Few-layer Phosphorene: An Ideal 2D Material For Tunnel Transistors

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2D transition metal dichalcogenides (TMDs) have attracted a lot of attention recently for energy-efficient tunneling-field-effect transistor (TFET) applications due to their excellent gate control resulting from their atomically thin dimensions. However, most TMDs have bandgaps ($E_g$) and effective masses ($m^*$) outside the optimum range needed for high performance. It is shown here that the newly discovered 2D material, few-layer phosphorene, has several properties ideally suited for TFET applications: 1) direct $E_g$ in the optimum range ~1.0–0.4 eV, 2) light transport $m^*$ (0.15 m$_0$), 3) anisotropic $m^*$ which increases the density of states near the band edges, and 4) a high mobility. These properties combine to provide phosphorene TFET outstanding $I_{ON}$ ~ 1 mA/µm, ON/OFF ratio ~ $10^6$ for a 15 nm channel and 0.5 V supply voltage, thereby significantly outperforming the best TMD-TFETs and CMOS in many aspects such as ON/OFF current ratio and energy-delay products. Furthermore, phosphorene TFETS can scale down to 6 nm channel length and 0.2 V supply voltage within acceptable range in deterioration of the performance metrics. Full-band atomistic quantum transport simulations establish phosphorene TFETS as serious candidates for energy-efficient and scalable replacements of MOSFETs.

Metal-Oxide-Semiconductor Field-Effect-Transistors (MOSFETs) have been the workhorse of most modern-day electronics. Although aggressive size scaling of MOSFETs has ushered in an era of ultra-fast miniature electronics, the advantages of scaling are fast disappearing as MOSFETs enter the sub-20 nm regime. In state-of-the-art MOSFETs, direct source to drain tunneling through the channel potential barrier degrades the OFF-state current and causes excessive power dissipation. Tunnel FETs (TFETs) have been proposed to be energy-efficient alternatives to the MOSFET that can reduce the supply voltage ($V_{DD}$) and satisfy the low power requirements in integrated circuits. Although TFETs, in principle, provide a steep OFF to ON transition needed to minimize power dissipation, the ON-currents of TFETs are quite low, which deteriorates their operational speed and energy-delay product. The current level in TFETs is the result of band to band tunneling (BTBT) of carriers, and hence, highly sensitive to the effective masses ($m^*$) and bandgaps ($E_g$) of the channel material. While a small $m^*$ and $E_g$ improve the ON-current ($I_{ON}$) and supply voltage scaling, the same also deteriorate the OFF-current and channel length ($L_{ch}$) scaling through direct source-to-drain tunneling. To meet the simultaneous requirement of the semiconductor industry of both power supply and size scaling, materials need to be carefully chosen with optimized $m^*$ and $E_g$. In this work, it is shown that the newly studied few-layer phosphorene provides the ideal material properties to obtain high performance in TFETs as well as to simultaneously achieve both $V_{DD}$ and $L_{ch}$ scaling.

There are several solutions to the low $I_{ON}$ challenge of TFETs. $I_{ON}$ depends exponentially on $E_g$/$m^*$, and the electric field $F$ at tunnel junction (i.e. log($I_{ON}$) $\propto$ $m^*$/$E_g$). Hence, $I_{ON}$ can be enhanced either by a) increasing $F$ or by b) using a channel material with optimum $E_g$ and $m^*$. A number of approaches for increasing the electric field $F$ were proposed before such as 1) atomically thin 2D channel materials that provide a tight gate control and small tunneling distance, 2) dielectric engineering with high- and low-k spacers, 3) internal polarization in Nitrides.

In addition to having an atomically thin channel that improves $F$, few-layer phosphorene also has the optimum $E_g$ and $m^*$ required for high performance TFETs. Moreover, the bandgap of phosphorene remains direct as the number of layers increases. In this regard, phosphorene has a great advantage over other 2D materials, such as graphene and transition metal dichalcogenides (TMDs). Graphene lacks a bandgap and even with engineered bandgaps, it remains unsuitable for transistor applications. Most monolayer TMDs have a bandgap larger than 1 eV. While the Eg of some multi-layer TMDs may reach below 1 eV, multi-layer TMDs are usually indirect gap materials in which the requirement of momentum change of the carriers by phonons causes very

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low ON-currents. Among TMDs, only WTe2 in 2H phase has a moderate $E_F$ of 0.75 eV, however it suffers from a large $m^*$, and the 2H phase of WTe2 has not been experimentally demonstrated yet. Density Functional Theory (DFT) calculations predict that $E_F$ of phosphorene varies from about 1.4 eV in monolayer to 0.3 eV in bulk. Also, phosphorene has lighter $m^*$ for both electrons and holes of $\sim$0.15 $m_0$. Hence, phosphorene is expected to provide the highest performance among all the 2D material TFETs considered so far.

In a few-layer phosphorene flake, each layer is a hexagonal honeycomb lattice with puckered surface, as shown in Fig. 1a. The electron and hole effective masses $m^*$ are highly anisotropic; $m^*$ is low in the armchair direction ($\approx 0.15 m_0$) and is very high in the zigzag direction ($> 1 m_0$). Since the tunneling probability decreases exponentially with the transport effective mass $m^*$, it is best to have the channel oriented along the armchair direction for high $I_{ON}$. In such a case, the very large $m^*$ in the transverse zigzag direction results in a high density of states near the band edges. This $m^*$ anisotropy ultimately leads to a large $I_{ON}$ as shown later in the paper. The scaling of TFETs to the sub-10 nm regime also require engineering $E_F$ and $m^*$ to keep the ON and OFF state performance intact. However, to achieve this in most conventional materials such as III-Vs, complicated experimental techniques need to be adopted such as application of strain or forming alloys, which can also introduce disorder in the device. In this regard, the layer dependent $E_F$ and $m^*$ in phosphorene already provides an additional knob to optimize the performance for sub-10 nm TFETs, as shown later.

Experimentally, phosphorene flakes as thin as a single layer have been realized recently by means of mechanical exfoliation. The experimental $E_F$ of a single layer phosphorene has been measured to be approximately 1.45 eV which is way higher than the bulk $E_F$ of black phosphorus ($\approx$0.3 eV). Measured few-layer phosphorene carrier mobility is very high in the armchair direction, it is $\approx$256 cm$^2$/Vs for few-layers and $\approx$1000 cm$^2$/Vs for bulk. In addition, strong anisotropy of $m^*$ was verified by angle dependent conductivity. Later, Saptarshi et al. reported experimental measurements of the thickness dependent transport gap and Schottky barriers of phosphorene. However, there are challenges to the development of phosphorene based electronics as well. Few-layer phosphorene is unstable in atmosphere and is prone to humidity and oxygen. Hence, it degrades within several hours when left in air. However, there are many efforts to solve this stability challenge; e.g. Junhong et al. stabilized phosphorene for two months by encapsulating it within Al$_2$O$_3$.

In this work, we performed full band atomistic quantum transport simulations of phosphorene TFETs based on the non-equilibrium Green’s function simulator NEM0S with a second nearest neighbor sp$^3$d$^5$s’ tight-binding (TB) Hamiltonian. The electrostatics of the device is obtained by solving a 3D finite-element Poisson equation self-consistently with the quantum transport equations described in the Methods section. The simulated phosphorene TFET assumes a double gated structure as shown in Fig. 1a. The channel length is 15 nm and the transport direction is oriented along the armchair direction. The source and drain doping levels are set to $10^{20}$ cm$^{-3}$.

Figure 1b,c compare the current-voltage ($I_{ON} - V_{gs}$) and capacitance-voltage ($C_g - V_{gs}$) characteristics respectively of bilayer-phosphorene (2L-phosphorene) with those of WTe2 and WSe2 (which have been identified as the best TMD material candidates for TFETs) for a supply voltage $V_{DD}$ of 0.5 V. 2L-phosphorene provides an inverse sub-threshold slope (SS) much lower than the other two TMDs (well below the Boltzmann limit of 60 mV/dec at room temperature), and provides an $I_{ON}$ of nearly 1 mA/um (about 7.5 times higher than WTe2 in 2H phase). The ON-state capacitance of 2L-phosphorene is also about 5 times lower than that of WTe2. The large $I_{ON}$ and small $V_{DD}$ and $C_g$ translate into a very small switching energy and switching delay for the 2L-phosphorene. The most important metric of performance for low power transistors is the product of the switching energy and the delay (energy-delay product or EDP). The lower the EDP, the more energy-efficient and faster the device is.
2L-phosphorene has 176 times lower intrinsic EDP compared to the best TMD TFET (WTe₂). The origins of these improvements are discussed next.

Figure 2a,b show $E_g$ and $m^*$ in the armchair direction ($m_{ac}^*$) as a function of the number of phosphorene layers extracted from phosphorene bandstructures computed with the atomistic tight-binding model of this work. In ref. 7, optimum $E_g$ and $m^*$ values needed to maximize $I_{ON}/I_{OFF}$ in TFETs were presented for various supply voltages and channel lengths $L_{ch}$. It was suggested that for $L_{ch}=15$ nm and $V_{DD}=0.5$ V, $E_g$ and $m^*$ need to be roughly about 0.7 V and 0.15 $m_0$, respectively. It is seen in Fig. 2b that the electron and hole $m^*$ are roughly about 0.15 $m_0$ and do not vary much with the number of layers. While the $E_g$ in Fig. 2a is seen to be strongly dependent on the number of layers, apart from the 1.4 eV value for monolayer phosphorene, $E_g$ is mostly in the range of 0.7 to 0.4 eV, with the optimum value of 0.7 eV reached for 2L-phosphorene. It is to be noted that there is still some experimental discrepancy about the actual values of $E_g$ in phosphorene with transport measurements yielding smaller bandgaps than optical measurements (as also seen in TMDs). DFT and TB calculations used in this work yield bandgaps closer to the transport measurements. Moreover, the bandgap of phosphorene varies about 1 eV from bulk to monolayer which provides a knob to tune $E_g$ to its optimum value by the right choice of channel thickness.

The bandgap alone does not explain why the phosphorene TFET significantly outperforms WTe₂ TFET since 2L-phosphorene has a similar $E_g$ as 1L-WTe₂. The difference actually originates from 2L-phosphorene having a light transport $m^*$ in the armchair direction ($m_{ac}^*$) and a heavy transverse $m^*$ in the zigzag direction ($m_{zz}^*$). This is conveniently illustrated in the complex bandstructure in Fig. 2c, which shows the energy-momentum dispersion of the carriers in the forbidden bandgap connecting the conduction and valence band states. The complex part of the bandstructure corresponds to the evanescent wavefunctions $e^{-iK\cdot r}$ in the bandgap with imaginary momentum $K_y$, and the area enclosed by the imaginary band and the energy axis corresponds to the band to band tunneling (BTBT) decay rate $\kappa$. The smaller the area, the larger is the transmission probability. Figure 2c compares the complex band structure of 2L-phosphorene with 1L-WTe₂. The complex bands are plotted at transverse wave-vector $K_\parallel = 0$ and $0.1\pi/b$ for both materials. 2L-phosphorene not only has smaller BTBT decay rate at $K_\parallel = 0$ due to small transport mass, but also at non-zero $K_\parallel$ due to large transverse $m^*$.
The total gate capacitances ($C_g$) of 1L- to 3L-phosphorene TFETs are shown in Fig. 4 for the same constant electric field scaling discussed before. As expected, the gate capacitances also scale quite well up to $L_{ch}=9$ nm. 2L-phosphorene offers the lowest capacitances. Although the capacitances for the $L_{ch}=6$ nm case are slightly larger than the 9 nm case, asymmetric doping can decrease the capacitance for 2L and 3L, as shown Fig. 4. The gate capacitances predicted here for phosphorene are much less (<10%) than those reported for TMDs. The lower $C_g$ in phosphorene originates from its optimum $E_g$ and $m^*$. The $I_{ds}-V_{gs}$ and $C_g-V_{gs}$ are shifted in voltage axis such that the current at zero gate voltage $I_{OFF}$ is set to 1 nA/um as required by ITRS. TMDs have lower $I_{60}$ currents (the current value where SS becomes 60 mV/dec) which is a result of their higher $E_g$ and $m^*$. This makes 0 gate voltage to be closer to threshold voltage if compared with phosphorene. Accordingly, TMDs operate closer to ON-state which results in a higher amount of charge in channel and a higher $C_g$. In summary, the benefits of optimum $E_g$, small transport $m^*$, and large transverse $m^*$ in phosphorene are two-fold: 1) higher $I_{ON}$, and 2) lower capacitance.

The outstanding $I_{ds}-V_{gs}$ and $C_g-V_{gs}$ characteristics of few-layer phosphorene translate into impressive intrinsic energy-delay products (EDP), which is used ultimately to compare ultra-fast energy-efficient transistors. Figure 5a shows the computed intrinsic energy and delay of phosphorene TFETs. In the energy-delay figure, the bottom left corner with the lowest EDP is preferred. It is worth mentioning that WTe$_2$ has been benchmarked as the best TMD TFET. Nevertheless, as seen in Fig. 5, the EDPs of phosphorene TFETs are much smaller than the best TMD TFET. Intrinsic EDP of 2L-phosphorene with $L_{ch}$ of 15 nm is two orders of magnitude smaller than the EDP of the WTe$_2$ TFET. Not only does phosphorene provide record $I_{ON}$ and $C_g$ but also a record energy delay product among 2D materials. The optimized asymmetric doping also improves the intrinsic EDP of TFETs specially for sub-9 nm channel lengths. Although intrinsic EDP is an important measure of the transistor's potential,

Figure 3. (a) The transfer characteristics of the mono- (1L), bi- (2L), and tri-layer (3L) phosphorene TFETs for 15 nm channel length $L_{ch}$. Transfer characteristics of constant electric field $E$ scaling (i.e. $E=V_{DD}/L_{ch}=30$ V/nm) for (b) 1L, (c) 2L, and (d) 3L phosphorene. For the $L_{ch}=6$ nm case, the $I_{ds}-V_{gs}$ can be optimized through asymmetric doping.
intrinsic EDP alone does not indicate how good the device is in a real circuit with interconnects and parasitic capacitances. For this reason, ED calculations of a 32-bit adder circuit based on these TFETs have been performed and shown in Fig. 5b. The 32-bit adder simulation has been performed using the software BCB 3.026. The scaling of circuit parameters as a function of gate length follows the ITRS roadmap22. As seen in the Fig. 5b, phosphorene 32-bit adder EDP is better than CMOS and WTe2 and improves further with scaling. These improvements are not as significant as the ones promised by the intrinsic EDP due to the presence of parasitics in smaller dimensions. For the 6 nm node, optimized 2L-phosphorene with asymmetric doping provides the lowest possible intrinsic EDP, such improvements are not felt in the adder EDP due to the dominance of parasitics.

In conclusion, few-layer phosphorene has a unique set of properties which makes it an excellent candidate for future ultra-scaled low power electronics: 1) atomistically thin body thickness, 2) tune-able $E_g$ and $m^*$ with number of layers within the optimum range for TFET applications, 3) anisotropic $m^*$, and 4) direct band gap even in multi-layer. These features make phosphorene an exceptional candidate among 2D materials for TFETs.
applications. The $I_{D}-V_{G}$ and $C_{G}$ characteristics of few-layer phosphorene exhibit significant improvements in energy-delay product compared to other 2D TFETs (e.g. TMD TFETs) and CMOS. Bilayer phosphorene shows optimum performance and is recommended for adoption as the future material of 2D-TFETs.

Methods

In the quantum transport simulations performed in this work, the phosphorene Hamiltonian employs a 10 band sp$^{3}$d$^{5}$s $2\text{nd}$ nearest neighbor tight binding model (TB). The TB parameters have been optimized to reproduce the band structures obtained from density functional theory (DFT) using HSE06. A general TB parameter set was obtained that captured the bandstructure of monolayer to bulk phosphorene. This DFT to TB mapping is a standard technique in semi-empirical TB$^{28}$. The Hamiltonian is represented with TB instead of DFT, since DFT is computationally expensive and is size limited. Our TB model agrees well with previous calculations of $m^{*}$ and $E_g$ of few-layer phosphorene obtained from DFT with Becke Johnson functional (DFT-mBJ)$^{18}$.

For transport simulations, a self-consistent Poisson-quantum transmitting boundary method (QTBMB) has been used with the TB Hamiltonian. QTBMB is equivalent to the non equilibrium Green's function (NEGF) approach in the ballistic case, but it entails the solution of a linear system of equations instead of obtaining the Green's function by matrix inversion which is more computationally inefficient$^{30}$. In QTBMB, the Schrödinger equation with open boundary conditions is given as,

$$\left( E - H - \Sigma \right) \Psi_{SD} = S_{SD},$$  \hspace{1cm} (1)

where $E$, $I$, $H$, and $\Sigma$ are the carrier energy, identity matrix, device Hamiltonian, and self-energy due to open boundaries and $\Psi$ and $S$ are the wave function and a carrier injection term respectively from either source (S) or drain (D). 3D Poisson equation is solved using the finite-element method. It should be noted that the dielectric tensor $\varepsilon$ of few-layer phosphorene is anisotropic and has been obtained from DFT calculations$^{30}$. The Poisson equation reads as follows:

$$\frac{d}{dx} \left( \varepsilon_s \frac{dV}{dx} \right) + \frac{d}{dy} \left( \varepsilon_y \frac{dV}{dy} \right) + \frac{d}{dz} \left( \varepsilon_z \frac{dV}{dz} \right) = -\rho,$$  \hspace{1cm} (2)

where $V$ and $\rho$ are the electrostatic potential and total charge, respectively. In this paper, the transport simulations have been performed with the Nanoelectronics Modeling tool NEMOS$^{31,32}$.

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T.A.A. and H.I. performed the simulations and analyzed the data. G.K. and R.R. supervised the work. All authors contributed to writing the manuscript.

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