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Black Phosphorous as an alternative to current Semiconductor materials

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Abstract: *It's been more than one hundred years since the black phosphorous (BP) was added as a new member to the Phosphorous family, joining the well-known Red and White members. However it is only in the recent years that BP has grasped attention from the varied fields of Physics, semiconductor engineering, Chemistry, and material science. This article provides a review on BP as an alternative to popular semiconductor materials including Silicon and Graphene. Furthermore, prospects of BP is also commented on.*

Keywords: **Semiconductor, Black Phosphorous, IOT, Silicon, Graphene**

Introduction:

There are at least 12 allotropes of Phosphorous, the most known being the White and Red Phosphorous. Black phosphorus (BP) is the most stable allotrope which is similar to graphite in structure and physical properties. BP has its origin in the year 1910 at the Harvard Lab, USA when Professor Bridgman, who was studying the effects of high pressure discovered BP by heating white phosphorus under high pressures (12,000 atmospheres) [1]. For years, BP was not recognized as a useful semiconductor material, mainly due to limited stability of the surface of BP under atmospheric conditions and due to layered structure [2]. However the ability to obtain the single-layer BP, termed as phosphorene, by microcleavage lead to its come back in the industry as a big challenger to the existing semiconductor materials [3]. Till now, the BP has been utilized in transistor devices [4], Efficient Singlet Oxygen Generation [5], sensors [6], and optoelectronics [7]

DISCUSSION

Black Phosphorous compared to Silicon

Silicon has ruled as a leader in the Semiconductor industry for a long time. There are several reasons that gives Silicon this status including abundant availability, low cost, easy doping, low band gap, stable surface properties, high mobility to name a few.

In recent years, BP has come as a close competitor to Silicon in the semiconductor industry. The key properties that makes BP a close competitor to Silicon is that black phosphorus has a higher mobility than silicon—that is, the speed at which it can carry an electrical charge. Also, BP has a bandgap, which gives the material an ability to act as a switch; meaning it can turn on and off in the presence of an electric field and act as a semiconductor.

The high mobility of BP has been explored by several researchers. In 2014, Qiao, J. et al studied theoretically that few-layer BP is a novel category of 2D semiconductor offering a direct bandgap, high carrier mobility and high transport anisotropy, all of which are tunable by controlling the layer thickness. [8]. In this study conducted by Qiao, J. et al, the monolayer of BP was found exceptional in having an extremely high hole mobility (of order 10,000 cm2 V−1 s−1). It was also found that the bandgap decreases from 1.51 eV for a monolayer to 0.59 eV for five-layer BP, a set of values fitting well into the gap between graphene nanoribbons and transition metal dichalcogenides (TMDCs). The 2D carrier mobility was calculated using the expression.

$$\mu_{2D} = \frac{e\hbar^3 C_{2D}}{k_B T m_e^* m_d (E_1^i)^2}$$

where m_e^* is the effective mass in the transport direction and m_d is the average effective mass determined by $m_d = \sqrt{m_x^* m_y^*}$. The term E1represents the deformation potential constant of the valence-band minimum for hole or conduction-band maximum for electron along the transport direction, defined by $E_1^i = \Delta V_i / (\Delta l / l_0)$. Here ΔVi is the energy change of the ith band under proper cell compression and dilatation (calculated using a step of 0.5%), l0 is the lattice constant in the transport direction and Δl is the deformation of l0. The elastic modulus C2D of the longitudinal strain in the propagation directions (both x and y) of the longitudinal acoustic wave is derived from (E−E0)/S0=C(Δl/l0)2/2, where E is the total energy and S0 is the lattice volume at equilibrium for a 2D system. All structural properties in the calculation of carrier mobilities were obtained from optB88-vdW and properties related to the electronic structure were computed with the HSE06 functional. The temperature used for the mobility calculations was 300 K.

Further, Xiao, J. et al. [9] investigated the electronic structures and the intrinsic charge carrier mobility of four type phosphorus sheets (α-P, β-P, γ-P and δ-P), using first-principles density functional theory and the Boltzmann

transport equation (BTE) with the relaxation time approximation and found that all four types of phosphorus sheets present anisotropy in carrier mobility. In the study, the carrier mobility was calculated by BTE method as expressed below-

$$\mu^{e(h)} = \frac{e}{k_B T} \frac{\sum_{i\in CB(VB)} \int \tau\left(i,\vec{k}\right) v^2\left(i,\vec{k}\right) \exp\left[\mp \frac{\varepsilon_i\left(\vec{k}\right)}{k_B T}\right] d\vec{k}}{\sum_{i\in CB(VB)} \int \exp\left[\mp \frac{\varepsilon_i\left(\vec{k}\right)}{k_B T}\right] d\vec{k}} \quad (1)$$

Where the minus (plus) sign is for electron (hole). $\tau\left(i,\vec{k}\right)$ is the relaxation time, $\varepsilon_i\left(\vec{k}\right)$ and $v\left(i,\vec{k}\right)$ are band energy and the component of group velocity at $\vec{k}$ state of the i-th band, respectively. The summation of band was carried out over VB for hole and CB for electron. Furthermore, the integral of $\vec{k}$ states is over the first Brillouin zone (BZ) [9].

In addition to the mobility studies, the bandgap tuning of BP has also been reported by the varied researchers. Kim, J. et al. has reported the tuning of doped few-layer BP through the adsorption of potassium atoms by photoemission spectroscopy experiments [10].

Inspite of the advantages of BP discussed above, BP is still not ready for large scale production. Currently, thin layers can be made only from scraping bulk crystalline BP samples, as no other manufacturing method exists yet. Tackling the scaling problem is already underway, with chemical vapor deposition (CVD) and other thin film growth techniques being investigated in labs across the world. Hence, given the low cost and abundant availability of silicon at the moment gives Silicon still an edge over BP. However, with the race for lighter and smaller devices across the technology world, BP poses as a strong a contender as a chip material for future technology.

Black Phosphorous compared to Graphene

BP shares similarities with Graphene in terms of scotch-tape delamination (exfoliation), resulting in phosphorene, a graphene-like 2D material with excellent charge and thermal transport properties. Graphene with a band gap of zero in its natural state behaves like a conductor. As the conductivity of graphene cannot be shut off, it is a challenge to use graphite as a semiconductor. Also the lack of band gap leads to "leakage" leading to inefficient applications.

Black Phosphorous application in Internet of Things (IoT) devices

The "Internet of Things" is expanding at a rapid pace. The technology is racing to create scalable functional devices to ever smaller sizes. It is anticipated that BP will find a position in autonomous transmitting and data devices that makes the IOT.

CONCLUSION

The exploration of black phosphorus devices is still in its infancy, with a lot of unique properties to be understood and exploited. However, with a tunable band gap, high-speed capability and extreme versatility, BP offers a tremendous opportunity in the world of electronics. The challenges in fabrication, scalability, and stability of phosphorus crystal (against degradation) still needs to be addressed by researcher across the globe.

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