Electron-hole asymmetry in the electron-phonon coupling in top-gated phosphorene transistor

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Abstract

Using in situ Raman scattering from phosphorene channel in an electrochemically top-gated field effect transistor, we show that phonons with $A_g$ symmetry depend much more strongly on concentration of electrons than that of holes, whereas phonons with $B_g$ symmetry are insensitive to doping. With first-principles theoretical analysis, we show that the observed electron–hole asymmetry arises from the radically different constitution of its conduction and valence bands involving $\pi$ and $\sigma$ bonding states respectively, whose symmetry permits coupling with only the phonons that preserve the lattice symmetry. Thus, Raman spectroscopy is a non-invasive tool for measuring electron concentration in phosphorene-based nanoelectronic devices.

1. Introduction

Few layer black phosphorus (BP) is a relatively new member of the family of 2D nanosystems with unique properties. Unlike gapless graphene, black phosphorus is a direct band gap material with gap ranging from 0.3 eV in bulk to 2 eV in monolayer, covering a wide range of the electromagnetic spectrum. This is distinctive from transition metal dichalcogenides (TMD) which exhibit a direct band gap of $\sim$1 to 2 eV only in their monolayer form. The narrow band gap of BP (in few layer form) bridges the gap between the zero gap graphene and large band gap TMDs, thus making BP a suitable candidate for near and mid infrared optics [8]. For possible applications in electronic devices, black phosphorus offers a good possibility with mobility of $\sim$1000 cm$^2$/V-sec at room temperature and on-off ratio of $\sim$10$^5$ with excellent current saturation characteristics [9].

Phosphorene (as monolayer BP is referred to) lattice structure is a 2-D puckered network (figure 1(a)) formed by phosphorus atoms with each atom covalently bonded to three neighbouring atoms. A unique feature of black phosphorus is its in-plane anisotropy. The puckered orthorhombic crystal structure of BP gives rise to asymmetric electronic and phonon dispersion relations: electronic bands are more dispersive along the armchair direction than along the zigzag direction, whereas the phonon dispersion is more dispersive along the zigzag direction [2, 10, 11]. Along the armchair direction, carriers are more mobile, as the effective mass along the zigzag direction is about 10 times larger than that of the armchair direction [12, 13]. Similarly, the Hall mobility along the armchair direction is 1.8 times the mobility along the zigzag direction [4]. Single and few layer BP absorb light (ranging from infrared to part of the visible spectrum) polarized along the armchair axis, whereas they are transparent for polarization along the zigzag direction [2]. Recent photoluminescence measurements on the monolayer show the existence of anisotropic excitons [5, 6, 14, 15].

For 2-D systems like graphene, electron-phonon coupling (EPC) plays a dominant role in the resistivity behaviour at high carrier densities [16]. For almost a decade, since the emergence of graphene [17, 18], Raman spectroscopy has scored over other techniques...
as an indispensable analytical tool for estimation of the number of layers in 2D materials like graphene and TMDs [19–23], to characterize EPC in 2-D graphene [24–26] and evaluating thermal conductivity of graphene layers [27–29] among various other properties. In-situ Raman scattering from monolayer MoS2 transistor have revealed the effect of doping on the EPC strength [30].

For BP too, Raman spectroscopy has shown its potential as a successful and noninvasive technique to determine the crystal orientation of black phosphorus flakes [4, 5, 31, 32]. Recently Luo et al [33] have reported anisotropic thermal conductivity using Raman spectroscopy: the thermal conductivity along the zigzag orientation exceeding that along the armchair direction by a factor of 2. The degradation of BP flakes due to environmental aspects have been probed by Raman spectroscopy [34]. With four atoms in the unit cell, out of nine optical modes, phosphorene has six Raman active modes, out of which three prominent modes with irreducible representations $A_g^1, A_g^2$ and $B_{2g}$ are observed in back scattering geometry. The eigen-vectors of these modes reveal that (figure 1(c)) $A_g^1$ mode involves out of plane displacements of atoms, while the atomic motions involved in $A_g^2$ and $B_{2g}$ modes are along armchair and zigzag directions, respectively.

We identify and quantify the effects of doping on the Raman active phonons in phosphorene, revealing characteristic EPC. While $A_g^1$ and $A_g^2$ phonons are affected by the doping, $B_{2g}$ mode is not. Further $A_g^1, A_g^2$ modes are soften and their linewidths broaden with electron doping while remaining unaffected by holes. Experimental results are supported by first-principle density functional theory (DFT) calculations, which show an enhanced (reduced) EPC for $A_g^1$ and $A_g^2$ modes with electron (hole) doping. We note that this is consistent with recent reports, [35, 36] which suggest a possibility of phosphorene to be a BCS superconductor by virtue of its enhanced EPC at high concentration of electron doping and strain.

![Figure 1](image-url), showing the crystal structure of monolayer BP showing the armchair (ac) and zigzag (zz) directions. (b) A schematic of the experimental set-up, with inset showing optical image of the BP flake and the monolayer region is marked by a dashed line. (c) Raman and (d) photoluminescence spectra recorded from the area dashed line. Laser wavelength used to record spectra is 532 nm. Inset of (c) shows the atomic displacements in normal modes. (e) Transport characteristics of the BP device.
2. Experimental results and discussions

Black phosphorus flakes were exfoliated from its single crystal (M/s Smart Elements), and transferred on to a 300 nm SiO₂ grown thermally on a heavily doped Si (M/s Nova Electronic Materials). Immediately after exfoliation, the substrate was coated with a bilayer resist consisting of PMMA 450 K/PMMA 950 K to avoid degradation of black phosphorus flakes [34]. After careful observation under a microscope, flakes were selected and photoluminescence (PL) measurement were done to confirm the layer thickness. Figure 1(b) shows the optical image of the selected flake. Raman spectrum showing the characteristic modes (namely A₁g, B₂g and A₄g ) and PL, recorded from the area marked by dashed line (figure 1(b)) are shown in figure 1(c) and d respectively. The observed PL peak at ∼1.53 eV confirms the marked portion to be a single layer phosphorene [4]. Source, drain and gate electrodes were fabricated by e-beam lithography followed by thermal evaporation of 5 nm/70 nm of Cr/Au and lift-off in acetone. A transparent solid polymer electrolyte gate consisting of lithium perchlorate (LiClO₄):polyethylene oxide (PEO) in the weight ratio of 1:8 is immediately drop casted to prevent the flake exposure. Due to the nanometer thick (∼2 nm) Debye layer, this polymer electrolyte enables doping with higher carrier concentration (almost by an order of magnitude) as compared to 300 nm oxide gating [26]. Confocal Raman and PL measurements using 532 nm excitation laser are carried out at room temperature using Labram HR-800 coupled with a Peltier cooled CCD and a spectrometer with 1800 lines/mm grating. Spectra are recorded using a long working distance 50X objective with numerical aperture 0.45. Spectra shown in figure 2 were acquired for 10 seconds using a laser power of ∼300 µW. Electrical measurements are done using Keithley 2400 source meters. Figure 1(b) shows the schematic of the experimental set up and the inset shows the device. The device transfer characteristic is shown in figure 1(e) displaying an on-off ratio of ∼10⁸ and a field effect mobility ∼100 cm²/V·sec and ∼35 cm²/V·sec for holes and electrons respectively. Similar asymmetric transfer characteristic curves were reported for the BP field effect transistors [9, 37–39]. In order to convert the applied gate voltage to carrier concentration n, we have used the standard MOSFET expression n = C_G (V_G - V_T), where C_G and V_T are top gate capacitance, applied top gate voltage and threshold voltage respectively, and C_G is taken to be 1.5µF cm⁻² [40]. It may be noted that the threshold voltage could be different for an isolated monolayer device and can introduce some errors in estimating n. However, the qualitative picture and the interpretation of the results would remain unaffected.

Figure 2 shows the evolution of the Raman modes of phosphorene as a function of gate voltage V_G. The peak positions and the full width at half maximum (FWHM) are obtained by fitting Lorentzian function (solid lines in figure 2) to the spectra. The changes in phonon energy ∆ω = ω(n ≠ 0) - ω (n = 0) are depicted in figures 3(a), (b) and (c). It can be seen that phonon softening is observed only for the A₁g and A₄g modes for electron doping (figures 3(a), (b)). Hole doping has no effect on the phonon frequencies. As can be seen in figures 3(c), the B₂g mode is not affected by either electron or hole doping. Figures 3(d)–(f) show FWHM of the three modes. The FWHM of A₁g and A₄g modes increase for the electron doping and do not change for the hole doping. The B₂g linewidth does not show any significant doping dependence. Similar phonon and linewidth trends are observed for multilayer BP device (see supplementary information). We will now compare our results with the DFT calculations.

3. Theoretical calculations

Our first-principles calculations are based on density functional theory as implemented in Quantum ESPRESSO package, [41] and norm-conserving pseudopotentials [42, 43] to model the interaction between valence electrons and ionic cores. The exchange-correlation energy functional is treated within a Local Density Approximation (LDA) with a parametrized form of Perdew and Zunger [44]. We use an energy cutoff of 60 Ry to truncate plane wave basis used in representing Kohn-Sham wave functions, and an energy cutoff of 240 Ry to represent charge density. Structures are relaxed till the Hellman–Feynman force on each atom is less than 0.03 eV/Å. We have used a periodic supercell to simulate a phosphorene sheet, with a vacuum of 15 Å (along y-direction) to separate its adjacent periodic images. Integrations over the Brillouin Zone (BZ) are sampled on 12 × 1 × 9 and 48 × 1 × 36 uniform meshes of k-points in the calculation of total energy and electron-phonon coupling respectively. For a few concentrations of hole doping (1.3 × 10¹³ cm⁻² and 1.8 × 10¹³ cm⁻²), we used 72 × 1 × 54 uniform mesh of k-points in the determination of electron-phonon coupling to ensure convergence.

Electronic structure of phosphorene (single layer BP) determined from our first-principles calculations exhibits a direct band gap of 0.89 eV (figure 4(a)) at the Γ point, in good agreement with earlier theoretical results [1]. We note that the electronic structure is remarkably different along zigzag (ΓX) and armchair (ΓZ) directions: linear dispersion along the armchair (ac) and parabolic dispersion along zigzag (zz) directions. Electronic states at conduction band minimum (CBM) and valence band maximum (VBM) at Γ point consist of pₓ orbitals of phosphorous (figure 4(b)). We note that symmetries of the wavefunctions at CBM and VBM are distinct.
We have simulated carrier (electron and hole) doping in phosphorene by adding a small fraction of electrons/holes (according to doping concentration) to the unit cell. From the changes in frequencies of the $A_{1g}^1$ and $A_{2g}^2$ modes (figures 3(g)–(i)), it is clear that $A_{1g}^1$ and $A_{2g}^2$ modes soften significantly with electron doping ($A_{1g}^1 \sim 3$ cm$^{-1}$ and $A_{2g}^2 \sim 2$ cm$^{-1}$ at $1.8 \times 10^{13}$ cm$^{-2}$) as compared to insignificant change with hole doping. In contrast, $B_{2g}$ is much less affected by doping. These results are in qualitative agreement with our experimental observations (see figures 3(a)–(c)). To understand these trends, we systematically determined electron-phonon coupling with carrier doping.

The electron–phonon coupling (EPC) of a phonon mode $\nu$ at wavevector $q$ (frequency $\omega$) is [30, 45]

$$\lambda_{\nu q} = \frac{2}{\hbar \omega_{\nu q} N(\epsilon_F)} \sum_{ij} |S_{ik+qj}^{\nu q}|^2 \times \delta(\epsilon_{k+qj} - \epsilon_F) \delta(\epsilon_{kj} - \epsilon_F),$$

where $N(\epsilon_F)$ is the density of states at Fermi energy. The electron-phonon coupling matrix element is

$$S_{ik+qj}^{\nu q} = \left( \frac{\hbar}{2M_0} \right)^{\frac{1}{2}} \langle \psi_{i+qj} | \Delta V_{\nu q} | \psi_{kj} \rangle,$$

where $\psi_{kj}$ is electronic wavefunction of $j$th band at wavevector $k$, $M$ is the effective mass associated with the phonon, and $\Delta V_{\nu q} = \frac{\partial V}{\partial q_{\nu}}$ is the change in the self-consistent potential associated with atomic displacements of phonon $q_{\nu}$.

From calculated $\lambda$ for all the Raman modes as a function of carrier concentration (figures 3(j)–(l)), it is seen that (a) $A_{1g}^1$ and $A_{2g}^2$ modes couple more strongly with the carriers than the $B_{2g}$ mode, and (b) all the modes couple more strongly with electrons than with holes. These results are indeed consistent with our experiments. Strong coupling of the $A_{1g}^1$ mode with electrons can be understood from symmetry arguments. $A_{1g}$ modes (see figure 1(c)) have the full symmetry of the lattice, (i.e. distortion along these modes does not break the symmetry of the lattice) and hence all the electronic states ($i = j$) have a non-zero matrix element (equation 2). Using the same argument, matrix element ($i = j$ in equation 2) vanishes for the $B_{2g}$ mode which breaks the symmetry of the lattice ($B_{2g}$ mode is orthogonal to the $A_{1g}$ modes). We do find an asymmetry in the EPC with hole and electron doping: EPC increases with increasing concentration of (see figure 4(c)), which lead to contrasting effects of electron and hole doping on the electron-phonon coupling (to be explained later).

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where $N(\epsilon_F)$ is the density of states at Fermi energy. The electron-phonon coupling matrix element is

$$S_{ik+qj}^{\nu q} = \left( \frac{\hbar}{2M_0} \right)^{\frac{1}{2}} \langle \psi_{i+qj} | \Delta V_{\nu q} | \psi_{kj} \rangle,$$
electron doping while it decreases with increasing hole concentration. This asymmetry follows from the symmetry of the electronic wavefunctions at the VBM and CBM at $\Gamma$ point. At the VBM, wavefunction is even under mirror reflection, while it is odd at the CBM. As a result, the magnitude as well as the sign of the coupling matrix \((\text{equation 2})\) can be different for electron and hole doping. It is evident in figures 3(g)–(h) and 3(j)–(k) that $A_{1g}$ mode is affected more strongly by electron doping than the hole doping. In contrast, $A_{2g}$ mode is affected by both electron as well as by hole doping, though the effect is stronger for electrons. To understand this, we obtained the energies of VBM and CBM at $\Gamma$ point as a function of structural distortions obtained by freezing the eigenvectors of these modes. It is evident (figure 5) that the CBM varies more strongly than the VBM with $A_{1g}$ mode, whereas freezing of $A_{2g}$ mode (figure 5) affects both VBM and CBM significantly, though its effect on the CBM is slightly stronger than that on the VBM. Therefore, the difference in the dependence of $A_{1g}$ and $A_{2g}$ modes on electron and hole doping originates from the matrix element $\langle \psi_{k_i} | \Delta V_{ij} | \psi_{k_j} \rangle$. The non-monotonous evolution of CBM as a function of distortion for $A_{1g}$ mode is further explained in the supplementary material.

We note that low levels of doping results in changes in the population of only the states that have energies close to the VBM and CBM at $\Gamma$ point. Thus, the states lining the band-gap along $\Gamma$–X direction are more relevant to our experiments than the ones along...
Our work demonstrates a phosphorene-based field effect transistor (P-FET) with a high on-off ratio, in which the carrier concentration in phosphorene channel can be effectively controlled by the top-gate electrode. We have shown how in-situ Raman spectroscopy can be a powerful tool in assessing the nature and concentration of carriers in the channel of P-FET. While the anisotropy in its properties is expected from its structural symmetry, we uncover a remarkable electron–hole asymmetry in the coupling between its charge carriers and phonons: phonons with $A_g$ symmetry couple much more strongly with electrons than with holes. Further, only the phonons preserving the symmetry of the lattice couple strongly with electrons. Our first-principles calculations reveal that the electron–hole asymmetry arises from rather different characters of conduction and valence bands involving $\pi$ and $\sigma$ bonding states respectively.

The angular dependence of the intensities of $A_1^g$, $A_2^g$ and $B_{3g}$ phonons in black phosphorus (BP) has been recently well studied [32]. It is shown that for reproducing experimental results for intensities of Ag modes, the Raman tensor has to be complex whereas for $B_{3g}$, real values of Raman tensor elements can explain the angular dependence. The complex values of the Raman tensor can arise both from electron–radiation as well as electron–phonon matrix elements. An interesting aspect brought out is that the imaginary part of the Raman tensor elements is different for the two totally symmetric modes $A_1^g$ and $A_2^g$, pointing out that electron–phonon interaction is a key factor responsible for the complex values of the tensor. In our work, we have shown that electron–phonon coupling (EPC) associated with $A_1^g$ and $A_2^g$ modes vary predominantly with electron doping. Our experiments did not focus on the angular dependence of the Raman intensities. The work of Ribeiro et al [32] points out an interesting future possibility to study the angular dependence of Raman intensities of $A_g$ modes as a function of carrier concentration and see how the relative phase factor (i.e. the imaginary part of the

$\Gamma-Z$ (energies of the states at Z-point are too far (figure 3(a)) from the gap to be affected by low levels of doping in phosphorene transistor). In figure SF5(a), we have shown iso-surfaces of wavefunctions of the valence and conduction bands at X-point and a diagram of their projections on p-orbitals of P. We note that the bands at X point are doubly degenerate, and are made from $p_x$ and $p_y$ orbitals of $P$, in contrast to the VBM and CBM at $\Gamma$ point made from $p_z$ orbitals. From the figure SF5(b), it is clear that the relative phases of p orbitals of the P sublattices are the same for wave functions at X and $\Gamma$ (figure 4(c)) points. Hence, our symmetry analysis of the coupling of Raman active phonons to the states along $\Gamma$ to X is similar. Since the orbitals involved in the VBM and CBM bands at X point are different from those at $\Gamma$ point, their relative phase factors are not simple. In fact, they involve rotations in the 3-dimensional space of bands made of two p-orbitals. Thus, their relative phases can be meaningfully described with a Hermitian matrix that is responsible for the complex Raman tensor element relevant to the polarization dependent Raman scattering [32]. To connect more closely with the results of [32], we determined optical dielectric constants of structures obtained by freezing $A_1^g$ and $A_2^g$ modes. $\Delta e_{xx}$ and $\Delta e_{zz}$ are 0.05 and 1.3 for $A_1^g$ and 0.2 and 1.5 for $A_2^g$ modes, respectively. This confirms a remarkable anisotropy in the Raman tensor, quite distinct for $A_1^g$ and $A_2^g$ modes, in qualitative agreement with the fitted parameters obtained from polarization dependent Raman spectra of phosphorene [32].

4. Conclusions

Our work demonstrates a phosphorene-based field effect transistor (P-FET) with a high on-off ratio, in which the carrier concentration in phosphorene

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\text{Figure 4. (a) Electronic structure of phosphorene with symmetry labels } B_{2g} \text{ at VBM (valence band maximum) and } B_{3g} \text{ at CBM (conduction band minimum) at } \Gamma \text{-point, (b) isosurfaces of wavefunctions at VBM and CBM at the } \Gamma \text{-point, and (c) a schematic showing the symmetry of the wavefunctions at VBM and CBM at } \Gamma \text{-point where dashed line shows a mirror plane. Note that wavefunctions at VBM and CBM are even and odd respectively, under mirror reflection } \sigma_{ac}.\]
Raman tensor elements) for the $A_g$ mode varies. This will further quantify the contribution of electron–phonon matrix elements to the real and imaginary parts of the Raman tensor elements. Our work is fundamental to understanding the transport in phosphorene and key to measurement of carriers in phosphorene-based nanoelectronic devices.

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