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Effects of plasma-treatment on the electrical and optoelectronic properties of layered black phosphorus

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KEYWORDS: phosphorene, black phosphorus, plasma thinning, etching, photoresponse

Abstract

Exfoliated few-layer black-phosphorus (BP) has been explored for a variety of electrical and optoelectronic applications. Plasma-assisted thinning of BP has emerged as an exciting pathway to achieve BP crystals of desired thickness. However, to fully realise the true potential of plasma-assisted thinning of BP and other emerging 2D materials, it is critical to understand the effects of different plasma environments on the electrical and optoelectronic properties of the resultant material. Here, we investigate the influence of Ar and O₂ plasma on the electrical and optoelectronic properties of plasma-treated BP flakes. It is revealed that by manipulating the environment under which BP is exposed to the plasma, it is possible to engineer defects that lead to new photoluminescence (PL) emission peaks without compromising the switching ratios or carrier mobilities of BP-based field effect transistors (FETs). Overall, our study finds the use of O₂ plasma as a more suitable approach to retain and enrich the intrinsic (opto)electronic properties of BP. Additionally, our study, for the first time, experimentally reveals the ability of BP to respond to UV excitation.

Introduction

Since the discovery of graphene, two-dimensional materials (2D) have received remarkable attention, in particular, due to their exceptional transport properties.[1] The weak inter layer and strong intra layer forces in the bulk form of these materials have enabled the realization of pristine, planar materials via seamless processes such as exfoliation. The fascinating properties that arise in planar materials due to the quantum confinement of carriers, makes them attractive for deployment as functional materials in transistors,[2-6] photodetectors,[7-12] solar cells,[9,13] batteries,[14,15] energy storage systems,[9,16,17] catalysis,[18] and sensing[15,19-21] to name a few. While graphene has been extensively investigated, a major limitation associated with its close to zero inherent band gap has subsequently sparked a

search for other 2D materials with natural band gaps. This led to the advent of transition metal dichalcogenides (TMDCs) such as MoS₂ that has direct band gap in its monolayer form but carrier mobilities that are inferior to that of graphene.[22,23]

More recently, elemental analogues have emerged as an exciting class of materials.[24] Amongst them, black phosphorus (BP) and its monolayer form commonly referred as ‘phosphorene’ have highly desirable intrinsic characteristics, with one of them being its direct bandgap that is independent of thickness but its value is tunable depending on the number of layers (0.2 eV in bulk to 1.5 eV in monolayer BP).[1,12] Furthermore, it possesses high carrier mobilities of the order of $10^3 \text{ cm}^2/\text{V.s.}$, [1] with theoretical predictions indicating that it can be as high as $20,000 \text{ cm}^2/\text{V.s.}$ [25] Additionally, its highly anisotropy-dependant thermal, electrical, and mechanical properties [26,27] are in striking contrast to other 2D TMDCs and graphene.

So far, the most common method of realising layered crystals of BP is mechanical exfoliation. The layers obtained are typically of different thicknesses which can be identified under the optical microscope and using atomic force microscopy (AFM). Generally, the highest proportion of flakes obtained using mechanical exfoliation are in the thickness range of 15-35 nm, with a scattered few that are less than 10 nm thick. This introduces a high degree of randomness in the thicknesses achieved. For several applications such as field effect transistors (FETs), a higher proportion of thinner layers are vital to fully capitalise on the quantum confinement effects.[22] Furthermore, even being the most stable allotrope of phosphorus,[28] BP is not environmentally stable and undergoes rapid photo-oxidation in ambient conditions, which is further expedited in the presence of humidity,[29-35] leading to surface defects and carrier scattering centres that compromise the promising electrical characteristics of this 2D material.

Plasma-assisted thinning of mechanically-exfoliated BP flakes has recently emerged as a promising route to control the number of layers in a BP crystal on-demand.[22,36,37] Two common gases involved in this approach include either argon (Ar) or oxygen (O₂); however their relative pros and cons are not investigated. To fully realise the true potential of plasma-assisted thinning of BP and other emerging 2D materials, it is critical to understand the effects of different plasma environments on BP thinning, its ambient stability and importantly, on the electrical and optoelectronic properties of the resultant material.

The current study focuses on these important aspects of plasma-assisted BP thinning, and, as such, offers new insights into the influence of Ar and O₂ plasma on the electrical and optoelectronic properties of plasma-treated BP flakes. Our investigations reveal that by manipulating the environment under which BP is exposed to the plasma, it is possible to engineer defects that lead to new photoluminescence (PL) emission peaks without compromising the switching ratios or carrier mobilities of BP-based field effect transistors (FETs). Overall, our study finds the use of O₂ plasma as a more suitable approach to retain and enrich the intrinsic (opto)electronic properties of BP. Additionally, our study, for the first time, experimentally reveals the ability of BP to respond to UV excitation.

Experimental Section

Sample preparation and storage: The BP flakes are mechanically exfoliated from a bulk crystal (Smart Elements) on to plasma-cleaned 300 nm SiO₂/Si substrates. The BP surface gets photo-oxidised in ambient air, so the samples were prepared and stored in a nitrogen atmosphere. BP flakes of uniform thicknesses of 25 nm to 30 nm were identified *via* optical contrast. Photo lithography followed by electron beam evaporation of metal electrodes (Au

90 nm with adhesion layer of Cr 10 nm), was carried out to realise two-terminal devices based on BP flakes.

Characterization:

AFM analyses are performed on a Veeco Dimension Icon in ScanAsyst mode. Plasma etching is performed with the PlasmaPro System100 Inductive Coupled Plasma (Oxford Instruments) system at room temperature. O₂ plasma is generated at ICP power of 400 W and RF power of 30 W with O₂ flow rate of 30 s.c.c.m. at a pressure of 10 mTorr. Ar etching is carried out at ICP power of 300 W and RF power at 30 W with Ar flow of 15 s.c.c.m at a pressure of 5 mTorr. The etch rates calculated for O₂ and Ar plasma are 0.12 nm/s and 0.50 nm/s, respectively. The Raman spectroscopy and photoluminescence characterizations were performed using a Horiba LabRAM HR Evolution Micro-Raman system equipped with a 532 nm laser source (50× objective). Photoexcitation was carried out using a 280 nm wavelength, high power excitation source (Thorlabs, Inc). The incident power at the sample surface is measured using the commercial UV power meter (Newport Corporation). All photoresponse experiments are performed in dark conditions in a customised environmental chamber (Linkam) at room temperature. The electrical measurements are performed using the Keithley 4200SCS semiconductor parameter analyser.

Results and Discussion

Few-layer BP is mechanically-exfoliated from a bulk crystal (Smart Elements) using a blue Nitto tape on to plasma-cleaned Si substrates with a 300 nm thermally-grown SiO₂ layer. We will refer to these as-exfoliated flakes as ‘pristine BP’ henceforth in the manuscript. The exfoliation process is carried out in UV deficient dark conditions and the samples are stored in an inert nitrogen (N₂) atmosphere to preserve the integrity of the samples during the exfoliation process (see Experimental for details).[29,38] For plasma treatment, BP flakes of

thicknesses in the range of 20-25 nm are initially identified using optical contrast with respect to the underlying SiO₂/Si substrate.

The thickness of the pristine BP flakes is confirmed using atomic force microscopy (AFM) (**Figure 1a,b**). To establish an optimal plasma etching recipe that provides controlled layer removal of BP without inducing significant damages on the morphology and crystal structure, various radio frequency (RF) and inductively-coupled plasma (ICP) power conditions at fixed pressure of 10 mTorr are initially investigated. After a series of etch cycles, each followed by AFM characterization, an optimal set of RF and ICP powers for both Ar and O₂ etching (see Experimental for details) are established, given their different ionization efficiencies. At these powers, no significant optical changes to the surface are observed following the etching process. The selected pristine BP flakes (as shown in Figures 1a,b) are plasma-treated in Ar and O₂ atmospheres individually. Both pristine BP flakes are etched down to sub-10 nm thicknesses (Figure 1c,d) with controlled exposure. We noted that the process can be implemented to successfully achieve monolayers however, we observed that thinner layers are prone to rapid degradation and further plasma-treatment will not allow for a valid comparison, especially in the case of Ar etched BP, where there is no process-generated P_xO_y protective coating. [36] Further, it is known that a thinner BP channel is more susceptible to potential variations in the substrate due to the formation of traps at the interface. The carrier mobility is known to increase monotonically in the thickness range 4-12 nm due to charge screening effects. However, further increases in channel thickness result in higher interlayer resistance of BP, thereby reducing the carrier conduction from the electrical contacts formed on the top surfaces of the BP.[37] It is also noted from the AFM characterisation that there is an increase in average surface roughness from 0.611 nm and 0.727 nm for the pristine BP flakes to 1.310 nm and 1.510 nm for the Ar and O₂ etched flakes, respectively. This surface roughness is comparable to the value reported previously.[37] The etch rate is calculated to

be 0.50 nm/s for Ar and 0.12 nm/s for O₂ plasma thinning, showing a faster etch rate for Ar plasma assisted thinning.

Figure 2 illustrates a schematic representation of the plasma bombardment and the BP layer removal process. In the case of O₂ plasma treatment, it has been reported[36] that a layer of P_xO_y forms on the BP surface which covers and protects the underlying layers of BP as shown in Figure 2. This is evident from a 4-times lower O₂ plasma layer-removal rate of BP in comparison to that of Ar plasma assisted thinning. Once an equilibrium is reached between the formation and etching of the surface P_xO_y layer, this slower etching process allows a highly controllable thinning of the underlying BP.[36] On the other hand, while Ar plasma removes any potentially pre-existing ambient oxide layer, the inability of Ar plasma to induce P_xO_y layer formation directly causes a more rapid layer-by-layer etching of BP atoms, which also manifests as a higher etching rate compared to O₂ plasma.[22,37]

To determine the effects of the plasma treatment process on the compositional integrity of BP, we conducted micro-Raman spectroscopic analysis on the same BP flakes before and after the etching processes. A comparison of the Raman spectra shows the presence of all three signature peaks of BP corresponding to A_g¹ (361 cm⁻¹), B_{2g} (438 cm⁻¹) and the A_g² (465 cm⁻¹) modes (**Figure 3a,b**).^[39] The A_g¹ mode originates from the out-of-plane vibrations of phosphorus atoms along the *c*-axis, while the B_{2g} and A_g² modes arise from the in-plane vibrations of phosphorus atoms along the *b*-axis (armchair) and *a*-axis (zigzag), respectively. It is known that the integrated Raman intensity ratio of A_g² to A_g¹ increases monotonically with decreasing layer numbers, and therefore, can be used as a reliable fingerprint to determine the thickness trend. In our case, the intensity ratios of A_g²/A_g¹ increases after plasma-assisted etching which indicates reduction in the thicknesses.[22,39] However, this ratio can be significantly influenced by surface oxidation and therefore AFM remains the best tool to directly measure the BP thickness.

To further investigate the effects of plasma treatment in different environments, we compare the photoluminescence (PL) spectra of the pristine and etched BP flakes (Figure 3c). Typically, only mono/bilayers of BP show PL in the visible region.[22] However, as seen from Figure 3c, the O₂ plasma treated flake reveals a prominent peak between 650 and 760 nm. There are no PL signals observed from the Ar plasma treated BP, which is also of a similar thickness as the O₂ etched BP. The emergence of this PL signature can be attributed to the presence of in-gap defect states. During the O₂ plasma etching, the oxygen ions create neutral and electrically metastable defects in BP.[36,40] These defects are expected to introduce an acceptor state near the conduction band, and consequently, a disturbed valence band state is formed by the hybridisation of the *p*-orbitals of O and P atoms.[40,41] These defects are energetically confined to one of the defect bands within the band gap of the material.[40] They can become electrically active when exposed to activation energies larger than their energy state. To verify this hypothesis, we conducted a transient photoresponse study on pristine, Ar and O₂ plasma etched BP flakes. Furthermore, the introduction of defects during the O₂ plasma etching process enables oxidation and the dissociation of oxygen dimers thereby facilitating the formation of a P_xO_y layer at the top surface.[42]

The photoresponse is acquired using a 280 nm excitation source. The low wavelength source will provide energy larger than the defect and the natural energy states and therefore induce a noticeable response. For this purpose, two terminal devices are fabricated (see Experimental) and the BP channel current is measured upon pulsed UV excitation. The measurements are carried out under constant channel bias of 100 mV. The illumination covers the whole active device area at a constant incident power of 1 mW/cm². **Figure 4a,b** shows the behaviour of the channel current under the exposure to 280 nm for two pristine BP flakes. It is seen that the current reversibly increases upon exposure. This is expected due to the photogeneration of carriers in the direct bandgap material such as BP. Furthermore, it should be noted that in the

case of elemental materials such as 2D BP, the interstitial P atom forms two bonds with other P atoms in adjacent layers and leaves one dangling bond.[40] Hence, the formation energies of the point defects are generally lower than other 2D systems, resulting in the creation of spin-polarized p-type states, which are predicted to be the origin of p-type conductivity. This also implies that such defects do not act as sinks for majority carriers (holes), due to the lack of compensating electrons and therefore an increase in current is seen upon photoexcitation with a 280 nm source.[40,43]

Following Ar plasma treatment, there is a distinctive change in the photoresponse trend. The channel current decreases upon illumination as seen from Figure 4c, in contrast to what is observed in the pristine BP flake before etching (Figure 4a). This intriguing behaviour is repeatedly observed in multiple devices following Ar etching. We explain this based on the thickness-dependent creation of reactive oxygen species (ROS), the formation of which results in a drop of electrical conductivity.[33] Thinner BP is more susceptible to the formation of oxide traps as a result of the interplay between light and environmental oxygen.[44-46] In every cycle of 280 nm exposure post-etching with Ar plasma, a decrease in conductivity is observed which is in contrast to the pristine BP device (Figure 4a and c). In the case of a pristine device, the energy gap of the thicker BP is relatively small (~ 0.2 eV), which makes the ROS formation due to photo-oxidation much slower and hence an expected increase in electrical conductivity is seen upon photo-excitation. However, when the BP is significantly thinned down and is not capped with any protective layer (as is the case after Ar etching), the larger energy gap allows an efficient formation of ROS that are known to degrade the electrical conductivity of BP.[29,42] This explanation is further supported with a model established by Martel and co-workers[47] which suggests that the rate of oxidation depends linearly on the oxygen concentration and light intensity and exponentially on the square of the energy gap.

On the other hand, following O₂ plasma treatment, the photoresponse in ambient conditions is observed to increase which is similar in trend to that of the pre-treated pristine BP flake (Figure 4d). However, the magnitude of response is relatively lower after etching. This can be attributed to the formation of an encapsulating surface P_xO_y layer,[36] which typically limits the incident photon energy. In contrast to the Ar-etched BP, there is no change in the photoresponse trend. This can be attributed to the protective nature of the P_xO_y layer that inhibits an efficient formation of ROS that could have otherwise degraded the electrical characteristics.

To evaluate the effect of the plasma process on the transport properties of BP, field effect transistors (FETs) are fabricated (see Experimental for details) and subjected to plasma etching. The transfer characteristics are acquired for two BP flakes pre- and post-treatment with Ar and O₂ plasma, as shown in **Figure 5** (see Supplementary Information **Figure S2** for the corresponding *I*–*V* curves). Optical micrographs of the devices pre- and post-treatment, are shown as insets. The thicknesses of the pristine BP flakes are 25-30 nm. The etched Ar and O₂ FET device have BP layers with thickness of ~9 nm and 5 nm, respectively. The switching ratio (*I*_{ON}/*I*_{OFF}) increases from 8 and 3 for the pristine BP-based FETs to approximately 2×10³ for the Ar and 1×10⁴ for the O₂ etched BP FETs, respectively. This is a dramatic increase of at least three orders of magnitude in both cases. Such an increase is in line with the previously reported values for FETs based on similar thicknesses of BP.[3,7,48] We also calculate the carrier mobilities using the following equation:[49]

$$\mu = \frac{\Delta I_{ds}}{\Delta V_{ds}} \times \frac{L}{W.C.V_{ds}} \quad (1)$$

where $\frac{\Delta I_{DS}}{\Delta V_{DS}}$ is the transconductance, *L* is the channel length, *W* is the channel width, *C* is the gate oxide capacitance (115 μFm⁻¹, see Supplementary Information, Figure S2 for this calculation) and the drain–source voltage (*V*_{DS}) is 50 mV. The carrier mobility for the Ar and

O₂ etched BP are found to be 336 cm²/V·s and 411 cm²/V·s, respectively. These values are in agreement with those reported for as exfoliated BP crystals of similar thickness at room temperature.[3,7,43,48] Based on these results, it can be concluded that the plasma process (Ar and O₂) has not resulted in any discernible change in the expected electronic properties of BP.[50]

In our study, we verify observations from previous studies that both Ar and O₂ plasma-treatment processes are viable and effective in controlling layer thickness. However, we reveal that O₂ plasma etching provides distinct advantages. Firstly, it offers an opportunity to controllably introduce defects that give rise to PL emission in the near infrared region, without compromising its electrical properties as demonstrated by fabricating a FET and a photosensor. Further, it results in the formation of a surface protective P_xO_y encapsulation layer thereby offering a better thickness control due to a slower etch rate. Based on known facts deduced from other reports[36,51] we also note that the formation of an encapsulation layer in the case of O₂ etching also offers higher ambient stability compared to the Ar-etched BP where the absence of a native encapsulation layer can in fact speed up the process of degradation and may require additional steps to protect the thinned BP flakes.

Conclusions

In summary, we have demonstrated the effects of plasma-assisted layer control of BP in Ar and O₂ atmospheres on the electrical and optoelectronic properties. Using spectroscopy, photoconductivity, and FET characteristics, it is shown that the O₂ plasma etching is favourable as it offers superior thickness control, primarily due to the formation of a surface P_xO_y encapsulation layer and the resultant defects can be exploited to generate PL emissions at new wavelengths while simultaneously retaining its electrical performance. A comparison of the structure and fundamental electronic characteristics before and after etching reveals

that both Ar and O₂ assisted thinning preserve the intrinsic properties of 2D BP. It is also shown that pristine BP could potentially be implemented as the functional layer for UV sensors, wherein the direction of resistance change can be manipulated using the etching process. Although a relatively slow response time may be beneficial in exploiting the UV response for applications in optically controlled memory devices.

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Figure 1: The AFM images of the pristine BP flakes (a), (b) and after plasma-assisted etching with Ar (c) and O₂ plasma (d) respectively along with their corresponding thickness profiles. The scale bars represent 2 μm.

Figure 2: A schematic representation of the plasma interaction with the BP. The O_2 plasma forms a P_xO_y layer which acts as a shield for the underlying BP, giving more control for the etching process compared to that of the Ar plasma. The Ar etching process results in a systematic layer-by-layer removal of any P_xO_y /BP layers.

Figure 3: A comparison of the Raman spectra for the pristine and (a) Ar-etched and (b) O_2 -etched BP. (c) Photoluminescence spectra comparison of the Ar- and O_2 -etched BP flakes on a SiO_2/Si substrate.

Figure 4: Photoresponse comparison of the BP flakes in air under pulsed illumination of 280 nm wavelength with a channel bias of 100 mV. The normalised current is plotted against time for two different devices based on pristine BP flakes (a and b) and with Ar-etched (c) and O₂-etched (d) BP flakes in. The ON (shaded areas) indicate that the 280 nm source is illuminating the device. The measurements are performed with cycles of 20 s exposure followed by 60 s recovery under dark conditions.

Figure 5: Transconductance comparison of (a) pristine and Ar-etched and (b) pristine and O_2 -etched BP FETs at a V_{DS} bias of 50 mV. The channel length and width of the devices are 2 μm and 3 μm , respectively. Optical micrographs of the devices pre- and post-etching are shown as insets.

Supplementary Information

Effects of plasma-treatment on the electrical and optoelectronic properties of layered black phosphorus

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S1: AFM images and thickness profile of the etched flakes.

Figure S1: The AFM images of the flakes after plasma-assisted etching with Ar (a) and O₂ plasma (b) respectively along with their marked areas of the thickness profiling. The scale bars of the image represent 2 μm . Thickness profiles of the Ar (c) O₂ (d) etched flakes across the flake as indicated in (a) and (b).

S2. I - V characteristics of the BP FETs before and after etching

Figure S2: The I - V characteristics of the devices with the as exfoliated BP (a) and (b). The O_2 -etched (c) and Ar^+ -etched (d) are shown with their respective gate voltages. The inset shows the optical image of the device in 100 $\times$ magnification.

The calculation of mobility was done using the equation[47]

$$\mu = \frac{\Delta I_{ds}}{\Delta V_{ds}} \times \frac{L}{W \cdot C \cdot V_{ds}}$$

Where $\frac{\Delta I_{ds}}{\Delta V_{ds}}$ is the transconductance, $L = 2 \mu m$ is the length of the channel, $W = 3 \mu m$ is the width of the channel, $C = 115 \mu F m^{-2}$ is the gate oxide capacitance, $V_{DS} = 50 mV$ is the voltage across drain and source. The gate oxide capacitance was calculated using equation[47] $C = \frac{\epsilon_0 \times \epsilon_r}{d}$, where $\epsilon_0 = 8.854 \times 10^{-12} F/m$, $\epsilon_r = 3.9$ for SiO_2 and d is the thickness of the gate oxide, here 300 nm.