Title:	Structural and Opto-electronic Study of 2D Black Phosphorus: A Perspective from Raman Spectroscopy
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Abstract: Two-dimensional black phosphorus (BP), having broad tunability in its direct bandgap and highest carrier mobility in single-layer con guration among all semiconducting two-dimensional (2D) layered materials, has attracted tremendous attention towards the development of high speed electronic and opto-electronic devices.[1 3] The lay- ered BP shows a wide bandgap variation from visible to near infra-red (NIR) region, which varies from 0.3 eV (in bulk con guration) to 2.0 eV (in single layer con gu- ration). The bandgap of BP falls within the semiconducting range of 2D materials family, lling the gap between Graphene [zero bandgap] and transition metal di- chalcogenides (TMDCs) [absorption in the visible range].[2, 4 6] Reports suggest the superiority of BP based eld-e ect-transistors (FETs) over TMDCs, exhibit- 2 −1 −1 ing very high hole mobility (μ e >1000 cm V s), large on-set current (I on μ A / μ m) □ 300 8 and the large on-o ratio (I on / I o >10).[7 9] However, the behavior of lay- ered BP under external perturbations like mechanical stress, optical exposure, and electrostatic eld is still unexplored, which are very crucial factors to extend its application in nano-electronic devices under harsh conditions. This thesis, entitled Structural and Opto-electronic Study of 2D Black Phosphorus: A Perspective from Raman Spectroscopy , provides a route to understand and monitor the key physical properties of BP for possible applications in opto-electronics and sensing. In order to understand the structural stability of layered BP ake, High-Pressure Ra- man spectroscopy of a few-layer BP ake has been carried out. The extensive study of Raman spectra under applied pressure con rms the structural stability of BP ake for mechanically harsh conditions as high as □ 4.2 □ 5.9 GPa. At applied pressure of GPa, an orthorhombic to a rhombohedral phase transition has been observed, which is simultaneously reversible and partial. The phase transition pressure has been identi ed experimentally from the abrupt change in blueshift to redshift of in- 2 plane Raman vibrational modes (B 2g and A g). The experimental results con rm the coexistence of both the crystal phases (orthorhombic and rhombohedral) is possible over the transition pressure (> 4.2 GPa) and reveals the possibility of a metastable state. Apart from mechanical stability, it is also necessary to understand the behavior ofBP ake upon optical exposure to explore its possible opto-electronic applications. In order to understand the light to matter interaction, the e ect of laser irradiation on BP ake has been investigated by acquiring the Raman spectra with the variation of laser power and laser energy. The variation in laser power produces a similar kind of shift in Raman vibrational modes, as observed in the conventional electrostatic eld gating e ect. Correlation between the transfer characteristics of BP FET de- vice with the variation of laser power and the corresponding shift in Raman modes concludes that the laser illumination dominates the n-type charge carriers. Such optically induced electronic gating can be as e ective as conventional electrostatic gating e ect and may pave a path for non-contact modulation of electrical conduc- tion in FET based devices. Though BP has been proven to be very promising in opto-electronic applications, whereas its poor stability in ambient conditions has become the major limitation for practical use. The instability of BP ake is mainly occurred due to the presence of lone pair electrons on each phosphorus atoms, and the saturation of lone pair elec- trons could be one possible way to enhance the stability in ambient condition. The limitation of having lone pair electrons may be used as a potential platform for in- situ growth of metal nanoparticles on BP ake, where layered BP ake itself acts as a reducing agent. A simple one-step protocol has been developed for the deposition of Ag and Au nanoparticles on BP ake, where the nanoparticles are uniformly dis- tributed and deposited over the BP surface. The Ag nanoparticle deposited BP ake (AgNP@BP) has shown enhanced stability as no degradation is observed for up to 72 hrs in ambient conditions. The structural and physical stability of AgNP@BP akes has been studied using AFM and Raman spectra measurements. Further study of the AgNP@BP ake suggests its potential application as an abundant SERS plat- form, where the plasmonic nature of the AgNPs enables the enhancement of the local electromagnetic eld, an essential requirement for SERS substrate. The as- fabricated SERS substrates have been used for the detection of Sepsis biomarkers with rapid detection capability as compared to the standard state-of-art protocols. The SERS enhancement factor has been achieved as high as in the order of - 10 14 □ 10 13 for all three biomarkers, i.e. , LPS, IL-3, and PCT, with a limit of detection (LOD) as low as 1 nM, 1 pM and 100 fM, respectively.Apart from the intrinsic properties of the 2D BP, the nano-structuring of BP has also opened up new aspects and potential applications, as atomic nanostructures open up novel characteristics to this material. For the practical uses of layered material in sensors and actuators development, it is essential to have a protocol for controlled nano-structuring of these materials to fabricate device arrays, which has not been established yet for unconventional materials like BP akes. Challenge lies within the nano-structuring process of such 2D atomic layers, where the replication of the standard microfabrication process ow, adopted by semiconductor industries, may induce unwanted alteration to the atomic structure. In our report, a simple route has been demonstrated for controlled and precise fabrication of nanostructures on the few-layer BP ake by focused laser (532 nm) irradiation. The feature size can be controlled using two mutually exclusive parameters, such as (i) laser power and (ii) exposure time. Using a 532 nm focused laser line, the minimum feature size is achieved □ 248 nm, which is close to the di raction limit of the laser used. This process does not require any photoresist coating and does not go through the stan- dard semiconducting multistep fabrication process ow, and hence the established process is considerably contamination free. By analyzing the geometrical shape of the nano-void, created due to laser irradiation, it is possible to identify the armchair and zigzag direction of BP ake. Experimental results reveal that by controlling the exposure time and laser power, it is also possible to perform the layer by layer thinning of BP akes. The proposed thinning process of the BP ake does not alter the pristine quality as no signs of oxidation is found in the Raman spectra, which signi es the reliability of this low power laser irradiation technique towards the fu- ture of nano-fabrication of BP based devices. Controlled formation of the nano-voids array on the few-layer BP ake induces enhanced local electric eld (hotspots) at the vicinity of the nano-voids, resulting in □ 30% Raman intensity enhancement. Such nano-voids induced hotspots demonstrate pronounced enhancement in Raman signal of Rhodamine B as high as of the order of (LOD) as low as □ 10 □ 10 6 and with a limit of detection nM. This low-power focused laser irradiation based nano-patterning technique is found to be replicable to other 2D materials such as MoS 2 , WS 2 ; however, it does not seem to work on Graphene due to its higher mechanical stability. However, on Graphene Oxide (GO) thin lm, the above mentioned nano-patterning process wassuccessfully optimized to create nanostructures of desired shape and size. More in- terestingly, it has been observed that the low power laser irradiation can bend the GO surface below a threshold laser power □ 1.59 mW, which leads to the experimen- tal realization of radiation pressure at the air-solid interface. The non-existence of a speci c experimental protocol for determining the photon momentum has led to a long-standing debate in physics as known as `Abraham-Minkowski controversy' on radiation pressure of light. Herein we have shown a direct experimental validation of Abraham's theory, where the GO surface bends in the propagation direction of the incident light, and the bending depth could be used as a linear calibration factor for radiation pressure. The AFM studies reveal that for very low laser power, ranges from 0.028 mW to 1.48 mW, the surface of the irradiated spot undergoes bending due to light radiation pressure with bending depth varying linearly from 14 nm to 97 nm. The calculated strain-stress curve also shows a very linear variation in this region, whereas for laser power > 1.59 mW, the linearity of the curve changes, which is identi ed as the Breaking Point. The real-time Raman spectra of the GO lm also validates the process, where the peak position of G-band ad D-band initially shows blueshift due to uniaxial strain induced in the GO thin lm, followed by a sudden redshift at the breaking point as the uniaxial strain is released abruptly due to etching of GO layers.

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