Ultrafast light-induced Coherent Optical and Acoustic Phonons in few Quintuple Layers of Topological Insulators Bi$_2$Te$_3$.

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Ultrafast lattice dynamics of few quintuple layers of topological insulator (TI) Bi$_2$Te$_3$ is studied with time-resolved optical pump-probe spectroscopy. Both optical and acoustic phonons are photogenerated and detected. Contrary to previous studies performed on confined systems like thin films, we show that there is no existing restriction to photogenerate the A1g(I) coherent longitudinal optical phonon in confined Bi$_2$Te$_3$ and that the photoinduced stress appears to be efficient even for nanostructures containing 10 quintuple layers (QLs). Remarkably, we also show that whatever the nanostructure of the film (single or polycrystalline arrangement), the A1g(I) optical phonon features are similar while clear differences exist between coherent acoustic phonons spectra. These latter spectra provide direct informations on the elastic properties of these few QLs assemblies.

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Topological insulators (TI) are a new electronic state in condensed matter with semiconducting bulk solid while conducting on the surface. Moreover, the surface Dirac electronic states exhibit natural spin-polarized current and appear to be robust regarding to backward non-magnetic scattering which is unique and heralds possible very attractive applications for next generation spintronic devices [1]. Beside the crucial spin-orbit coupling effect on the features of surface and bulk electrons dynamics [2] and the features of confined electrons in 2D TIs [3], the large electron-phonon coupling mechanisms is the object of active discussions and appear to play a peculiar role in the transport properties of the TI. This is also of prime importance for the thermoelectric properties for this class of materials. Among dominant scattering mechanisms of electrons by phonons, it has been observed recently in Bi$_2$Se$_3$ (BS) that the longitudinal optical phonon (LO) with an energy of 8 meV plays a crucial role in the surface electrons scattering and sets a limit in the conductivity [4]. This LO mode is the Raman active mode A1g(I) (2.13 THz in Bi$_2$Se$_3$ [5] and 1.85 THz in Bi$_2$Te$_3$[6]). Additionally, some theoretical reports suggest some driving contributions of this electron-phonon coupling in the appearance of the topological state [7]. Witnessing probably the large electron-phonon coupling, it is remarkable that this A1g(I) longitudinal optical phonon is the one which is efficiently photoexcited by a femtosecond laser optical pulse in bulk Bi$_2$Te$_3$[8,9] or Bi$_2$Se$_3$[10]. However, Wang et al [11] recently reported that the large confinement of light-induced hot electrons in Bi$_2$Te$_3$ films (BT) as thin as 5 to 10 nm cannot lead to sufficient large photoinduced force to induce lattice displacement. Knowing if hot electrons couple differently in bulk BT than in thin films made of few BT quintuple layers (QLs shown in Fig. 1) is a fundamental question as well as crucial for applications.

In this Letter, femtosecond pump-probe spectroscopy has been used to demonstrate that contrary to what has been previously proposed, it is actually possible to generate coherent optical phonons in BT nanostructures and a discussion of the driving force is developed. These observations are then a confirmation of the strong coupling of hot electrons with the LO mode that plays a particular role in the transport properties [4]. Furthermore, the mechanism of excitation is remarkably efficient whatever the nanostructure of the system is (single crystalline film, polycrystalline film or crystallized islands). Additionally to optical phonons, coherent acoustic phonons have also been laser generated and detected with this technique. The clear observation of coherent acoustic phonons provides rich informations about the electron-acoustic phonon coupling mechanism as well as about the sound velocity (i.e. elastic modulus) along the [001] direction, which is the direction along which the QLs are connected with Van der Waals bonds (Fig. 1(c)).

All studied films of Bi$_2$Te$_y$ with various compositions

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have been grown on Si(100) or mica (muscovite) substrates by thermal evaporation with the use of Molecular Beam Epitaxy (MBE) system from Prevac. The growth was performed in the co-deposition mode. The electronic and crystallographic characterizations were carried out in situ with the use of x-ray photoelectron spectroscopy (XPS), the reflection high energy electron diffraction (RHEED), the low energy electron diffraction (LEED) and the atomic force microscopy (AFM). Additionally, the ex-situ x-ray reflectivity (XRR) measurements were performed. The Fig. 1 show some characteristics. Preparation of the Si substrate and details of the films grown on Si (samples A and B) are given in our earlier work [12]. The film C was deposited on the (110) freshly cleaved Muscovite mica substrate (Ted Pella, Inc.) which was then annealed at 230°C in the MBE chamber by 1.5 hour. For both types of the substrate it was kept at 130°C during the deposition. The deposition rate has been controlled by the quartz crystal micro balance. The film A shows a polycrystalline structure while for the sample B the well visible streaks in the RHEED pattern indicate to at least partial long range atomic order on the surface (Fig. 1(a)). For that sample we found no oscillations in the XRR results (Fig. 1(b)) which can be related with a large roughness detected in the AFM tests where the value of RMS up to 5-6 nm (per 1 μm²) was obtained. This film is then more arranged according to some crystallized islands induced by the growing process. It is worth to mention that the value of RMS for the substrates was lower than 1 nm. For the film C deposited on mica, the electron diffraction experiments (RHEED in Fig. 1(a) and LEED in Fig. 1(d)) show that this film is single crystalline. The thickness of the films was derived from the quartz crystal micro balance and XRR data. For the sample C grown on mica a good agreement was found between the data obtained from two methods (about 15 nm). For the sample A, the BT layer has a thickness close to 10 nm but fitting of the XRR data indicates the presence of an overlayer of lower density, probably tellurium oxide, and thickness of about 7 nm. The upper layer is formed probably by Te and tellurium oxides. The XPS analysis (not shown) allowed to determine the atomic composition and chemical state of the components. All the films appear to be free of any contamination and the atomic composition characterized by the Bi/Te ratio varied from 34/66 (film A), through 44/56 (film B) to 46/54 (film C). The analysis of the Bi and Te most prominent photoemission lines showed for films B and C only one chemical state with the positions of the lines characteristic for Bi₂Te₃ [12]. For the sample A an additional line in the Te 3d spectrum was found which could be assigned to pure Te. The Bi₂Te₃ system is known to form many layered nanostructures especially for the compositions y/x < 3/2. The stacking sequence of the quintuple layers (QL), characteristic for Bi₂Te₃ and additional layers of Bi leads to formation of many structures [13].

The pump probe technique used here is based on a 80 MHz repetition rate Ti:sapphire femtosecond laser. The beam is split with a polarizing beam splitter into a pump and a probe beams. The probe beam is introduced in an synchronously pumped OPO that allows to tune the wavelength and finally permit to do two-color pump-probe experiments (pump and probe linearly and circularly polarized respectively). The transient optical reflectivity signals are obtained thanks to a mechanical stage delay (delay line) which enables a controlled arrival time of the probe beam regarding to the excitation of the pump one. The experiments were conducted with the front-front configuration (Fig. 2(a)) with incident pump and probe beams perpendicular to the surface as shown in Fig. 1(c). In our experiments, the pump wavelength was fixed at 830 nm (1.495 eV) and the probe fixed at 582 nm (2.13 eV) with a corresponding absorption length of 8 nm and 10 nm [13]. The pump and probe are focused with a microscope objective providing a typical spot radius of 5 micrometers. Additional details of the setup can be found in previous recent articles [15].

The time resolved optical reflectivity obtained for the 3 samples are shown in Fig. 2(a). The signals are composed of different contributions. A first sharp variation of the optical reflectivity R corresponds to the electronic excitation by the pump light with a following decay of the out-of-equilibrium carriers. Within the first picoseconds, several oscillatory components appear. The high frequency component, as shown in Fig. 2(b), is the sig-
crystallographic order. All these observations have been done for the investigated pump fluence range of 0.005-0.1 mJ.cm$^{-2}$. We actually know how sensitive the optical phonons are to the unit cell forces distribution. As a matter of fact, this FFT features is thus a direct proof that the detected coherent optical phonon A1g(I) comes from the right BT structure with the right chemical environment in agreement with our XPS analysis. Consequently, the slight excess of Bi in film B and C and the excess of Te in film A might be isolated in the structure within probably interlayers as already suggested by XRR for the film A and probably within an interlayer between QL for Bi as suggested in the literature [13].

The efficient generation of the A1g(I) mode even with ten QLs has to be discussed. Despite the A1g(I) mode does not have the largest Raman cross section [6, 11], the ultrafast generation of this longitudinal optical mode is actually efficient. Furthermore, it is important to underline that despite the random distribution of the BT grains in the films A or the existence of crystallized islands (film B) (see REED images in Fig. 1(a)), the generation/detection of the A1g(I) mode is still efficient. Then we believe that the emission is a result of a large and local coupling between hot electrons and the A1g(I) mode. Recent calculations have shown that the isotropic electron/optical phonon deformation potential actually is as large as $d_{e-op} \approx 40 \text{eV}$ [16]. Following the convention used in semiconductors physics [17] (but different expressions of the electronic pressure containing the same physics also exist [18]), the associated photoinduced stress driven by deformation potential can be written as $\sigma_{e-op} = -d_{e-op} N$ where N is the photoexcited carriers concentration. Since $d_{e-op}$ is positive this indicates first that in the early stage of excitation there is an expansion of the BT lattice. With a concentration of photoexcited carriers of $N \sim 0.5 \times 10^{27} \text{m}^{-3}$ (typically that achieved with our maximum absorbed pump fluence of 0.1mJ.cm$^{-2}$) the photoinduced stress becomes as large as $\sigma_{e-op} \sim -3 \text{ GPa}$. This value is in accordance with the estimate of Wang et al done following the Fermi pressure approach [11]. It is to be mentioned that this electron-optical deformation potential stress is roughly one order larger than the polarization stress (electrostriction) previously estimated [11]. As a consequence this electron-optical deformation potential mechanism is likely the driving mechanism for coherent LO excitation and the gradient of this stress which is proportional to the induced force is intrinsically dependent on the exponential decay of pump light absorption that does not depend on the thickness of the system. The gradient can of course be smeared because of hot electrons diffusion, but we think that this diffusion should be somehow limited within a QL. It is then interesting to discuss that LO excitation in the real space and in that particular situation. If we consider, as a first approximation, that each QL are nearly isolated (or poorly connected, i.e. weak electron wavefunction overlapping) due

Figure 2: (color online) (a) Time resolved optical reflectivity obtained for Bi$_2$Te$_3$ thin films deposited on various substrates: film A, B and C (see text for details about samples). The curves have been normalized to the largest magnitude point for clarity. (b) A1g(I) optical phonon signals. (c) corresponding Fast Fourier Transform (FFT) of curves shown in (b).
The ultrafast light-induced coherent acoustic phonons (THz) that has been observed in bulk BT \cite{6, 8, 9}. The analysis of the photo-induced coherent acoustic phonons signals extracted from the transient optical reflectivity signals. For clarity, the curves have been scaled in amplitude. The dotted lines are numerical adjustments (see the text for more details). (d)-(e)-(f) corresponding coherent acoustic phonons spectra obtained by a Fast Fourier Transform (FFT).

Figure 3: (color online) (a)-(b)-(c) Coherent acoustic phonons signals extracted from the transient optical reflectivity signals. For clarity, the curves have been scaled in amplitude. The dotted lines are numerical adjustments (see the text for more details). (d)-(e)-(f) corresponding coherent acoustic phonons spectra obtained by a Fast Fourier Transform (FFT).

The oscillatory components detected for film C actually are not explain of course the generation of the A1g(II) (3.8 GHz and \(f_n = 115 \text{ GHz} \) where \(\lambda = 582 \text{ nm}, n = 4 \) [22], in agreement with the observations (Fig. 3(e)). A numerical adjustment with a damped cosine function gives \(\Delta R_{\text{ac}}(C) \sim \cos(2\pi f_B t + \phi_B) e^{-t/\tau_B} \) with \(f_B = 111 \text{ GHz} \) and \(\tau_B = 24 \text{ ps} \) (dotted line in Fig. 3(b)). On the other hand, for the film C, the mode that is detected is not that of Brillouin nature in the mica substrate (a similar estimate shows that the Brillouin frequency is expected at \(f_{\text{mica}} = 2n_{\text{mica}} V_{\text{mica}} / \lambda = 27 \text{ GHz} \), with \(n_{\text{mica}} = 1.6 \) [24]). The oscillatory components detected for film C actually correspond to a mechanical resonance eigenmodes due to the confinement of acoustic phonons (\(R_{\text{ac}} \sim 0.17 \)).

The FFT shown in Fig. 3(f) evidences two modes (\(f_1 \approx 80 \text{ GHz} \) and \(f_2 \approx 160 \text{ GHz} \) with \(f_2 \sim 2 f_1 \)). This is the sequence of the expected harmonics of our resonator whose frequency is given by \(f_n = n V_C / 2C \) with \(n = 1, 2, 3, \ldots \) and where \(V_C \) is the longitudinal sound velocity of the BT film and \(H_C \) its thickness. A numerical adjustment with only the fundamental mode gives \(\Delta R_{\text{ac}}(C) \sim \cos(2\pi f_1 t + \phi_C) e^{-t/\tau_C} \) with \(\tau_C = 14 \text{ ps} \) (Fig. 3(c)). Thanks to this resonator model, we immediately obtain \(V_C = 2460 \text{ m.s}^{-1} \) which is consistent with theoretical estimates in bulk BT (~2300 m.s\(^{-1}\)) \cite{25} and with previous estimates obtained in pump-probe experiments carried on Bi\(_2\)Te\(_3\)/Sb\(_2\)Te\(_3\) superlattice (~2600 m.s\(^{-1}\)) \cite{21}. Considering the mass density of the stoichiometric BT film \(\rho = 7642 \text{ kg.m}^{-3} \), this leads to an elastic constant \(C_{33} = \rho \times V^2 \approx 36-46 \text{ GPa} \) also in accordance with recent calculations \cite{10}. Finally, according to this model, and because film A was grown on silicon too, we should observe only Brillouin mode in the silicon substrate. The spectrum in Fig. 3(d) shows a small Brillouin signal in Si with additional modes not resolved yet. An numerical adjustment (Fig. 3(a)) has been done with two damped cosine (frequencies indicated by vertical dotted lines in Fig. 3(d)) and hardly reproduces the experimental sig-
nal. Because of complex interfaces and multilayers composition as well as polycrystalline texture (the relevant sound velocity is probably a mixture of out-of-plane and in-plane sound velocity), this spectrum requires further investigations which are not the topic of the present paper.

It is necessary now to discuss the physical origin of the acoustic phonon emission. A rapid estimate shows that the driving mechanism of coherent acoustic phonon generation is of electronic nature. The evaluation of the photoinduced thermoelastic stress ($\sigma_{ph}$), due to a rapid lattice heating that follows the electronic decay, can be accounted following the standard model \[26\]. We find $\sigma_{ph} = -3\beta B \Delta T \approx 0.1-0.2$ GPa with $B \approx 37$ GPa the bulk modulus \[16\], $\beta=2.10^{-5}$K$^{-1}$ \[27\] the out-of-plane BT thermal expansion and $\Delta T = \Delta E/C_L \approx 60$ K the lattice heating where $C_L=1.5.10^6$ J.m$^{-3}$.K$^{-1}$ \[28\] is the BT lattice heat capacity and $\Delta E=N \times 1.495$ eV$\cdot$10$^8$ J.m$^{-3}$ the total laser pump energy per unit of volume absorbed by the material (this maximum temperature increase is obtained with a fluence of 0.1 mJ.cm$^{-2}$ and without considering the heat conductivity at film/substrate interface). This thermoelastic stress is much smaller than the electron-acoustic phonon deformation potential stress given by \[26 \, 29\] $\sigma_{e-ac} \approx -a_{e-ac} N=2.5$ GPa, were $a_{e-ac}=35$ eV \[10\] is the electron/acoustic deformation potential (four times larger than that in GaAs \[17\]) and $N \sim 0.5.10^{27}$ m$^{-3}$.

Finally, probing the assemblies of QLs with the coherent acoustic phonons could provide new insights on the QLs Van der Waals interactions. Usually in Van der Waals bonded solids \[20\] the macroscopic/mesoscopic elastic modulus is driven by the Van der Waals contacts, as a matter of fact if we consider it is the case for the 1D assemblies of QLs, then we obtain a Te-Te Van der Waals force elastic constant of the order of $C_{V,AW} \sim C_{33} \times a_{Te-Te} \sim 12-16$ N.m$^{-1}$, where the Te-Te distance between two QL is $a_{Te-Te}=0.364$ nm \[30\]. These estimates are 1.5 to 2 times larger than previous estimates obtained thanks to macroscopic estimate \[30\]. As noticed previously, we have to keep in mind that these constants $C_{V,AW}$ remains ten times larger than real Van der Waals interactions existing in rare gas solids \[16\].

As a conclusion, thanks to a complete ultrafast two-colors pump-probe investigation performed on various films grown by MBE, we show that it is possible to excite coherent Al$_{13}$I(1) LO mode in thin films containing ten QLs and no restriction appears. It is remarkable that the Al$_{13}$I(1) LO phonon dynamics is nearly not disturbed by the nanostructure of the films. Our estimates show that the LO deformation potential photoinduced stress appears to be as high as -3 GPa for a photoexcited carriers concentration of $N \sim 0.5.10^{27}$ m$^{-3}$ which is quite large and likely to launch the atomic motion of Al$_{13}$I(1) mode. Our results confirm the strong coupling of hot electrons with the LO mode that plays a particular role in the transport properties \[4\]. We also show, before the LO mode decay, the birth of coherent acoustic phonons whose spectrum drastically depends on the films nanostructure contrary to that of the LO mode. The generation mechanism of these acoustic phonons is also attributed to the deformation potential mechanism. Finally, the measurement of the time of flight (sound velocity) of these longitudinal acoustic phonons in the single crystalline film (C) provides an evaluation of the out-of-plane elastic modulus (36-46 GPa) of these assemblies of QLs. As a final perspective, the coexistence of both optical and acoustic phonons could make these systems as a rich playground for studying the LO-LA anharmonic couplings.

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