

Physical Insights into Phosphorene Transistor Degradation Under Exposure to Atmospheric Conditions and Electrical Stress

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Abstract— In spite of promising properties like high mobility, tunable band gap, etc. Phosphorene’s promise to be a beyond CMOS material is hindered by its instability and fast degradation when exposed to ambient conditions. In this work, we performed a systematic study of Phosphorene degradation, under different influencing parameters, using detailed atomistic (DFT) computations and electrical, optical (Raman and PL) as well as physical (high resolution TEM) experiments. We observed that O₂ dominates over other gases to degrade phosphorene. O₂ is adsorbed chemically and dissociates over Phosphorene while other gases like, Ar, CO₂, H₂O and N₂, have physical adsorption over it with weak van der Waals (vdW) interactions. The degradation rate is anisotropic with maximum and minimum along [001] and [010] planes, respectively. Gate bias plays a significant role in Phosphorene FET instability. The degradation is enhanced under positive gate bias due to enhanced oxidation by gate field induced electron in the FET channel. The degradation however was found to be missing when channel was populated with holes under negative gate bias.

Index Terms— DFT, Phosphorene, QuantumATK, Raman.

I. INTRODUCTION

Phosphorene is a promising two-dimensional (2D) material with potential to fill the gap between Graphene and Transition Metal Dichalcogenides (TMDs) due to its exceptional properties, including high carrier mobility, wide range of tunable direct band gap, and in plane anisotropy [1]. Despite of these properties, instability (fast degradation) of Phosphorene is a big hurdle for its Field Effect Transistors (FET) application. While initial reports show that the oxygen and water play a significant role in Phosphorene degradation [2]-[4], impact of (i) other ambient gases like N₂, O₂, Ar, CO₂ & H₂O, (ii) Phosphorene anisotropy, and (iii) external factors like voltage bias, on its degradation have not been deeply explored yet. In this work, we have done systematic study

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and have developed physical insights into these issues with help of micro-Raman, Photoluminescence (PL), Transmission Electron Microscopy (TEM) characterization along with Density Function Theory (DFT) computational method. We have seen that O₂ dominates over other gases to degrade phosphorene in ambient atmospheric condition. The degradation is anisotropic, maximum along [001] plane and boosted further for Phosphorene FET due to inverted channel under positive gate bias.

II. EXPERIMENTAL DETAILS

Phosphorene was exfoliated using scotch tape method, transferred onto SiO₂/Si substrate and scanned for thin flacks (2-5 layers). All the Raman measurements were done using Horiba Lab Ram HR with 532 nm laser source at room temperature. TEM images were recorded at an 80 kV electron acceleration voltage in Oxygen environment of 2.7×10^{-6} Torr. QuantumATK computational package was used for all the DFT computations [5]-[7]. 5x5 supercells of phosphorene along different planes were created followed by ~ 15 Å vacuum space was added on the both sides of the plane to avoid interlayer wave function interaction. All the simulating modules were optimized with 0.01 eV/Å and 0.001 eV/Å³ force and energy cutoffs respectively. Perdew-Burke-Ernzerhof (PBE) form of generalized gradient approximation (GGA) functional was used in the computations with 5x5 k point sampling. Grimme DFT-D2 Van der Waals (vdW) correction was considered to capture long range vdW interactions.

III. RESULTS AND DISCUSSION

Phosphorene flakes were first observed in ambient and N₂ rich environment at different time using Raman spectroscopy (Fig. 1) to see its stability. A_g² peak reduces with time in ambient environment while it is relatively stable in the N₂ rich environment. Faster A_g² peak reduction confirms instability of Phosphorene in ambient environment [8]. We need to explore and understand further, which ambient gas is responsible for

the degradation, corresponding degradation mechanism and influencing parameters as well.

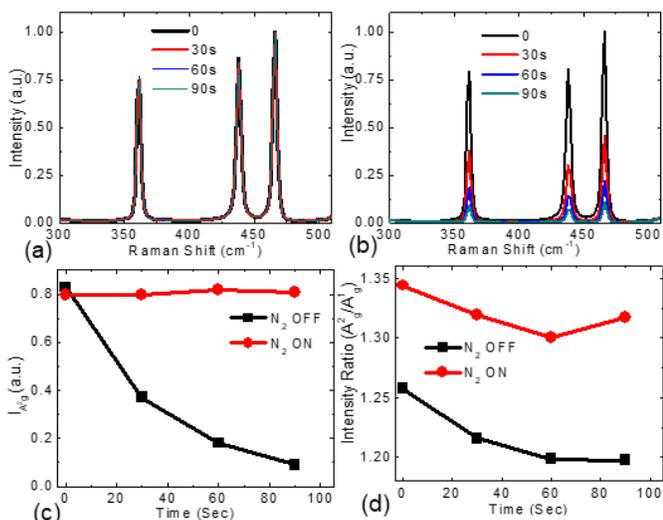


Figure 1: Raman degradation analysis of few layer Phosphorene with time: (a) Raman peaks in N₂ rich environment, (b) Raman peaks in ambient environment, (c) Change in A_{2g} peak, (d) Change in A_{2g} and A_{1g} peaks ratio. All peaks decay fast in ambient environment which confirms that Phosphorene degrades fast in ambient condition [8].

A. Phosphorene Under Ambient Gas Molecules

N₂, O₂, Ar, CO₂ and H₂O have major presence in atmosphere which can influence Phosphorene degradation in ambient condition. Computational (DFT) study of Phosphorene under these gases has been done to explore and understand physical and chemical properties of the gases over phosphorene surface. Optimized structures of the Phosphorene in presence of these gas molecules, and corresponding binding energy and bound distances confirm that O₂ is adsorbed chemically over Phosphorene while other gases are adsorbed physically (Fig. 2). O₂ dissociates over Phosphorene (Fig. 2e), sits ~0.62 Å above the plane (Fig. 2f) and releases ~5.12 eV energy (Fig. 2g) while other gases sit more than 2 Å above the plane and release less than 0.5 eV energy. Bond distance of Oxygen with Phosphorene surface (~0.62 Å) and corresponding bond energy (~5.12 eV) confirms covalent interaction of Oxygen with Phosphorene while other gases bond lengths and corresponding bond energies confirm Van der Waals (vdW) interaction of these gas molecules with Phosphorene. Among these gases, H₂O shows strongest physical (vdW) interaction, it sits 2.08 Å above the plane (Fig. 2c & 2f) and releases ~0.42 eV energy (Fig. 2g) while Ar, N₂ and CO₂ sit 3.41 Å, 3.14 Å and 3.18 Å above the plane (Fig. 2c & 2f) and release 0.18 eV, 0.26 eV and 0.38 eV of energy respectively (Fig. 2g). The analysis confirms that among significantly present atmospheric gases (N₂, O₂, Ar, CO₂ and H₂O), O₂ is primarily responsible for degradation initiation of Phosphorene in ambient atmosphere. Next we need to explore how Oxygen interacts with different Phosphorene plane to understand whether Phosphorene degradation is isotropic or anisotropic.

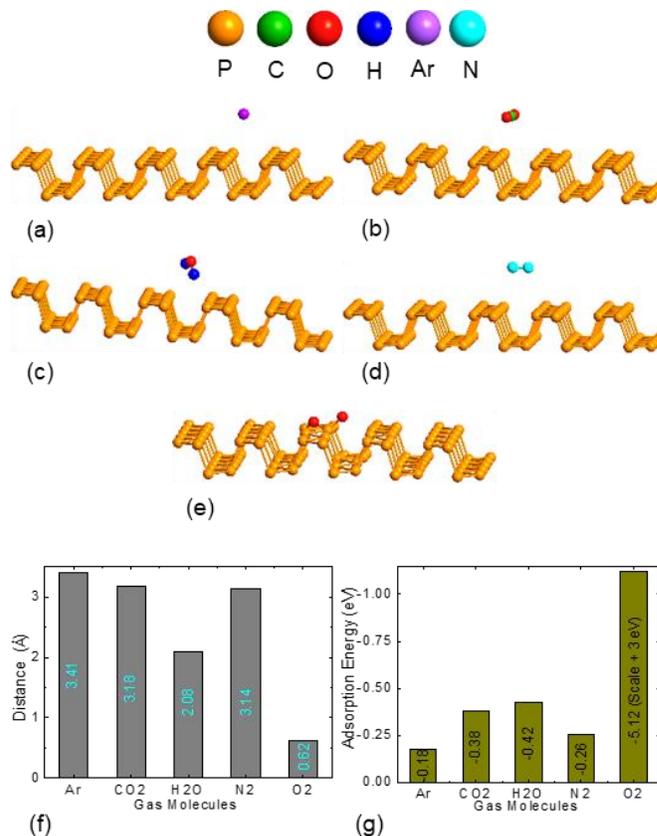


Figure 2: Computational study of atmospheric gaseous adsorption over Phosphorene using DFT. Optimized structure of (a) Ar, (b) CO₂, (c) H₂O, (d) N₂, and (e) O₂ with their (f) distance from Phosphorene plane and (g) adsorption energy reveal that O₂ is chemically adsorbed over Phosphorene while other gases are physically adsorbed. O₂ dissociates over Phosphorene plane, releases ~5.12 eV energy in reaction and seats ~0.62 Å above Phosphorene plane. Ar, CO₂, H₂O and N₂ seats ~3.41 Å, ~3.18 Å, ~2.08 Å and ~3.14 Å above phosphorene respectively with ~0.18 eV, ~0.38 eV, ~0.42 eV and ~0.26 eV corresponding energy release. From analysis, O₂ is responsible for Phosphorene degradation in ambient atmosphere.

B. Anisotropic Degradation Under Oxygen

O₂ dissociation over different Phosphorene planes (directions) has been studied using DFT and TEM (Fig. 3 & 4) to understand effect of phosphorene anisotropy over degradation rate. Modules of Oxygen molecule over different Phosphorene planes have been optimized (Fig 3a-d) and corresponding energies have been evaluated (Fig 3e-f). Dissociation energy of Oxygen is different over different Phosphorene planes (Fig. 3f), it is maximum for [001] plane and minimum for [010] plane (Fig. 3f and inset). If reaction kinetics is driven by thermodynamics (high energy condition), [001] plane degrades fast whereas [010] plane is relatively inert.

TEM image of degraded phosphorene (Fig. 4a) and corresponding etching rate (Fig. 4b) confirm anisotropic degradation rate as predicted computationally. The dumbbell shape of image (Fig. 4a) is due to different degradation rate along different direction of the Phosphorene sample.

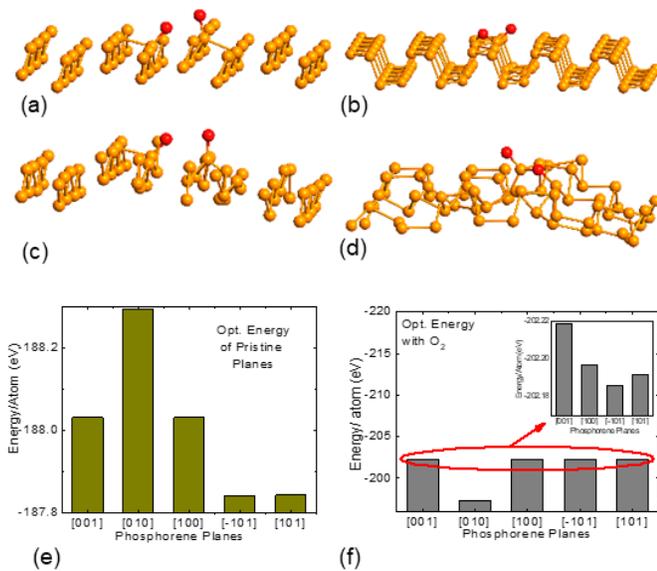


Figure 3: Computational study of anisotropic degradation of Phosphorene under O_2 using DFT. Optimized structure of O_2 with (a) [001], (b) [010] (c) [100] and (d) [101] planes confirms that O_2 dissociates over Phosphorene planes in all the studies orientation. Figure (e) and Figure (f) represent optimized energy of different Phosphorene planes in pristine and with O_2 molecules respectively. [010] pristine plane has most negative energy (e), hence, it is most stable than other planes. [001] and [100] planes have same stability which is higher than similar stabilities of [-101] and [101] planes. Under O_2 (f), [010] plane has least negative energy than other planes which means [010] plane has least affinity towards O_2 among all studies planes. Further analysis (figure (e) inset) says that [001] plane is most stable with O_2 followed by [100], [101] and [-101] planes respectively. If reaction kinetic is driven by thermodynamics (in high initial energy condition), Phosphorene degradation rate is anisotropic, it degrades relatively faster in [001] plane while the rate is relatively very slow in [010] direction.

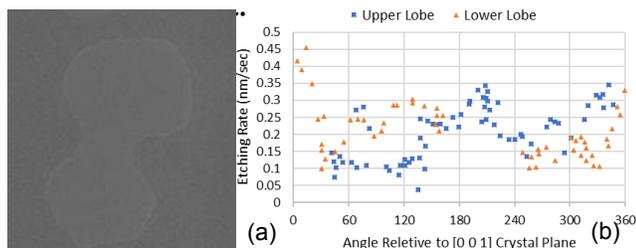


Figure 4: (a) TEM image of degraded Phosphorene, kept in O_2 environment. The dumbbell shape is image of degraded part which is an anisotropic image. It is clear from image that Phosphorene degradation rate in Oxygen is anisotropic. (b) Etching rate of different planes (directions). Different angles in the plot represent different directions, 0° is corresponding to [001] while 306° corresponds to [101] plane, 54° is corresponding to [-101] while 270° corresponds to [100] plane. It is clearly seen that [001] plane has maximum etching rate, as studies computationally as well.

C. Impact of Light Exposer and Laser Power

Investigation has been done under different laser power in ambient and N_2 rich environment using Raman and Photoluminescence (PL) spectra (Fig. 5). Raman peak first decreases with increase in laser power in ambient condition while it increases consistently in N_2 rich environment. Initial peak reduction is due to dominance of degradation, which is overtaken by laser power later. PL peak always increases with

increase in laser power, peak intensity is always higher and narrower in N_2 rich environment than in ambient condition.

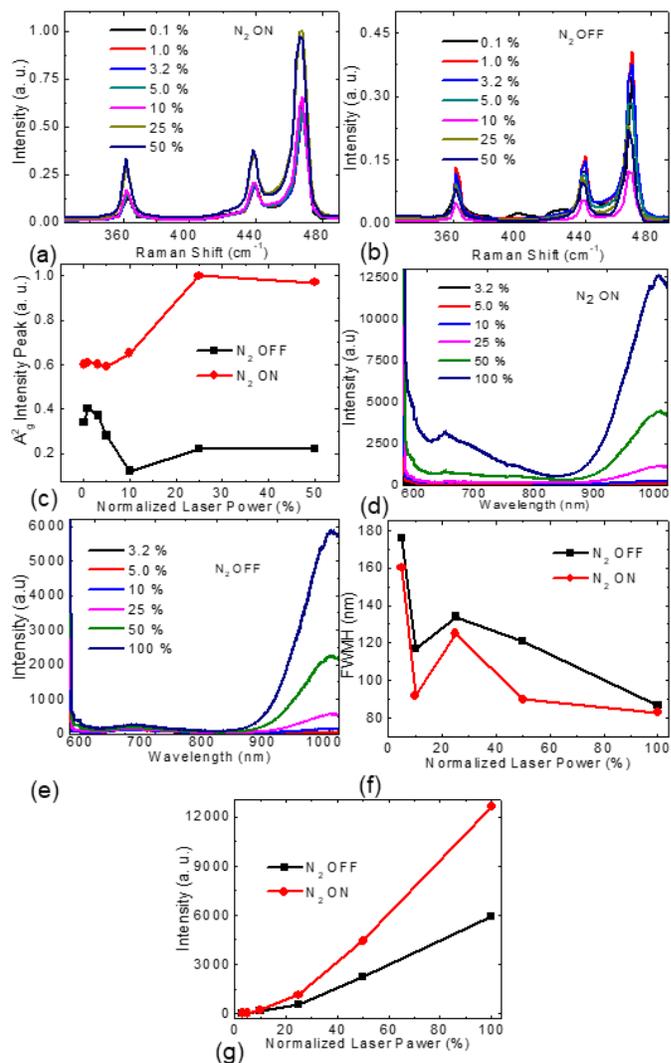


Figure 5: Study of Phosphorene degradation with laser power density. Raman spectra of Phosphorene under different laser power in (a) N_2 rich, (b) ambient, environment. (c) A_2g peak intensity with laser power. Photoluminescence (PL) spectra under different laser power in (d) N_2 rich, (e) ambient, environment. (f) FWHM of individual PL peak, (g) PL peak intensity (985 nm), under different laser power density in N_2 rich and ambient condition. In ambient condition, Raman peak first decreases followed by increases with increase in laser power while it increases consistently in N_2 rich environment (a-c). PL peak increases with increase in laser power, peak intensity is always higher and narrower in N_2 rich environment than in ambient condition (d-g).

D. Voltage Bias Enhanced Degradation

Phosphorene Field effect transistor (FET) has been investigated by Raman scanning in channel region under back gate bias (Fig. 6). The Raman peaks are almost constant under negative gate bias (Fig. 6a and 6c) while they decrease consistently (Phosphorene degrades fast) with time under positive gate bias (Fig 6b and 6d). FET channel has excesses electron in the channel under positive gate bias. These excess electrons can enhance oxidation of Phosphorous by Oxygen which causes fast degradation of Phosphorene. In negative

gate bias, the channel has excess hole which slows down the oxidation process and makes the Phosphorene FET relatively inert to ambient exposure. Corresponding photo response (Fig 6e and 6f) has also shown fast degradation of phosphorene FET under positive gate bias. On the other hand, it shows that the degradation accelerates with light only above a certain power, possibly due to increased phonon population by laser heating. These findings show presence of electrons to be the necessary condition for Phosphorene degradation.

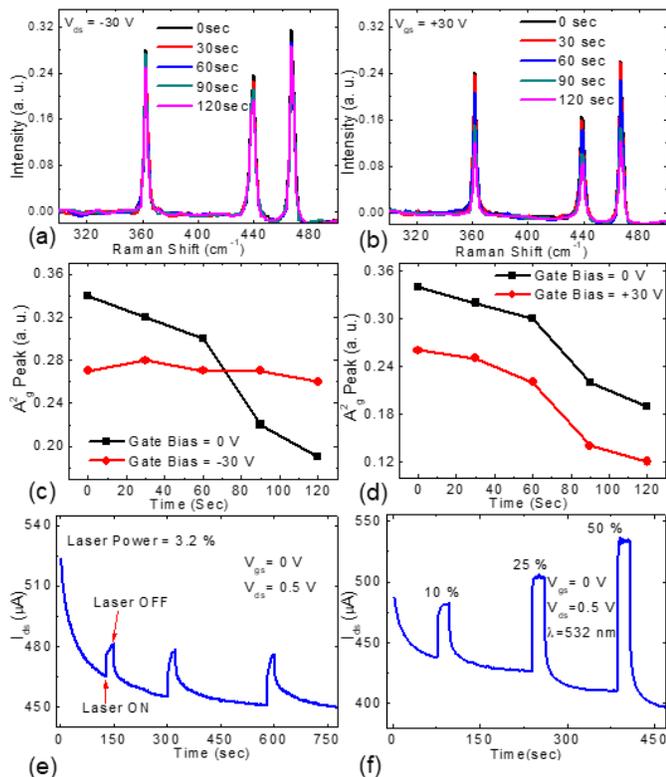


Figure 6: Degradation study under different gate bias voltage: Raman spectra of Phosphorene FET at different time under (a) -30 V, and (b) +30 V gate bias. A_2^g peak comparison between (c) zero and negative gate bias, and (d) zero and positive gate bias. (e) Photocurrent with constant laser power under zero gate bias, (f) Photocurrent with variable laser power under zero gate bias. Raman peaks are almost constant with time in negative gate bias (a,c) while they decay with time in positive gate bias (b, d). A_2^g peak is lower under positive than zero gate bias (d). Phosphorene degrades relatively fast in positive gate bias, but it is relatively inert in negative gate bias. Photo response of the FET is also analyzed under different laser power. The dark current decreases with time, photo current initially rise fast and then slow under laser illumination. When the illumination is OFF, the current does not fall back to its dark value immediately rather a slow exponential decay of current is observed which could be due electron trapped by trap states due to dangling bond created during phosphorene degradation.

IV. CONCLUSION

We have found that O_2 is responsible among major ambient atmospheric gases (N_2 , O_2 , Ar, CO_2 and H_2O) for Phosphorene degradation initiation in ambient condition. We have also seen that the degradation rate is anisotropic, which is maximum along [001] plane and minimum along [010] plane among the studied, [001], [100], [010], [-101] and [101] planes. Positive gate bias accelerates Phosphorene degradation due to enhanced oxidation by gate bias induced

electron in the Phosphorene FET channel while negative gate bias mitigates degradation due to presence of holes in the channel. These results show that while exposure to O_2 dominates the degradation, it is catalyzed by the phonon and electron population.

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