

# Few-Layer Black Phosphorous PMOSFETs with BN/Al<sub>2</sub>O<sub>3</sub> Bilayer Gate Dielectric: Achieving I<sub>on</sub>=850μA/μm, g<sub>m</sub>=340μS/μm, and R<sub>c</sub>=0.58kΩ·μm

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**Abstract**—In this paper, high-performance few-layer black phosphorus (BP) PMOSFETs have been demonstrated by using MOCVD BN and ALD Al<sub>2</sub>O<sub>3</sub> as the top-gate dielectric as well as the passivation layer. Highest I<sub>on</sub> of 850μA/μm (V<sub>ds</sub> = -1.8V) and g<sub>m</sub> of 340μS/μm (V<sub>ds</sub> = -0.8V) have been achieved with the 200nm channel length (L<sub>ch</sub>) devices. Record low contact resistance (R<sub>c</sub>) of 0.58kΩ·μm has been obtained on BP transistors by contact engineering. The gate leakage of the BN/Al<sub>2</sub>O<sub>3</sub> bilayer gate dielectric is less than 10<sup>-12</sup>A/μm<sup>2</sup> (V<sub>g</sub> = -1V) with an EOT of 3nm. SS and hysteresis voltage as low as 70mV/dec and 0.1V have been achieved, indicating a high quality interface between BP and BN.

## I. INTRODUCTION

BP is an exceptional two-dimensional (2D) material for high-performance transistor applications due to its excellent transport properties: i) intrinsically high electron and hole mobilities, i.e., hole mobility as high as 300-1000cm<sup>2</sup>/Vs at room temperature [1,2]; ii) direct bandgap semiconductor with the bandgap of 0.35-2.0eV depending on the number of layers, which can find wide applications in electronics and photonics [3,4]. However, the device performance of BP PMOSFETs such as I<sub>on</sub>, g<sub>m</sub>, EOT, and R<sub>c</sub> in literature are still far below what is expected due to the instability of BP in ambient reacting with O<sub>2</sub> and/or H<sub>2</sub>O [5,6].

In this work, a bilayer gate dielectric of 1.6nm MOCVD sp<sup>2</sup>-BN and 1.3nm ALD Al<sub>2</sub>O<sub>3</sub> was used to passivate the BP channel from oxidation. Compared with un-passivated devices, the passivated devices showed significant performance improvement. Hysteresis as low as 0.1V and SS as low as 70mV/dec are achieved. Record high I<sub>on</sub> of 850μA/μm (V<sub>ds</sub> = -1.8V) and g<sub>m</sub> of 340μS/μm (V<sub>ds</sub> = -0.8V) have been demonstrated with a 200nm L<sub>ch</sub> device. The gate leakage is less than 10<sup>-12</sup>A/μm<sup>2</sup> (V<sub>g</sub> = -1V) with an EOT of 3nm. Meanwhile, R<sub>c</sub> as low as 0.58 kΩ·μm has also been demonstrated by contact engineering. It is shown that BN/Al<sub>2</sub>O<sub>3</sub> is a high quality and scalable gate dielectric as well as an effective passivation layer for BP.

## II. EXPERIMENT

Fig. 1 shows the schematic diagram of a BP MOSFET with BN/Al<sub>2</sub>O<sub>3</sub> as gate dielectric. A top view SEM image of two connected 100nm L<sub>ch</sub> BP MOSFETs is shown in Fig. 2(a). Fig. 2(b) shows the element analysis along the gate stack direction,

namely AA' in Fig. 1. Fig. 3 illustrates the STM image of a 4.5nm by 4.5nm freshly cleaved BP surface with 0.3V scanning bias showing the puckered structures with atomic resolution. The detail of fabrication is shown in Fig. 4. The sp<sup>2</sup>-BN was grown by MOCVD at 1050°C on 1/4 2'' sapphire wafers. The roughness of BN on sapphire is less than 0.1nm and the film thickness is ~1.6nm measured by AFM, as shown in Fig. 5(a) and (b). Bulk BP was synthesized from red phosphorus using SnI<sub>4</sub>/Sn as catalyst in sealed ampoules. Firstly, PMMA A10 and PDMS were coated on BN/sapphire wafers. The sapphire substrate was peeled after a few hours' soak in BOE. BP flakes (thickness of 4-12 nm) were exfoliated onto a 90nm SiO<sub>2</sub>/p<sup>++</sup> Si substrate. The PDMS/PMMA/BN film was transferred to the substrate after baking at 120°C for 30 minutes. The processes of BP exfoliation and BN transfer were all performed in a glovebox with H<sub>2</sub>O and O<sub>2</sub> concentration less than 0.5ppm. The sample was baked at 100 °C for 30 minutes to improve the adhesion between BP and BN. PMMA and PDMS was removed by solvent cleaning followed by N<sub>2</sub> annealing at 180°C. After Source/Drain pattern, an optional low power O<sub>2</sub>/Ar plasma etching was used to open the BN windows at the S/D regions. The samples were immediately loaded into a metallization chamber after etching. 5nm Pt/ 8nm Ni/ 30nm Al or 12nm Ni/ 30nm Al was deposited as the contact metals. Fig. 6 shows a cross-sectional TEM image of the S/D region with BN etched. After metal lift-off, 1.3nm Al<sub>2</sub>O<sub>3</sub> was deposited with ALD at 200 °C. Finally, 10nm Ti/50nm Au was deposited as the top gate metal.

All patterns were defined with a VISTEC VB6 UHR e-beam lithography. Dry etching was performed with a Panasonic E620 high density plasma etcher. A HORIBA LabRAM HR800 Raman spectrometer was used for the Raman measurement with a 632.8nm wavelength He-Ne laser. All the devices were measured with a Keithley 4200 semiconductor parameters analyzer at room temperature.

## III. RESULTS AND DISCUSSION

BP has anisotropic hole mobilities as the hole effective mass of armchair direction is 6-8 times larger than that of zigzag direction from DFT calculation [1]. Consequently, the armchair direction is identified with polarized Raman spectra and used as the channel direction for all devices, as shown in Fig. 7(a). Fig. 7(b) shows the time dependence of integrated intensity of A<sub>1g</sub> Raman mode of BP samples without BN, with BN, and with

BN/Al<sub>2</sub>O<sub>3</sub>, respectively. Laser illumination is used to accelerate the degradation of BP [7]. Exposed in air, the normalized A<sub>1g</sub> Raman intensity of the freshly cleaved BP flake decreases exponentially within one hour, indicating its fast degradation in ambient. The degradation speed slows down when it is covered by BN only. Interestingly, no sign of degradation is observed when BP is covered by BN and Al<sub>2</sub>O<sub>3</sub> with EOT of 3nm thick. It is shown that BN/Al<sub>2</sub>O<sub>3</sub> bilayer dielectric can effectively suppresses the degradation of BP in ambient.

Fig. 8 (a) shows the C-V characteristics of 1.6nm BN and 6nm Al<sub>2</sub>O<sub>3</sub>. The extracted relative dielectric constant of the MOCVD BN is about 3.0, which is in agreement with the reported dielectric constant of CVD BN [8]. In Fig. 8 (b), the leakage current density of the 1.6nm BN/1.3nm Al<sub>2</sub>O<sub>3</sub> gate dielectric is less than 10<sup>-12</sup>A/μm<sup>2</sup> at V<sub>g</sub> = -1V, which is comparable to SiO<sub>2</sub> with the same EOT.

Typical transfer curves of a back-gate (7.5nm HfO<sub>2</sub>) BP transistor without any passivation techniques are shown in Fig. 9. The I-V hysteresis is as large as 2.5V [ $\Delta E_{BP} = 6.0\text{MV/cm}$ ;  $\Delta E_{BP}$  is defined as  $(\Delta V_g/EOT) \cdot (3.9/6.1); k_{BP}=6.1; k_{SiO_2}=3.9$ ]. Fig. 10 shows the transfer curves of a 500nm L<sub>ch</sub> BP MOSFET with BN/Al<sub>2</sub>O<sub>3</sub> as top gate dielectric, showing hysteresis of 0.25V ( $\Delta E_{BP} = 0.6\text{MV/cm}$ ). SS<sub>min</sub> as low as 70mV/dec is achieved indicating a low-defect interface between BP and BN. The drain current is low because the BN above the S/D region was not etched avoiding the interface degradation due to the dry etching process. The transfer curves of a 200nm L<sub>ch</sub> BP MOSFET with BN etched are shown in Fig. 11. The hysteresis is as low as 0.1V ( $\Delta E_{BP} = 0.25\text{MV/cm}$ ), which is reduced by a factor of 24, compared to the back-gated devices.

Table 1 summarizes different BP passivation techniques in literature [9-11]. Unfortunately, conventional ALD Al<sub>2</sub>O<sub>3</sub> is not a viable method to reduce hysteresis since ALD usually needs H<sub>2</sub>O as precursor and grows at high temperature. Vacuum annealing is reported to be an effective way to reduce hysteresis but it doesn't completely solve the degradation problem. It is also reported that hysteresis can be completely eliminated by sandwiching BP with thick exfoliated BN, but it cannot achieve the required EOT scaling. In this work, low hysteresis and small EOT can be achieved at the same time by using MOCVD BN and ALD Al<sub>2</sub>O<sub>3</sub> bilayer dielectric.

Fig. 12 shows the linear I<sub>d</sub>-V<sub>g</sub> curve as well as the g<sub>m</sub>-V<sub>g</sub> curve of a 200nm L<sub>ch</sub> BP MOSFET with V<sub>ds</sub> = -0.8V. The peak g<sub>m</sub> is about 340μS/μm, which is the highest reported value among all BP transistors. The threshold voltage is ~0.65V extracted by linear extrapolation. The field effect hole mobility is calculated to be 144 cm<sup>2</sup>/Vs with C<sub>g</sub> = 1.15μF/cm<sup>2</sup>. It is known mobility could be under-estimated from short channel devices. The I<sub>on</sub>/I<sub>off</sub> is about 10<sup>4</sup> and 10<sup>3</sup> for V<sub>d</sub> = -0.1 and -0.8V

The I<sub>d</sub>-V<sub>d</sub> curves of the same device are shown in Fig. 13. Record high I<sub>on</sub> = 850μA/μm is achieved at V<sub>d</sub> = -1.8V and V<sub>g</sub> = -2V. No clear current saturation is observed when the channel current is along the high mobility direction. Fig. 14 shows the I<sub>d</sub>-V<sub>d</sub> curves of the same device with different back biases (V<sub>bg</sub> = 0, -20, and -40V). Interestingly, the ON state is nearly independent of V<sub>bg</sub> although the OFF state is still affected by

V<sub>bg</sub>. This indicates that the drain current flows through the top few layers which are strongly controlled by the top-gate. The contact resistance of top-gated devices doesn't change significantly through electrostatic doping from back gate.

To get a better understanding of the increase of I<sub>on</sub>, R<sub>c</sub> and sheet resistance (R<sub>s</sub>) are extracted with a 12nm thick BP TLM structure, as shown in Fig. 15. Record low R<sub>c</sub> of 0.58kΩ·μm for BP transistors has been obtained, which is one fifth of the previous reported value of Ni/BP contact at zero gate bias [12]. There are three factors that contribute to the low R<sub>c</sub>: (i) protected by BN, no oxides of phosphorus exhibit at the BP/metal interface during the fabrication process; (ii) there is less interlayer resistance due to the top gate structure, which is an important part of R<sub>c</sub> for back gate structure; (iii) high work-function metal Pt is used to form a lower Schottky barrier at the BP/metal contact. Fig. 16 shows the transfer curves of two BP MOSFETs with (a) Pt/Ni/Al and (b) Ni/Al as contact metals. The I<sub>on</sub> of the device with Pt/Ni/Al contact is about 1.6 times higher than that of device with Ni/Al contact.

The anisotropic characteristics of BP is also investigated. Fig. 17 and 18 depict the output and transfer characteristics of a 200nm L<sub>ch</sub> BP MOSEFT along the zigzag direction. Unlike the armchair devices, the drain current of zigzag device starts to saturate at V<sub>d</sub> = -1V due to its lower mobility. The hole mobility is calculated to be 51 cm<sup>2</sup>/Vs, which is about one third of the armchair mobility. The I<sub>on</sub>/I<sub>off</sub> is as high as 10<sup>5</sup> and 10<sup>4</sup> for V<sub>d</sub> = -0.1 and -1V due to the smaller thickness. The time dependent I<sub>d</sub>-V<sub>g</sub> curves are presented in Fig. 19. The device still works properly after 20 days although minor V<sub>th</sub> shift is observed. Finally, Table 2 benchmarks the device metrics such as EOT, I<sub>on</sub>, g<sub>m</sub>, R<sub>c</sub>, I<sub>on</sub>/I<sub>off</sub> of this work with other BP transistor results in literature [12-15].

#### IV. CONCLUSION

High-performance BP MOSFETs with I<sub>on</sub> = 850μA/μm, g<sub>m</sub> of 340μS/μm, EOT = 3nm, and R<sub>c</sub> = 0.58kΩ·μm have been successfully demonstrated in this work. The significant performance improvement is attributed to the BN/Al<sub>2</sub>O<sub>3</sub> bilayer dielectric, which served as a top gate dielectric and a passivation layer. I-V hysteresis and SS as low as 0.1V and 70mV/dec have also been demonstrated.

#### ACKNOWLEDGMENT

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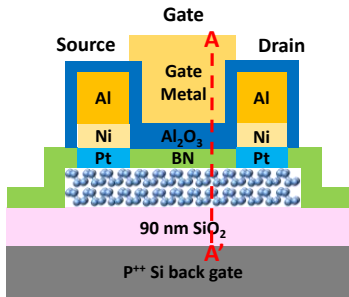


Fig. 1. Schematic diagram of a BP PMOSFET with BN/Al<sub>2</sub>O<sub>3</sub> gate dielectric.

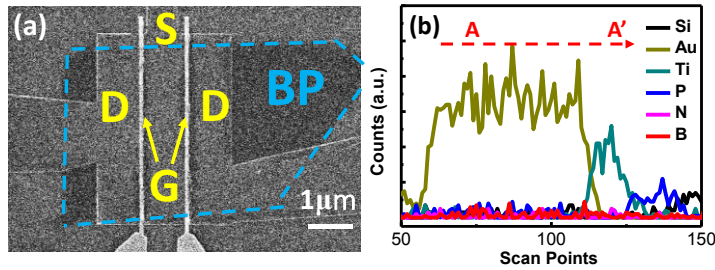


Fig. 2. (a) Top-view SEM image of two BP MOSFETs with BN/Al<sub>2</sub>O<sub>3</sub> top gate dielectric. (b) EDS element analysis along the AA' gate direction.

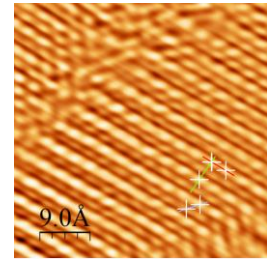


Fig. 3. STM image of a freshly cleaved BP surface showing atomic puckered structures.

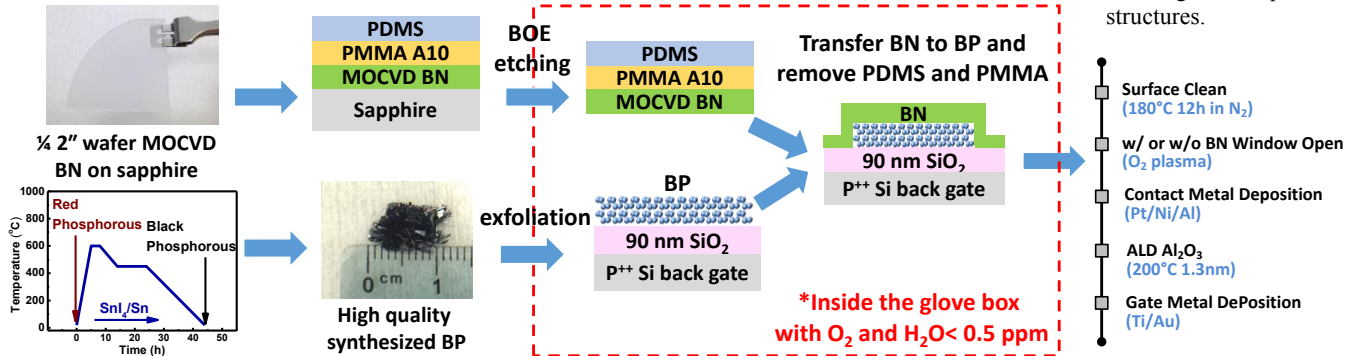


Fig. 4. Fabrication process flow for the BP MOSFET. Key steps include: (i) MOCVD BN; (ii) bulk BP growth; (iii) BP exfoliation; (iv) BN transfer; (v) BN dry etching; (vi) ALD Al<sub>2</sub>O<sub>3</sub>. BP exfoliation and BN transfer were performed in glovebox filled with high purity Ar.

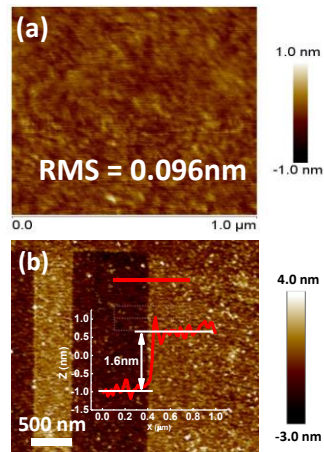


Fig. 5. AFM image of (a) BN on sapphire with RMS = 0.096 nm and (b) BN after dry etching. The thickness of BN is 1.6 nm.

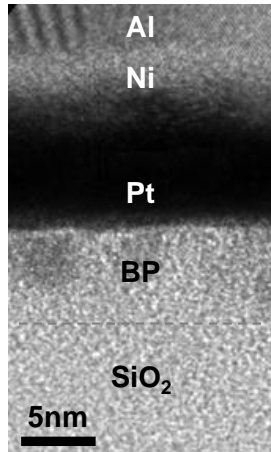


Fig. 6. Cross-sectional TEM image of the Pt/BP contact after BN etching.

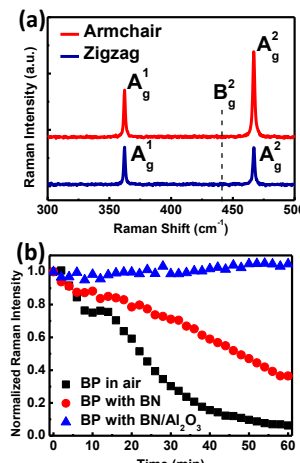


Fig. 7. (a) BP anisotropic Raman. (b) Time dependence of A<sub>1g</sub> Raman intensity of BP w/o BN, w/ BN, and w/ BN and Al<sub>2</sub>O<sub>3</sub>.

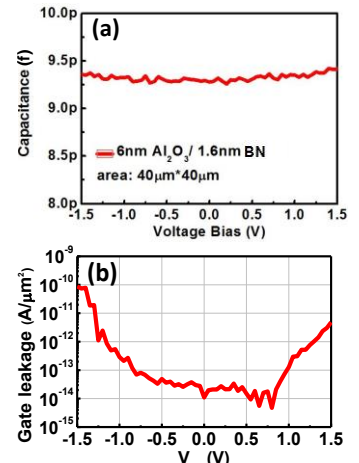


Fig. 8. (a) C-V of a BN/Al<sub>2</sub>O<sub>3</sub> capacitor; (b) gate leakage vs. V<sub>g</sub> of 1.6 nm BN/1.3 nm Al<sub>2</sub>O<sub>3</sub>.

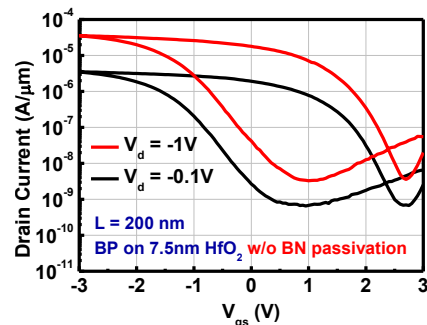


Fig. 9. Typical due sweep I<sub>d</sub>-V<sub>g</sub> of a 200 nm L<sub>ch</sub> BP MOSFET with 7.5 nm HfO<sub>2</sub> as back gate oxide. No passivation technique is used.

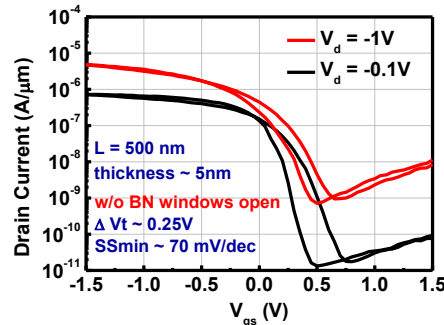


Fig. 10. I<sub>d</sub>-V<sub>g</sub> of a 500 nm L<sub>ch</sub> BP FET with BN/Al<sub>2</sub>O<sub>3</sub> as gate dielectric without source/drain BN etching.

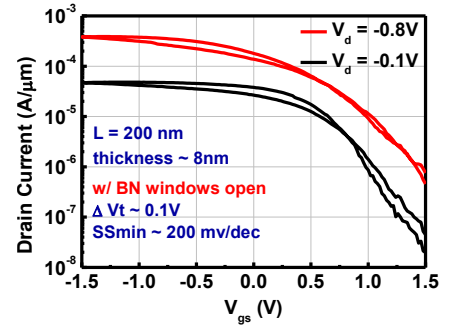


Fig. 11. I<sub>d</sub>-V<sub>g</sub> of a 200 nm L<sub>ch</sub> BP MOSFET with BN/Al<sub>2</sub>O<sub>3</sub> as gate dielectric. The source/drain BN was etched. Hysteresis is as low as 0.1V.

	Gate Oxide/ passivation	$\Delta V_g$	$\Delta E_{bp}$	Remarks
1* without passivation	7.5nm HfO <sub>2</sub> as back gate, no passivation	2.5V	6 MV/cm	Large hysteresis due to oxidation
2* ALD Al <sub>2</sub> O <sub>3</sub> only [9]	5nm Al <sub>2</sub> O <sub>3</sub> as front gate and passivation layer	2.5V	6 MV/cm	No obvious improvement
3* vacuum annealing [10]	10nm SiO <sub>2</sub> as back gate; annealed in vacuum	0.4V	0.3 MV/cm	Hysteresis is reduced but it requires vacuum
4* BN sandwich + annealing [11]	Exfoliated thick BN as back gate and front passivation layer	0	0	No hysteresis but difficult to scale down
5* this work: BN/Al <sub>2</sub> O <sub>3</sub>	1.6nm BN/1.3nm Al <sub>2</sub> O <sub>3</sub> as front gate and passivation layer	0.1-0.25V	0.25-0.6 MV/cm	low hysteresis and small EOT

Table 1. Comparison of BP passivation techniques: 1) no passivation; 2) ALD Al<sub>2</sub>O<sub>3</sub> as top gate; 3) vacuum annealing; 4) sandwiched with top and bottom BN and annealing; 5) this work.

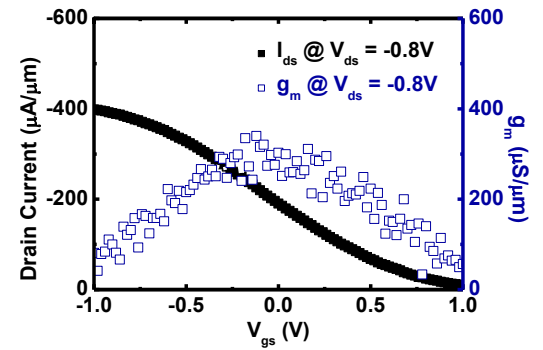


Fig. 12. Linear  $I_d$ - $V_g$  and  $g_m$ - $V_g$  curve ( $V_d = -0.8V$ ) of the same device in Fig. 11.

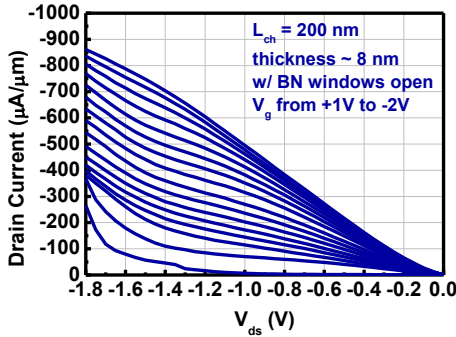


Fig. 13.  $I_d$ - $V_d$  of the same device in Fig. 11.  $I_{on}$  of  $850\mu A/\mu m$  was obtained with  $V_d = -1.8V$  and  $V_g = -2V$ .

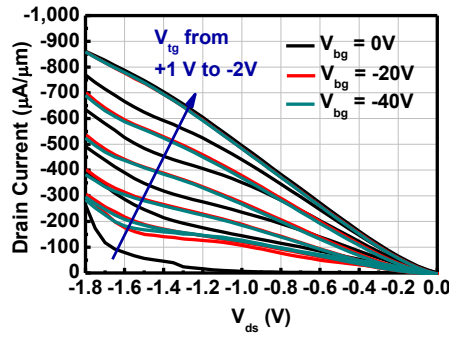


Fig. 14. Back gate bias dependence of  $I_d$ - $V_d$  of the same device in Fig. 11.  $I_{on}$  is nearly independent of  $V_{bg}$ .

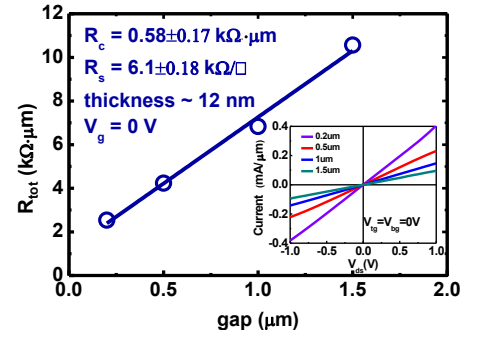


Fig. 15. TLM resistance on BP with Pt/Ni/Al contact. Inset shows the I-V curves between two contacts with different gap length.

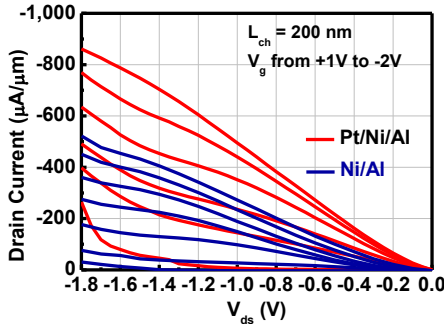


Fig. 16.  $I_d$ - $V_d$  of 200nm  $L_{ch}$  BP MOSFETs with Pt/Ni/Al and Ni/Al contacts.

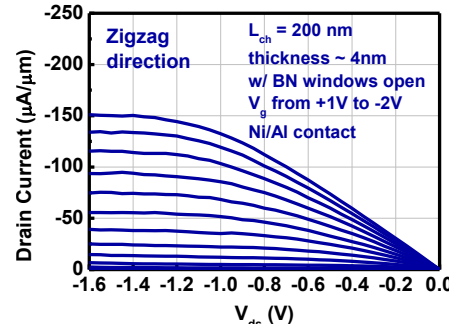


Fig. 17.  $I_d$ - $V_d$  of a 200nm  $L_{ch}$  BP MOSFET with Ni/Al contact along the zigzag direction.

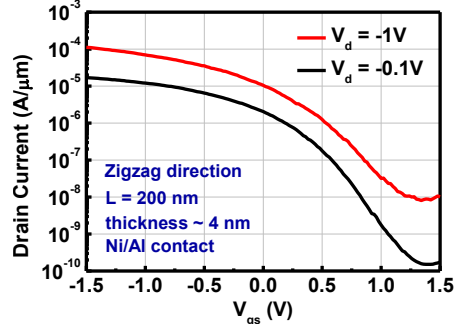


Fig. 18.  $I_d$ - $V_g$  of the same device in Fig. 17.  $I_{on}/I_{off}$  is about  $10^5$  and  $10^4$  at  $V_{ds} = -0.1$  and  $-1V$ , respectively.

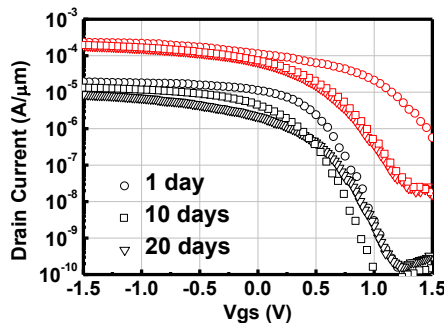


Fig. 19. Time dependence of  $I_d$ - $V_g$  of a 200nm  $L_{ch}$  BP MOSFET with Ni/Al contact.

	1# Purdue	2# Purdue	3# Uni. of Minnesota	4# USC	5# Stanford	6# This Work
$L_{ch}$	0.5µm	1.5µm	170nm	300nm	1µm	200nm
Gate Oxide	16nm Al <sub>2</sub> O <sub>3</sub>	90nm SiO <sub>2</sub>	7nm HfO <sub>2</sub>	21nm HfO <sub>2</sub>	10nm SiO <sub>2</sub>	1.6nm BN/1.3nm Al <sub>2</sub> O <sub>3</sub>
S/D Metal	Ni/Au	Ni	Ti/Au	Ti/Pd/Au	Sc/Au	Pt/Ni/Al
$I_{on}$	144µA/µm ( $V_d = -1V$ )	210µA/µm ( $V_d = -2V$ ) *w/o doping	300µA/µm ( $V_d = -2V$ )	270µA/µm ( $V_d = -2V$ )	482µA/µm ( $V_d = -2V$ )	850µA/µm ( $V_d = -1.8V$ )
$g_m$	3.3µS/µm ( $V_d = -0.5V$ )	NA	250µS/µm ( $V_d = -2V$ )	180µS/µm ( $V_d = -2V$ )	NA	340µS/µm ( $V_d = -0.8V$ )
$R_c$	NA	1.3kΩ·µm ( $V_g = -40V$ )	1.14kΩ·µm ( $V_g = -1.5V$ )	NA	NA	0.58kΩ·µm ( $V_g = 0V$ )
$I_{on}/I_{off}$	$\sim 10^3$ ( $V_d = -0.1V$ )	$\sim 10^3$ ( $V_d = -0.01V$ )	$\sim 10^3$ ( $V_d = -0.1V$ )	$\sim 2 \cdot 10^3$ ( $V_d = -2V$ )	$\sim 10^3$ - $10^5$ ( $V_d = -0.7V$ )	$\sim 10^3$ - $10^5$ ( $V_d = -0.1V$ )

Table 2. Benchmark of device metrics of this work with other results in literature [12-15].