Black Phosphorus N-Type Field-Effect Transistor with Ultrahigh Electron Mobility via Aluminum Adatoms Doping

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Owing to the absence of an energy gap in graphene, 2D layered materials (2DMs) such as transition metal dichalcogenides (TMDC), boron nitride, and black phosphorus (BP) are being investigated intensively due to their appealing electronic, optoelectronic, and mechanical properties.[1-28] Among other 2DMs, BP shows superior carrier transport properties that hold promise for nanoelectronic device applications because of its much higher mobility as compared to that of TMDC.[29] For bulk BP single crystal, the impressive electron and hole mobilities reaching ~15 000 and ~50 000 cm² V⁻¹ s⁻¹, respectively, have been reported.[6] In addition, unlike graphene, the presence of a tunable bandgap ranging from 2.0 eV for monolayer to 0.3 eV for bulk BP[7] allows the achievement of high on/off ratio over graphene transistors.[1,2] To date, various top-gated and bottom-gated BP-based field-effect transistors (FETs) utilizing different gate dielectrics such as SiO₂, HfO₂, and Al₂O₃ have been reported.[12-21] Although p-type BP FET with mobility up to ~1000 cm² V⁻¹ s⁻¹ has recently been experimentally demonstrated,[7] the complementary n-type BP FET is rarely reported due to the lack of a controllable n-type doping technique. Until now, only a few previous reports were dedicated to the experimental demonstration of conductance conversion from pristine p-type BP into n-type by employing Al contacts.[12,13] Cu adatoms diffusion,[14] and surface functionalization by Cs₂CO₃,[15] respectively.

In recent work, Koenig et al. demonstrated electron doping of ultrathin BP using Cu adatoms, which realizes n-type BP FET with electron mobility reaching ~380 cm² V⁻¹ s⁻¹.[14] Such metal adatoms doping technique is perceived to be superior over the surface electron donation from Cs₂CO₃, as its low mobility would reduce the effectiveness of electron transfer into the BP channel. However, Cu adatoms have a large atomic size of 2.7 Å that is deemed challenging to diffuse into the BP lattice and could potentially result in crystal defects. Additionally, the Cu doping was performed using a transient one-second sputtering, which comes with limited controllability of the Cu impurity concentration. For enabling practical device applications, there is a compelling need to develop a simple and controllable doping technique that can tune the electronic properties of BP for enabling conductivity type control. Moreover, to achieve device performance optimization, it is fundamentally important to gain an insight into its carrier transport properties especially for n-type BP FET, where the mechanisms are not well understood.

Here, we report on a novel aluminum (Al) adatoms doping that enables the realization of complementary n-FETs in few-layer BP, which achieved a record high electron mobility of >1495 cm² V⁻¹ s⁻¹ at 260 K. The incorporation of Al-adatoms in the few layer BP channel has been found to transform the pristine p-type conductivity of BP into n-type. We perform first-principles calculations, which reveal Al-adatoms as effective electron donors that shift the Fermi level into the conduction band, thereby inducing an n-type conductance in the Al-phosphorene system. We further conduct a carrier transport study that shows clear evidence of charged-impurity scattering at low temperature, where the incorporated Al can act as localized sites for 2D Mott variable range hopping transport. At high gate voltage, metallic-like conduction is observed and corroborated to enhanced electron–phonon interactions, which confirms the origin of phonon scattering at high temperature.

To understand the effect of Al-doping, theoretical electronic structure of Al-doped phosphorene was calculated by first-principles calculations within the density functional theory (DFT) framework. Details of the calculations are described in the Experimental Section. We found that Al adatoms at both the surface adsorbed site and the intercalated site would donate electrons to the host phosphorene, which induces n-type conductance in the Al-phosphorene system.

As shown in Figure 1a, the Al atom locates at about 1.60 Å above the monolayer sheet and forms three covalent Al–P bonds (two of 2.68 Å and the other of 2.60 Å) by connecting the two neighboring zigzag phosphorus chains. The Al adatom is strongly absorbed by the phosphorene with a binding energy of ~2.04 eV (calculated via $E_b = E_{\text{Al} + \text{phosphorene}} - E_{\text{Al}} - E_{\text{phosphorene}}$), leading to a significant distortion of the phosphorene lattice (Figure 1b). The new Al–P bonds result in tension strain up to 2.11% and compressive strain up to
−1.35% of the phosphorene lattice around the Al dopant atom. Because of the puckered structure of phosphorene, the strain field is anisotropic, attenuates slower in the zigzag direction than along the armchair direction. As shown in Figure 1b, the strain field triggers a broadening of the peaks of the P–P bond length distribution. Figure 1c,d shows the electronic band structures and the corresponding density of states (DOS) of the pristine and Al-doped phosphorene, respectively. Comparing with the Fermi level for pristine phosphorene that is in the middle of the bandgap, the Fermi level in Al-doped phosphorene shifts upward into the conduction band, or in other words, the Al adatom can act as an effective electron donor in the Al-phosphorene system, and a hybridized state forms between Al and phosphorus atoms in the conduction band crosses the Fermi level. In the case of a multilayer system where the Al adatom is intercalated between two phosphorene layers, we further confirm that the Fermi level is also shifted upward into the conduction band, thereby transforming the p-type conductivity of pristine BP into n-type. Moreover, the incorporation of Al adatoms in phosphorene has also been theoretically calculated to result in a higher Al–P binding energy ($E_b = −2.18$ eV) as compared to the weak van der Waals interactions between P–P bond, thus leading to thermal stability improvement.[27] This can be evidenced by the significantly improved thermal coefficients of $A_{1g}$, $B_{2g}$, and $A_{2g}$ phonon modes by two orders of magnitude as compared to the pristine phosphorene.

Next, we move on to experimentally demonstrate the Al-doped BP n-FET using a low temperature fabrication flow as described in Figure 2a. After exfoliation of BP onto p+-Si/SiO$_2$ substrate, the sample was immediately transferred to the atomic layer deposition (ALD) chamber where trimethylaluminum (TMA) precursor was pulsed at a low substrate temperature of 120°C. This resulted in the incorporation of Al-adatoms into the BP channel, which altered the p-type conductivity of pristine BP into n-type. It is important to note that this method is simple and involves ALD, which offers better controllability of the Al doping in a homogenous BP nanosheet. Further details of the sample preparation and device fabrication are described in the Experimental Section. The final device structure of the BP n-FET and its biasing condition are schematically shown in Figure 2b. The atomic force microscope (AFM) image of the BP n-FET together with the S/D electrodes made of Ti/Au is depicted.
in Figure 2c. A high resolution cross-sectional transmission electron microscopy (TEM) image confirms a thickness uniformity of ≈5 nm as well as good interface properties with the underlying SiO$_2$ gate dielectric (Figure 2d). It also explicitly shows the layered crystal structure of the few-layer BP, which was encapsulated by a ≈20 nm Al$_2$O$_3$ passivation layer. By employing energy dispersive X-ray (EDX) spectroscopy, the Al adatoms depth profile in BP can be obtained (Figure 2e). The incorporation of Al adatoms is found to be responsible for the conductivity change from p- to n-type where electrons become the dominant carriers. The spatially controlled Al doping was found to peak at the Al$_2$O$_3$/BP interface and decrease along the BP thickness toward the BP/SiO$_2$ interface. We further confirm that in a multilayer system where Al adatoms are intercalated between two phosphorene layers, the Fermi level is also shifted upward into the conduction band. This is well corroborated to the experimental results demonstrated in this work, in which Al adatom remains an effective electron donor that transforms the pristine p-type BP into n-type conduction.

To study the effect of Al-adatoms on the electrical performance of BP n-FET, detailed measurements were carried out in a closed cycle cryogenic vacuum probe station with a pressure of ≈10$^{-6}$ mbar. Figure 3a shows the comparison of transfer curves ($I_D-V_G$) for both pristine and Al-doped BP FETs. Conspicuously, the dominant n-type conduction behavior is attributed to the Al-adatoms doping, which can be explicitly seen with higher drain current ($I_D$) at positive gate bias (+$V_G$). Figure 3b shows the temperature dependent conduction curves ($G$–$V_D$) of the Al-doped BP n-FET measured at an increasing cryogenic temperature from 30–265 K. The device was functional at all temperatures, which confirms its thermal stability and robustness. It was also observed that the device demonstrates a high ON current ($I_{ON}$) to OFF current ($I_{OFF}$) ratio of >10$^3$ at <120 K and remains >10$^5$ even at 260 K (Figure 3c). It is worthy to note that a low OFF current on the order of sub-10$^{-10}$ A was measured at low temperature (<120 K) and only slightly increased to a few nA at a higher temperature of 260 K, showing good electrostatic control of the source-to-drain leakage current due to an ultrathin BP channel.

Figure 3d plots the field-effect mobility ($\mu$) as a function of temperature ($T$) calculated from the $G$–$V_D$ curves after decoupling the S/D contact resistance estimated by assuming a fully conducting channel at very high $V_D$ from the $G$–$V_D$ curve.$^{[28]}$ The field-effect mobility ($\mu$) of the BP n-FET can be calculated based on the equation$^{[5]}$ $\mu = \frac{dG}{dV_D} \times \frac{L}{W} \times \frac{W}{(\varepsilon_0_e \varepsilon_r d)}$, where the channel length ($L$) is 2 μm, the channel width ($W$) is 2 μm, the relative permittivity ($\varepsilon_r$) is 8.854 × 10$^{-12}$ Fm$^{-1}$, the dielectric constant for SiO$_2$ ($\varepsilon_0$) is 3.9, and the thickness of SiO$_2$ gate dielectric ($d$) is 300 nm. As can be seen, the $\mu$ peaks at a value of >2150 cm$^2$V$^{-1}$s$^{-1}$ at ≈120 K and remains at a fairly high value of >1495 cm$^2$V$^{-1}$s$^{-1}$ even at 260 K. This is believed to be the record high field-effect mobility as compared to other BP n-FET reported in the literature.$^{[12,14–16]}$ Comparing to the Al contact work,$^{[12]}$ a better device performance is achieved using Al adatoms due to an improved channel conductance and a reduced contact resistance as a result of electron doping under the metal electrode, which would lower the Schottky barrier height. Our carrier transport analysis reveals that the mobility was corroborated to charged-impurity and phonon scattering at low and high temperature, respectively. An increase in carrier mobility is observed when the temperature is increased up to 120 K.
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Such a transport behavior shows good agreement with the mobility limited by charged-impurity scattering, which depends on the speed of the carriers and the concentration of the ionized impurity. This is because when temperature increases, the average thermal speeds of the carriers are also increased. Hence, the carriers spend less time near the ionized impurity and thus the scattering effect of the ions is reduced, which concomitantly leads to higher mobility. However, a further increase in temperature above 120 K has been shown to result in a suppression of mobility from the peak value due to phonon scattering limited transport, which follows a power law dependence $\mu \propto T^{-\gamma}$, where the exponent $\gamma$ depends on the dominant phonon scattering mechanism. A $\gamma$ value of $\approx 0.5$ was extracted from the fit to this part of the curve, which is comparable to that reported in pristine BP p-FET that has a $\gamma = 0.5$.\[7\]

To understand the mechanism, a comprehensive carrier transport investigation was performed. Figure 3a shows the conductance ($G$) as a function of temperature ($T$) at various gate voltage ($V_g$). The $T$- and $V_g$-dependent $G$ for the BP n-FET clearly shows the different transport mechanism with semiconducting behavior observed in the lower temperature regime ($80 < T < 200$ K) and at low $V_g < 35$ V, as evidenced by the increase in conductance with temperature. On the contrary, metallic-like behavior is observed at high $V_g > 35$ V and high temperature ($T > 200$ K), as shown by the reduction in $G$ with increasing $T$. Notably, for $80 < T < 200$ K, the $T$-dependent $G$ agrees well with the 2D Mott variable range hopping (VRH) model where the variation of $GT^{0.8}$ weakens with decreasing temperature ($T > 200$ K), as shown by the reduction in conductance at high $V_g > 35$ V. It is noted that the temperature variation of $G$ in this low gate voltage regime can be fitted linearly, which shows good agreement with the above model. This implies that the incorporated Al can act as the localized trap sites in the BP channel, which accounts for the VRH conduction that dominates in this temperature range. However, when the temperature increases beyond $T > 200$ K, there is an observable deviation from the linear fit to the $\mu T^{0.8}$ versus $(1/T)^{1/3}$ plot, which implies a change in the carrier transport mechanism, as shown in Figure 3c.

Interestingly, the carrier transport mechanism in the high temperature regime ($T > 200$ K) demonstrates a clear dependence on the applied gate voltage $V_g$. A thorough analysis of the $G-T$ curves reveals two distinct mechanisms under both low and high $V_g$. Figure 4d plots the semilog plot of $G$ as a function of $1/T$ for low $V_g < 35$ V. It is noted that the temperature variation of $G$ in this low gate voltage regime can be modeled with thermally activated transport that follows the Arrhenius law\[25,26\] $G = G_0(T)e^{-E_a/RT}$, where $E_a$ is the

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**Figure 3.** a) Comparison of the transfer curves for pristine and Al-doped BP FETs explicitly shows the dominant n-type conduction behavior in the Al-doped device. b) Conduction curves ($G$) versus gate voltage ($V_g$) measured at different cryogenic temperatures ranging from 30 to 265 K, showing stable device operation. c) OFF current and ON/OFF current ratio as a function of operation temperature. A high ON/OFF ratio of $\approx 10^5$ was achieved at $120$ K and remained $>1$ up to $260$ K. A low OFF current on the order of sub-$10^{-10}$ A was also measured at low temperature ($<120$ K and increases to only few nA at higher temperature ($260$ K). d) Field-effect mobility ($\mu$) dependence on operation temperature ($T$). A record-high $\mu$ of $>1495$ cm$^2$V$^{-1}$s$^{-1}$ was achieved at $260$ K. At low temperature (below $120$ K), a decrease in the mobility is observed as the temperature is lowered to $\approx 30$ K, showing good agreement with the mobility limited by charged-impurity scattering. Increasing the temperature above $120$ K has resulted in a suppression of mobility from the peak value due to phonon scattering limited transport, which follows a power law dependence $\mu \propto T^{-\gamma}$, where the exponent $\gamma$ depends on the dominant phonon scattering mechanism. A $\gamma$ value of $\approx 0.45$ was extracted from the fit to this part of the curve, which is comparable to the pristine BP p-FET that has a $\gamma = 0.5$.\[7\]

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activation energy, $k_B$ is the Boltzmann constant, and $G_o(T)$ is the temperature-dependent parameter extracted from the fitting curves. The good agreement of data fitting with the activation transport model suggests that the carrier transport is thermally activated at $T > 200$ K. Figure 4e plots the calculated activation energy ($E_a$) values, which show a linear

**Figure 4.** a) The conductance ($G$) as a function of $1/T$ at various $V_g$ of the BP n-FET. The $T$-dependence on $G$ at various $V_g$ clearly shows the different carrier transport mechanism of semiconducting and metallic-like. b) $G^{0.8}$ versus $(1/T)^{1/3}$ curves for $V_g < 30$ V and corresponding linear fit shows good agreement with 2D Mott VRH model for a temperature range of 80 K $< T < 200$ K. c) $\mu T^{1.8}$ versus $(1/T)^{1/3}$ plot of the fabricated BP n-FET shows deviation from 2D Mott’s VRH for $T > 200$ K, suggesting other transport mechanism (as marked by arrow). d) Semilog plot of conductance versus inverse of temperature for $V_g < 30$ V. The fitting data (lines) show good agreement with the thermal activation transport for $T > 200$ K. e) Carrier activation energies ($E_a$) calculated from the slope of curves in panel (d) as a function of gate voltage. Linear dependence of $E_a$ with $V_g$ can be observed. f) The dependence of conductance ($G$) on temperature ($T$) for $V_g > 35$ V. Metallic-like conduction behavior is observed as $G$ decreases with increasing $T$. 

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decrease with increasing $V_g$ except for $V_g > 15$ V. Similar carrier transport behavior was also observed in the monolayer MoS$_2$ FETs, in which thermally activated transport also dominates at higher temperature. However, for higher $V_g > 35$ V and high $T > 200$ K, the transport behavior shows a deviation as evidenced by the variation in conductance at higher temperature (Figure 4f). It is worthy to note that $G$ decreases monotonically with increasing $T$ at higher $V_g$, confirming the presence of a metallic-like carrier transport. In other words, enhanced electron–phonon interaction is expected in this temperature regime due to an increased carrier density, as induced by the high gate electric field. The increase in temperature further promotes carrier generation and results in a more pronounced decrease in the BP conductance where electron–phonon scattering becomes the dominant scattering mechanism at higher temperatures. In summary, high-performance few-layer BP n-FETs were demonstrated via a novel Al-adatoms doping technique that achieved a record-high mobility of $>1495$ cm$^2$V$^{-1}$s$^{-1}$ at 260 K. The EDX depth profile confirms the incorporation of Al in the few-layer BP channel. First-principles calculations prove the effectiveness of Al-adatoms as electron donors that lift the Fermi level into the conduction band, thereby transforming the predominantly p-type conductivity of BP into n-type. Carrier transport analysis reveals the suppression of electronic mobility to charged-impurity scattering at low temperature, where Al can act as localized sites for 2D Mott variable range hopping transport. At high gate bias regime with increased carrier density, metallic-like conduction is observed due to enhanced electron–phonon interactions at high temperature. This work demonstrated a viable route to realize complementary n-type FET in few-layer BP and provided an insight into its carrier transport mechanism, paving the way toward the development of high-performance BP-based nanoelectronic devices.

### Experimental Section

**Device Fabrication:** Few-layer black phosphorus was mechanically exfoliated from bulk single-crystal BP (purity 99.998%, HQ graphite) onto thermal oxide (300 nm) on a degenerately p-type doped Si substrate. The exfoliation was performed in an argon-filled glovebox with an O$_2$ and H$_2$O (concentration less than 1 ppm). After exfoliation, the sample was immediately transferred to the ALD chamber where TMA precursor was pulsed at low substrate temperature (120 °C). The few-layer BP devices were then contacted with thermally evaporated Ti/Au (60 nm/20 nm) that was patterned by standard electron-beam lithography and lift off. Next, a Al$_2$O$_3$ passivation layer (20 nm) was deposited using trimethylaluminum and water precursors in an atomic layer deposition system with vacuum chamber attached to an argon-filled glovebox.

**Computational Details:** Spin-polarized first-principles calculations were performed using the plane wave code VASP (Vienna ab initio simulation package) within the framework of DFT. Both the PBE (Perdew–Burke–Ernzerhof) functional with the projector augmented wave and hybrid functionals (HSE06) are used as the exchange-correlation functional with a cutoff energy of 350 eV. The relaxed lattice constant of the unit cell of monolayer phosphorene is $a = 3.305$ Å and $b = 4.617$ Å. The effect of Al dopant is considered by adsorbing an Al adatom into a 5 × 4 supercell of monolayer phosphorene, together with a vacuum of 15 Å, and a 3 × 3 × 1 MP (Monkhorst–Pack) grid for k-point sampling is adopted. The lattice constant is relaxed until the stress exerted on the cell is less than 0.1 kbar and the force exerted on the atoms are less than 0.01 eV Å$^{-1}$.

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