

# Dopants induced structural and optical anomalies of anisotropic edges of black phosphorous thin films and crystals



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## ABSTRACT

A detailed experimental investigation of dopants modified black-phosphorus and methodology to deposit film on glass substrate have been conducted in order to improve the optical properties and wider utility. It was observed that Raman peaks were less intense for film, compared to separately grown black-P crystals. It was also observed that when synthesis duration was reduced to four hours, all Raman peaks became broader. A non-uniform material luminescence with dominance of green luminescence was observed when black-P crystals were irradiated with light of wavelength  $\sim 565\text{--}575$  nm. The sulfur doped black-P illustrated fascinating rod-and-globule like deposits on the parent nano-coral black phosphorous substrate, whereas selenium doped black-P exhibits a localized concentration of Se in the near homogeneous phosphorous coverage. The boron and sulfur doping increased the band gap. In contrast, Se, In, and Ga doping resulted in a significant decrease in band gap energy. Frequency dependent dielectric functions of the anisotropic zig-zag and armchair edges of phosphorene suggest that doping of black-P causes a diminution in the first peak position for the zigzag electric field polarization demonstrating a gradual red shift. The red shift in the first peak position was perceived to be greatest for doping with boron exhibiting a band edge at 0.65 eV and least in the case of doping with sulfur, resulting in a band edge at 1.09 eV.

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## 1. Introduction

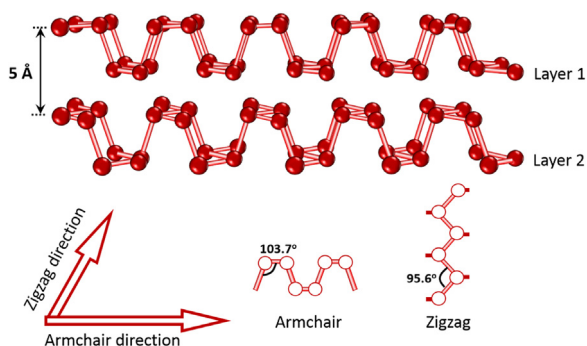
Polymorphism of materials is often advantageous if it offers improved electronic and physical properties, better crystal structures, and adequate handling [1]. In a special case of chemical elements (polymorphism is often referred as allotropy), associated allotropes behave differently due to the nature of the bonding and the lattice arrangement. Many different metallic (such as Sn, Fe, and Po) and non-metallic (Such as C, P, O, and S) allotropes exhibit different behavior and stability. Among all these polymorphs, black phosphorus (black-P) research was almost dormant for 100 years since its date of first synthesis in 1914 [2]. Recently it was re-explored due to its unique puckered single layer geometry (See Fig. 1) [3]. Some of the great advantages of black-P are the tunability of direct energy bandgap (from 0.3 eV to 2.0 eV), enhanced charge carrier mobility, and anisotropic in-plane properties. These properties make black-P a special candidate for research associated with nanophotonic devices incorporating 2D layered materials and moderate band gap based nanoelectronic applications.

Apart from all these properties, recently the possibility of black-P for terahertz applications has been explored [4]. It was computed that the intraband and interband optical transition frequencies were entirely different as the occurrence of the former one was in the microwave-to-terahertz range and the latter ones in the visible frequency segment (with application of magnetic field), respectively [4].

Graphene was the only single element material that could be fabricated using exfoliation techniques and it exhibited stability, until the discovery of few layers of phosphorene [5]. In the case of single layer graphene, several novel phenomena were encountered such as anomalous room temperature quantum hall effects that has provided several new dimensions to Fermi-Dirac physics [6]. Silicene, also a 2D elemental material, degrades rapidly in the presence of low concentrations of oxygen. The deposition of black-P into a substrate will create a substrate-material interaction and subsequent appearance of a band gap opening at the K point. Such a substrate-material interface behavior due to adatoms and defect can significantly affect the associated inherent properties [6]. Black-P exhibits mobility on the order of  $\sim 10,000$  cm<sup>2</sup>/V s and 1000 cm<sup>2</sup>/V s, in case of bulk crystals and exfoliated flakes, respectively. One of the great advantages of black-P is its small and direct band gap, which can enable research in new dimensions of broadband photodetection [7]. Many 2D materials such as TMDCs

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**Fig. 1.** Layered structure of Phosphorene. In this structure, weak interlayer (van der Waals) forces are responsible for holding the unit containing systematic arranged lamellae of phosphorus atoms. Figure also shows a front view (armchair) and top view (Zigzag) structure of phosphorene and corresponding bond angles.

are not very suitable for this application, due to their large band-gap. Additionally, the broadband response of black-P based FET extends from visible to NIR region light excitation. In contrast such a response was narrow and confined to the visible portion of the spectrum in the case of TMDCs [7]. Apart from these unique characteristics of pristine phosphorene, doped phosphorene can also be useful to tune the properties for better molecular adsorption, desorption, enhanced chemical activity, and its utility in sensing [8].

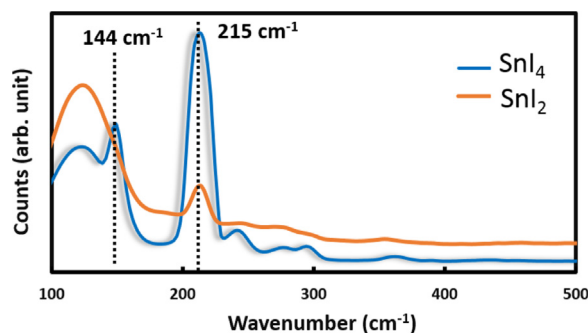
### 1.1. Synthesis challenges

Black-P was first prepared by Bridgman, who used a high pressure (above 1.2 GPa) method to transform the white phosphorus into black-P polycrystals [2,9]. Similarly, black-P was synthesized using red-P with the application of high pressure  $\sim 8.0$  GPa [9]. Another method utilized white-P solution in liquid bismuth for synthesis of needle shaped black-P crystals [10]. Large black-P crystals were grown using red or white P and their subsequent conversion into black-P at high pressure and temperature [9]. One of the challenges in preparing black-P using liquid bismuth is the use of high quality white phosphorus, that is highly reactive, flammable in air, and poisonous [11]. Some new methods have been demonstrated where red-P is used as a starting precursor material, that is converted into white phosphorus using an electric furnace. The pure white phosphorus was reacted with the lumps of bismuth at elevated temperature, in a sealed vessel. Such a process takes at least two days to synthesize the black-P crystals [9]. Recently, various new methods have been proposed and demonstrated where low pressure synthesis of black-P was achieved using various mineralizing agents [12] including Sn, Au, Ag, and SnI<sub>4</sub> [13,14]. Hence, we are investigating doped black-P in a similar line of investigation, using a low pressure synthesis technique.

## 2. Experimental

### 2.1. Materials

Red Phosphorus of purity  $\sim 99.9\%$  was purchased from Alfa Aesar (USA). Tin powder (purity  $\sim 99.8\%$ ) was obtained from Sigma Aldrich. Iodine was purchased from Mallinckrodt Inc. (USA). Tin (IV) Iodide or SnI<sub>4</sub> was synthesized as discussed in the literature [15]. In summary, stoichiometric proportions of iodine and tin were dissolved in dichloromethane and mildly heated. The results of this reaction provides SnI<sub>4</sub> as a principal product and SnI<sub>2</sub> as a side product. It has been observed that the melting point of our synthesized SnI<sub>4</sub> were very close to that reported for pure SnI<sub>4</sub>.



**Fig. 2.** Raman spectra of SnI<sub>4</sub> and SnI<sub>2</sub>.

Raman characterizations of SnI<sub>4</sub> was conducted to evaluate the phase purity of compound (See Fig. 2). It was observed that strong and distinct peaks at  $\sim 144$  cm<sup>-1</sup> and 215 cm<sup>-1</sup> match well with the reported Raman spectrum [16] of pure SnI<sub>4</sub>.

### 2.2. Synthesis

Sn (20 mg metallic), SnI<sub>4</sub> (10 mg) and red phosphorus (500 mg) were weighed in a silica glass ampoule of 10 cm length, an inner diameter of 1.0 cm and a wall thickness of 0.1 cm. The ampoule was evacuated, sealed, and placed horizontally, with the starting materials mixture located at the hot end and the empty ampoule side towards the colder middle section of a tube furnace, set to a temperature of 750 °C and then cooled during 10 h to 550 °C. The resulting black-P crystals were then treated with toluene to remove other phases. The FTO substrate was then cooled to room temperature to facilitate deposition of the thin film.

In order to grow black-P on a transparent conducting substrate, a Sn thin film was grown over it. For the growth of a Sn thin film, an electrochemical approach was used. In a typical experiment, an electrochemical bath containing Na<sub>2</sub>SnO<sub>3</sub> · 3H<sub>2</sub>O and tin chloride was used with a 3-electrode system. Electrodeposition was carried out at a potential of  $\sim -1.8$  eV. We have used sodium potassium tartrate as a complexing agent. Electroplating was carried out at a controlled temperature of  $\sim 55$  °C. Other details about Sn electrodeposition can be found in earlier reports [17]. After growth of Sn, we have deposited Sn iodide over it. For such deposition, tin iodide was first dissolved in toluene solution and sonicated for 30 min. A homogeneous mixture obtained after sonication was coated over Sn coated FTO-glass substrate using a doctor-blade technique. After complete drying, the substrate was kept inside a quartz ampoule containing Sn, SnI<sub>4</sub>, and Red-P as discussed in the preceding section. Most of the other processing parameters were kept similar except, annealing was performed at relatively low temperature in order to protect the quartz ampoule. A completely sealed and evacuated quartz tube was heated using a furnace, where half of the tube was in direct contact with the heating surface of a furnace. Such a tube was first heated up to 680 °C, followed by a lowering of temperature to  $\sim 550$  °C. The ramp rate was adjusted in such a manner so that it took seven hours for reduction in temperature. Once it reached  $\sim 550$  °C, it was kept at constant temperature for 1 h. After that it was slowly cooled down to room temperature. Fig. 2 shows the digital photographs of the quartz tube captured during the reaction (t<sub>i</sub> represent the time interval in sequence). A sequential change in reaction tube evident in Fig. 3, illustrates that most rigorous transformation and reaction starts only after certain period of time (the temperature reaches  $\sim 600$  °C). It can be observed that most of the red color residue was deposited in the upper portion of tube (cold end) whereas the lower end shows the deposition of black-P. Similarly for Sn-coated glass substrate, the black portion was only observed at the lower

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