Direct Growth of $\text{Al}_2\text{O}_3$ on Black Phosphorus by Plasma-Enhanced Atomic Layer Deposition

B. B. Wu$^{1,2}$, H. M. Zheng$^2$, Y. Q. Ding$^{1\ast}$, W. J. Liu$^{2\ast}$, H. L. Lu$^2$, P. Zhou$^2$, L. Chen$^2$, Q. Q. Sun$^2$, S. J. Ding$^2$ and David W. Zhang$^2$

Abstract

Growing high-quality and uniform dielectric on black phosphorus is challenging since it is easy to react with O$_2$ or H$_2$O in ambient. In this work, we have directly grown $\text{Al}_2\text{O}_3$ on BP using plasma-enhanced atomic layer deposition (PEALD). The surface roughness of BP with covered $\text{Al}_2\text{O}_3$ film can reduce significantly, which is due to the removal of oxidized bubble in BP surface by oxygen plasma. It was also found there is an interfacial layer of PO$_x$ in between amorphous $\text{Al}_2\text{O}_3$ film and crystallized BP, which is verified by both X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) measurements. By increasing temperature, the PO$_x$ can be converted into fully oxidized P$_2$O$_5$.

Keywords: Black phosphorus, Plasma-enhanced atomic layer deposition, Oxygen plasma, $\text{Al}_2\text{O}_3$

Background

Two-dimensional (2D) semiconductor materials, such as graphene [1, 2], MoS$_2$ [3, 4], WSe$_2$ [5], WS$_2$ [6], MoTe$_2$ [7, 8], SnSe$_2$ [9], and black phosphorous (BP) [10–18], have been widely studied for the potential applications in the next generation devices including field emitters [10–12], gas sensors [13, 14], solar cells [17], field-effect transistors [18], optoelectronics [19], and light-emitting diodes [20]. Among these 2D materials, BP is found to be more thermodynamically stable under the ambient conditions [14]. BP is an anisotropic lamellar semiconductor and has a direct band gap of $\sim$0.3–1.5 eV from the bulk to monolayer structure [21–25]. BP transistors also have high carrier mobility up to 1000 cm$^2$/(V·s) at room temperature, on/off current ratio over $10^4$ [18, 26]. Thus, BP may be a promising candidate for electronic and optoelectronic device applications [27]. However, exfoliated BP films will degrade in the air ambient owing to the possible reactions between BP and the adsorbed water and oxygen, thus leading to a significant reduction of BP carrier mobility and on/off current ratio [27, 28]. Therefore, efficient and reliable isolation/passivation layers are necessary for BP to preserve its inherent structure and property.

So far, many efforts on passivation for BP have been made, such as an encapsulation layer for BP with boron nitride ($\text{h-BN}$) [29–33], creating saturated P$_2$O$_5$ on BP surface [34–36], atomic layer deposited dielectric capping [27, 37–40]. Nevertheless, $\text{h-BN}$ passivation requires complicated environmental conditions and has extremely low yield [29–33]. The P$_2$O$_5$ which was created on BP surface provides only the short-time protection since the oxygen and moisture in the air can erode it slowly [34–36]. It is also quite tough for atomic layer deposition (ALD) to form a high-quality and uniform top dielectric film on BP because of no dangling bonds. Therefore, it is important to prevent BP-based devices from degradation in the air ambient by covering a protective oxide dielectric. Moreover, uniform and reliable dielectrics are also essentially needed for the top-gate BP devices.

In this work, uniform $\text{Al}_2\text{O}_3$ was directly grown on BP flakes using plasma-enhanced atomic layer deposition (PEALD) with the help of O$_2$ plasma as an oxygen...
**Fig. 1** (a) Optical microscope image of the BP sample acquired by Raman measurements. (b) Raman spectra of pristine BP for different exposure time. All Raman measurements were done in the air ambient with the same laser excitation.

**Fig. 2** (a-f) Optical images of accelerated BP degradation on SiO$_2$/Si exposed to air for different time. (g-i) AFM images of BP flake exposed to the air ambient for 2, 3, and 4 h. All three BP samples for AFM measurements were taken from the same batch. The average thickness of BP in (g-i) was 130 nm. (j) The average RMS roughness of BP samples versus the exposure time, the same samples as shown in (g-i).
precursor, instead of H₂O, to react with trimethylaluminum (TMA) [41]. The composition and properties of the interfacial layer between Al₂O₃ and BP have been examined by physical characterizations, and the mechanisms behind are analyzed.

**Methods**

Few-layer BP (purity: 99.998%, Smart Elements) was transferred onto a Si substrate with thermally grown 285 nm SiO₂ using a micromechanical method with polydimethylsiloxane (PDMS) [1, 28, 42]. Prior to transfer, the SiO₂ surface was ultrasonically cleaned in turn by acetone and isopropyl alcohol (IPA) and piranha solutions for 10 min each, followed by 100% O₂ annealing at 500 °C for 3 min using rapid thermal annealing (Annealysys As-One). The optical images of BP were acquired by an optical microscope (BA310Met, Motic) equipped with a camera. Raman spectroscopy measurements were performed using LabRam-1B (the Raman spectral resolution was 1.1 cm⁻¹) with an excitation wavelength of 532 nm at room temperature in the air ambient. The laser power was maintained at around 0.5 mW to prevent any heating-induced damage during the measurement. Al₂O₃ films on BP were deposited using PEALD with O₂ plasma and TMA precursors at different temperatures. The freshly exfoliated BP samples were transferred to Picosun 200R ALD chamber (the vacuum pressure was 12 hPa). PEALD of Al₂O₃ was carried out with successive cycles of O₂ plasma and TMA precursors, with an Ar carrier gas (99.9997%, Airgas) at a flow rate of 300 sccm, 15 s pulse + 10 s Ar purge time for O₂ plasma (The O₂ plasma RF Power was 2000 W), 0.1 s pulse + 5 s Ar purge time for TMA (the precursor temperature was 18 °C) at a substrate temperature of 200 °C. The surface and interfacial properties of Al₂O₃ on BP were physically characterized using atomic force microscopy (AFM, Dimension Edge, Bruker), XPS (AXIS ULDLDTRA, Shimadzu), and TEM (Tecnai G² F20 S-TWIN, FEI) measurements at room temperature.

**Results and Discussion**

Figure 1a shows the optical image of transferred BP sample prepared by mechanical exfoliation from its bulky crystalline. The Raman spectra of thin-layer BP, as denoted by a red circle in Fig. 1a, were examined as a function of exposure time in the air ambient at room temperature, as shown in Fig. 1b. It is noted that all Raman spectra measured in Fig. 1b are calibrated using a Si peak of 520 cm⁻¹. It can be clearly seen one out-of-plane modes (A1g) and two in-plane modes (A2g and B2g) in thin-layer BP [43]. Both A2g and B2g peak positions keep almost unchanged. While for A1g mode, it has redshifted as the exposure time goes up to 30 min and then seems to be stable up to 20 h. This may be attributed to the oxidation of surficial BP in the initial stage and a relatively saturation of oxidation up to 20 h. This is evidenced by the time evolution of BP surface morphology examined by optical microscopy, as shown in Fig. 2a–f. It was markedly observed that BP flake exposed to the air ambient degrades as the exposure time extended and then exhibited a fare rough BP surface with bubbles, as presented in Fig. 2d–f. Figure 2g–i shows AFM images of exfoliated BP flake exposed to the air ambient for 2, 3, and 4 h, respectively. All three BP samples for AFM measurements were taken from the same batch and their RMS roughness is summarized in Fig. 2j. The RMS roughness of BP surface increases as the exposure time increases, indicating the formation of oxidative phosphorus species.

![Figure 3](image-url)  
Fig. 3 RMS roughness of BP samples before and after PEALD deposition at various temperatures. For each deposition temperature, more than five samples were measured for an accurate assessment.

| Temperature (°C) | The average roughness (before/after) (nm) | Standard deviation (before/after) (nm) |
|-----------------|------------------------------------------|---------------------------------------|
| 150             | 8.33/1.20                                | 0.46/0.76                             |
| 200             | 6.13/2.52                                | 0.16/1.80                             |
| 250             | 7.55/1.66                                | 0.71/0.24                             |
| 300             | 7.95/3.56                                | 3.34/2.73                             |
| 350             | 11.05/2.63                               | 7.10/1.44                             |
variations; however, the RMS reduces to ~3 nm after 100 cycles Al$_2$O$_3$ deposition. This infers that O$_2$ plasma as an oxygen precursor can effectively etch the oxidized bubbles in the top-layer BP thin film, thus leading to a significant reduction of RMS, while H$_2$O as an O source may not have this benefit (discuss later).

To understand the impact of the pretreatment of O$_2$ plasma and different oxygen precursors on Al$_2$O$_3$ growth in freshly exfoliated BP samples, Al$_2$O$_3$ deposition on BP was realized by three approaches: (1) 20 cycles O$_2$ plasma pretreatment + 100 cycles TMA/O$_2$ plasma, (2) 100 cycles TMA/O$_2$ plasma, and (3) 100 cycles TMA/H$_2$O, as shown in Fig. 4a, b, and c, respectively. Figure 4a, b depicts AFM images of the 100 cycles Al$_2$O$_3$ grown on BP samples by PEALD with and without an oxygen plasma pretreatment, respectively. Using PEALD for Al$_2$O$_3$ growth in BP flakes, it has demonstrated a highly uniform surface morphology of Al$_2$O$_3$/BP. The average RMS roughness of Al$_2$O$_3$/BP samples prepared by PEALD is only 0.4 nm regardless of an oxygen plasma pretreatment, as shown in Fig. 4a, b. For freshly exfoliated BP samples, PEALD (with and w/o pretreatment) can achieve a good uniformity and coverage of Al$_2$O$_3$ films. While for BP samples exposed to the air ambient for certain time, 4 h for example, PEALD with O$_2$ plasma pretreatment is much preferred. O$_2$ plasma pretreatment can create enough nucleation sites for ALD growth. On the other hand, it also has an “etching” effect for thinning BP samples. O$_2$ plasma may penetrate the PO$_x$ layer and oxidize the underlying BP, then increase the thickness of PO$_x$ layer [35]. On the contrary, Al$_2$O$_3$ films on freshly exfoliated BP grown by ALD with H$_2$O as an oxygen precursor nucleate to an isolated “island” and exhibit a remarkable nonuniform surface profile, resulting in a large RMS roughness of 0.8 nm, as shown in Fig. 4c. It is attributed to the insufficient dangling bonds or nucleation sites in BP surface for ALD growth with H$_2$O as an oxygen precursor [37]. It is worthwhile to mention that BP flake was covered uniformly by Al$_2$O$_3$ film and can prevent O$_2$ or H$_2$O in

Next, chemical analysis of the interfacial characteristics near BP film was examined by XPS characterizations. Figure 5 shows photoelectron spectroscopy measurements of the P 2p core level at different deposition temperatures. Middle and top panels present
the P 2p core level after growth of 100 cycles Al2O3 by PEALD at 250 and 350 °C, respectively. The peaks which labeled as P1a and P1b correspond to P-P bonds. The phosphorus core level contains only the characteristic doublet representing the P 2p3/2 (P1a) and P 2p1/2 (P1b) orbitals with peak positions of 130.06 eV and 130.92 eV, respectively, consistent with the report [34]. Two peaks of P2 and P3 were observed at 134.07 and 135.03 eV, corresponding to the POx and P2O5, respectively, as shown in the middle panel. It can be seen that the POx peak locates at 134.07 eV, smaller than that of reported P2O5 (134.2 eV) [44], which may be caused by less O concentration in the interfacial POx layer. The P3 represents the most dominant oxide component and appears at 135.03 eV, in good agreement with the reported P2O5 binding energies which are between 135.0 eV [45] and 135.15 eV [37]. When the temperature goes up to 350 °C, interestingly, P2 peak disappears. This is due to the conversion from POx to P2O5 with the help of reactivity of O2 plasma at high temperatures. However, there is no P3 peak for natively oxidized BP at room temperature and its peaks of P1a; P1b and P2 locate at 130.06 eV (P 2p3/2), 130.87 eV (P 2p1/2), and 134.05 eV, respectively. The absence of P3 peak is due to low temperature or insufficient exposure time for the formation of fully oxidative top layer, which may prevent POx from converting into P2O5 film.

Finally, the interface properties of Al2O3/BP samples were also characterized by TEM measurements. It can be clearly seen for Fig. 6a that the interfacial POx layer between Al2O3 and BP was formed during PEALD process with the 20 cycles O2 plasma pretreatment. Figure 6b shows high-resolution TEM (HRTEM) image of the Al2O3/BP sample after the deposition of 100 cycles Al2O3, same scanned region marked by a red square in Fig. 6a. The thickness of POx and Al2O3 is 6.1 and 10.7 nm, respectively. It is worth noting that Al2O3 and POx film is amorphous, while our BP sample is single crystalline which is verified by results of selected area electron diffraction (SAED) pattern, as seen from Fig. 6c. This interfacial layer POx was evidenced by TEM results, indicative of O2 plasma penetrating into POx layer and reacting with underlying BP.

Conclusions
In summary, we have demonstrated the direct growth of Al2O3 film on BP by using PEALD. The A1g peak of freshly exfoliated BP sample shifts downwards owing to the formation of POx in the BP surface. The uniform Al2O3 film on BP can be achieved by PEALD with O2 plasma and TMA precursors, which may be attributed to the etching and reactivity of O2 plasma with BP at high temperatures. The interfacial layer of POx between Al2O3 and BP was converted into P2O5 as the deposition temperature increases to 350 °C, revealed by XPS characterizations. These findings provide insightful information on passivation and top-gate dielectric integration for future applications in BP devices.

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Authors’ Contributions
BBW and HMZ carried out the BP fabrication and Al2O3 growth and measurements. YQD and WJL supervised the work and drafted the manuscript. HLL, PZ, LC, QQS, SJD, and DWZ helped to analyze the experimental results. All authors read and approved the final manuscript.

Competing Interests
The authors declare that they have no competing interests.

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