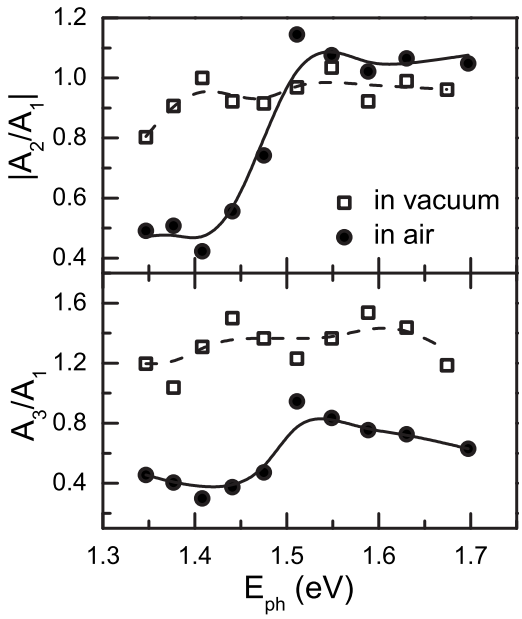

FIG. 4. $|A_2/A_1|$ and A_3/A_1 as a function of E_{ph} for Bi_2Se_3 crystals exposed to air (filled dots) and in vacuum (open squares). Solid and dashed lines are the guides to the eye.

which impacts the ultrafast dynamics of the material. Further experimental and theoretical work is needed to understand our observation. Finally, we find that the extracted A_{1g}^1 optical phonon energy (ν=2.13 THz) from the in-vacuum samples is slightly, but consistently, lower than that obtained for the samples exposed to air (2.15 THz) at all E_{ph} measured. Given that the theoretical value of this energy is 2.03 THz for a perfect Bi_2Se_3 crystal,[14] Se vacancies may also underlie the observed difference.

In conclusion, we have performed ultrafast time-resolved optical spectroscopy measurements on Bi_2Se_3 crystals and observed the contributions from three exponential relaxation processes with distinctive time constants. The origin of the three processes can be attributed to electron–phonon interactions and defect-induced charge trapping. Our work also shows that air exposure can significantly affect the carrier and phonon dynamics in Bi_2Se_3 crystals by altering the relative strength of these three processes.

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