nature portfolio

Peer Review File

A clean transfer approach to prepare centimetre-scale black phosphorus crystalline multilayers on silicon substrates for field-effect transistors

Corresponding Author: Professor Jianhua Hao

Reviewer comments:

Reviewer #1

(Remarks to the Author)
In this study, the authors introduce a wet transfer method utilizing ethylene-vinyl acetate polymer and ethylene glycol solution to transfer high-crystalline black phosphorus films onto various substrates, such as silicon wafers. The transferred black phosphorus films are then used to fabricate and study back-gate field-effect transistors, demonstrating that the wet transfer method effectively maintains the significant electrical performance of the material.

The topic is timely and of wide interest, and the proposed transfer method is both useful and original.
The manuscript is clear and well-organized but may benefit from some revisions:

1. Regarding the statement "After wet transfer, the thickness of the BP thin film remains unchanged (see Fig. 3b)," the conclusion could be strengthened by providing additional profiles or a histogram with thickness measurements before and after transfer to support this claim.
2. “To investigate the homogeneity and electrical performance of the transferred BP thin film, an array of stripe electrodes connected all together with different channel lengths was fabricated.” Although clarified in the Methods section, specify here which is the metal of the electrodes that is in contact with BP and make it clear that the electrodes were deposited prior to the BP transfer.
3. “This suggests that the contact between the electrodes and the BP layers exhibits an ohmic contact.” This conclusion is contradicted by the observed rectifying behaviour in the output curves over the -3/+3 V range. The authors should revisit this conclusion.
4. To assess the surface cleanliness and quality of the BP layer, the authors could study the hysteresis in the transfer characteristics of the BP transistor. Have they measured the transfer curve over a back-gate voltage loop (i.e., with a forward and reverse sweep)? If so, discussing hysteresis in the transfer characteristics would be beneficial.
5. “2D black phosphorus BP exhibits exceptional carrier mobility and the ability to support 42 high current density, making it ideal for incorporation into advanced functional devices.15–17” About BP-based advanced functional devices, the authors may want to consider this recent article in which BP-based transistors are used for neuromorphic vision: https://doi.org/10.1039/D4MH00027G

Reviewer #2

(Remarks to the Author)
Zhao et al demonstrated a wet transfer method utilizing ethylene-vinyl acetate (EVA) polymer and an ethylene glycol (EG) solution to transfer high-crystalline PLD-BP films on SiO_2/Si substrate. Following the successful wet transfer, large-scale BP-based bottom-gate field-effect transistor (FET) arrays exhibiting excellent uniformity and continuity were fabricated and studied. This reviewer had checked the previous work of BP published in Nature Mater. (2021) done by the group. It is impressive that the results of BP film grown from less commonly used mica in NM paper to the widely used silicon in this manuscript present an encouraging advance in this field. The authors employ a novel and convenient strategy to transfer centermetre-size on-substrate 2D BP for the fabrication of large-scale FET arrays, which offers the opportunities for the future integration of BP-based multifunctional nanoelectronic devices and also expanding this technique further to other as-grown 2D materials. In general, the manuscript is well-organized and the authors have done inspiring work. Acceptance of the work is highly recommended after necessary improvement. There are some questions which need to be addressed before suitable for publication in Nature Communications.
1.The authors fabricated FET arrays to investigate the homogeneity and electrical performance of the transferred BP thin film

and claimed that the wet transferred BP film can still allow efficient transport of charge carriers and exhibit reliable switching behaviors compared to original as-grown BP. However, only the results for a single device were presented. The authors should include additional data from more BP devices to demonstrate the repeatability of the electrical performance.
2.The authors should clarify the condition of the Ids -Vds curves under different passivation conditions of BP FET arrays presented in Fig. 4c whether the BP film is before or after wet-transfer process.
3.Furthermore, it is suggested that the authors include a comparison of the effect of passivation on the electrical transfer properties of as-grown BP on mica substrate and wet-transferred BP on SiO2/Si substrate under the same conditions.
4.The authors stated that EVA swelled when immersed in IPA solvent, and no obvious changes was observed when immersed in EG solvent. However, Fig. S2 shows noticeable variations in the initial thickness of EVA before immersion, with approximately 1.03 μm and 0.21 μm, respectively. Is it possible that the initial thickness of the EVA polymer could impact its extent of swelling in different solvents?
5.The units and description should be included in Table. S1.
6.The authors successfully demonstrated the transfer of BP thin films and suggested that this transfer strategy could be expanded to other as-grown 2D materials. Considering the importance of universality, it is suggested the author to demonstrate and expand this transfer approach to other on-substrate 2D materials.
7.There are some typos on Fig. 4d, 'Before removing the polyer.'.

Reviewer #3

(Remarks to the Author)
This manuscript reports on a wet transfer approach to prepare centimeter-scale black phosphorus (BP) mono-layered crystalline films on silicon substrates for fabrication of field-effect transistors (FET) arrays. Detailed characterization indicated that as-transferred BP films possess uniform morphology and crystallinity, enabling the fabrication of large-scale bottom-gated FET arrays with high carrier mobility and current on/off ratios, although the values are smaller than that in reported literature (Nat. Mater. 22, 717-724 (2023)). The results are interesting and convincing for further development of scalable integration of 2D materials into electronic device applications. Before its further consideration, the following issues need to be addressed:
1. Although the authors have developed a wet transfer approach for their PLD grown BP films to apply them to device applications, the previous reported direct preparation of subcentimeter-scale BP films on SiO2/Si substrate (Nat. Mater. 22, 717-724 (2023)) should be properly acknowledged in the introduction part.
2. When benchmark the device performance, the values in the literature of Nat. Mater. 22, 717-724 (2023) should be included.
3. The channel lengths of the BP devices are too long (>70 μm) to extract the size effect of the BP films, which weakens the advantages of 2D BP channel over that of silicon when scaling down to nanometer limit. A shorter channel length (Such as 1 μm or shorter) in BP devices is required.

<u>Reviewers' Comments and Authors' Response</u>

Reviewer #1 (Remarks to the Author):

In this study, the authors introduce a wet transfer method utilizing ethylene-vinyl acetate polymer and ethylene glycol solution to transfer high-crystalline black phosphorus films onto various substrates, such as silicon wafers. The transferred black phosphorus films are then used to fabricate and study back-gate field-effect transistors, demonstrating that the wet transfer method effectively maintains the significant electrical performance of the material.

The topic is timely and of wide interest, and the proposed transfer method is both useful and original.

The manuscript is clear and well-organized but may benefit from some revisions:

Thanks for the reviewer's very positive comments. We have carefully addressed all the comments from all the reviewers in the revised manuscript.

1. Regarding the statement "After wet transfer, the thickness of the BP thin film remains unchanged (see Fig. 3b)," the conclusion could be strengthened by providing additional profiles or a histogram with thickness measurements before and after transfer to support this claim.

<u>Answers:</u> Thanks for the reviewer's good comments.

We have added the thickness profiles to Fig. 3a and 3b to demonstrate more clearly that the thickness of the BP thin films remains almost the same before and after the transfer process.

In the revised version: "

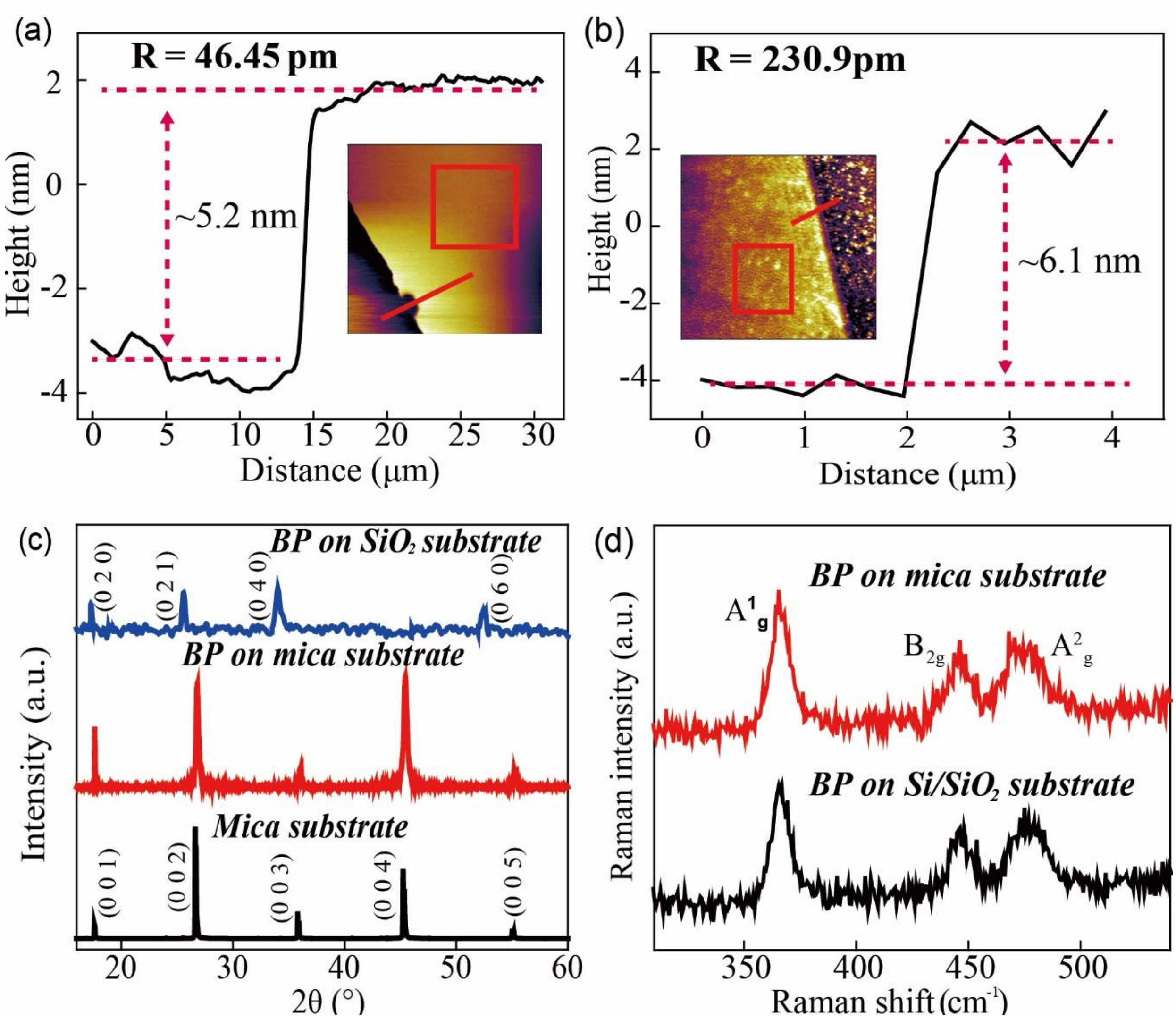

Fig. 3 AFM height profile of BP thin films (a) directly grown on mica substrate and (b) wet-transferred onto the SiO_2/Si substrate. Inset: corresponding AFM images showing the topography of BP thin films. The squared areas marked in the AFM images were used to deduce the roughness presented in (a) and (b). (c) XRD patterns of bare mica substrate, as-grown BP and wet-transferred BP. (d) Raman spectra of BP thin films before (on mica substrate) and after (on SiO_2/Si substrate) wet transfer."

2. "To investigate the homogeneity and electrical performance of the transferred BP thin film, an array of stripe electrodes connected all together with different channel lengths was fabricated." Although clarified in the Methods section, specify here which is the metal of the electrodes that is in contact with BP and make it clear that the electrodes were deposited prior to the BP transfer.

Answers: Thanks for the valuable comments from the reviewer. In the revised manuscript, we have included additional information regarding the metal of electrodes. Furthermore, we have provided supplementary explanations in the Methods section to clarify that the BP thin film is in direct contact with the Au.

Page 8, line 16 in the revised version: "To investigate the homogeneity and electrical performance of the transferred BP thin film, an array of stripe Ti/Au electrodes connected all together with different channel lengths was fabricated."

Page 14, line 11 in the revised version: "The BP thin film prepared through PLD was then wet-transferred onto the SiO_2/Si substrate with Ti/Au electrodes for construction of the FET arrays, while direct contact was established between Au and the BP thin film."

3. "This suggests that the contact between the electrodes and the BP layers exhibits an ohmic contact." This conclusion is contradicted by the observed rectifying behaviour in the output curves over the -3/+3 V range. The authors should revisit this conclusion.

Answers: Thanks a lot for the reviewer's insightful comments.

We observed that the output curves demonstrate a satisfactory linear trend within a small voltage range. However, we also agreed and noted that when a large negative gate bias is applied within the voltage range of -3/+3 V, some rectifying behavior becomes apparent. This finding suggests the existence of a small Schottky barrier between the BP film and the Au electrodes, which can also be observed in the BP FET devices characterized in previous study (*Nano Lett.* 2016 16, 6870−6878). We have addressed and rectified this issue in the revised text to ensure clarity and accuracy.

Page 9, line 17 in the revised version: "The inset figure depicts the I_{ds} –V_{ds} output characteristics of a FET near origin, illustrating a linear interaction between gate voltage (V_g) modulation and current flow. However, when a large negative gate bias is applied, a non-linear trend is observed, suggesting the presence of a small Schottky barrier between the BP layers and Au electrodes."

4. To assess the surface cleanliness and quality of the BP layer, the authors could study the hysteresis in the transfer characteristics of the BP transistor. Have they measured the transfer curve over a back-gate voltage loop (i.e., with a forward and reverse sweep)? If so, discussing hysteresis in the transfer characteristics would be beneficial.

Answers: Thank you for the precious comments from the reviewer.

We have measured the transfer curve with application of the back-gate voltage loop according to the suggestion of the reviewer, and the transfer characteristics measured is shown in Fig. R1. The BP transistor exhibits only a negligible hysteresis and domenstrates excellent stability.

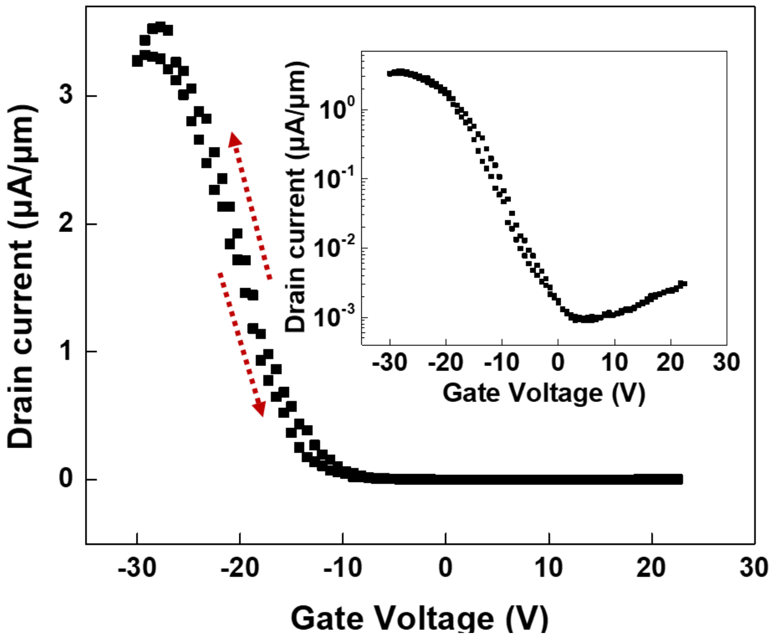

Fig. R1 Transfer characteristics of BP FET with 75 µm channel length in linear scale with -0.1 V drain voltage. Inset: transfer characteristics in logarithmic scale.

5. "2D black phosphorus BP exhibits exceptional carrier mobility and the ability to support high current density, making it ideal for incorporation into advanced functional devices.[15–17]" About BP-based advanced functional devices, the authors may want to consider this recent article in which BP-based transistors are used for neuromorphic vision: https://doi.org/10.1039/D4MH00027G

Answers: Thanks for the reviewer's good suggestions.

The following reference papers have been added in the revised version.

Page 2, line 18 in the revised version: "2D black phosphorus BP exhibits exceptional carrier mobility and the ability to support high current density, making it ideal for incorporation into advanced functional devices.[15–18]…"

Page 16, line 19 in the revised version: "18. Kumar A. *et al.* Memory effect and coexistence of negative and positive photoconductivity in black phosphorus field effect transistor for neuromorphic vision sensors. *Mater. Horiz.* **11**, 2397-2405 (2024)."

Reviewer #2 (Remarks to the Author):

Zhao et al demonstrated a wet transfer method utilizing ethylene-vinyl acetate (EVA) polymer and an ethylene glycol (EG) solution to transfer high-crystalline PLD-BP films on SiO_2/Si substrate. Following the successful wet transfer, large-scale BP-based bottom-gate field-effect transistor (FET) arrays exhibiting excellent uniformity and continuity were

fabricated and studied. This reviewer had checked the previous work of BP published in Nature Mater. (2021) done by the group. It is impressive that the results of BP film grown from less commonly used mica in NM paper to the widely used silicon in this manuscript present an encouraging advance in this field. The authors employ a novel and convenient strategy to transfer centermetre-size on-substrate 2D BP for the fabrication of large-scale FET arrays, which offers the opportunities for the future integration of BP-based multifunctional nanoelectronic devices and also expanding this technique further to other as-grown 2D materials. In general, the manuscript is well-organized and the authors have done inspiring work. Acceptance of the work is highly recommended after necessary improvement. There are some questions which need to be addressed before suitable for publication in Nature Communications.

Thanks for the reviewer's very positive comments and strongly recommending the publication of the paper. In response to the valuable feedback provided by the reviewer, we have diligently addressed all of the comments in the revised manuscript.

1. The authors fabricated FET arrays to investigate the homogeneity and electrical performance of the transferred BP thin film and claimed that the wet transferred BP film can still allow efficient transport of charge carriers and exhibit reliable switching behaviors compared to original as-grown BP. However, only the results for a single device were presented. The authors should include additional data from more BP devices to demonstrate the repeatability of the electrical performance.

Answers: Thanks so much for the reviewer's comments.

We have fabricated and characterized several BP FET devices in this study. For demonstration of repeatability in the electrical performance of our BP devices, we additionally provided the I_{ds}-V_{ds} curves of two more BP FETs, which tested under different back-gate voltages, as depicted in Figure R2a and R2b. Moreover, the transfer characteristics of the three different BP devices are compared in Fig. R2c, which indicates excellent repeatability of the FETs prepared. This repeatability demonstrates the consistent and reliable performance of the fabricated BP FET devices.

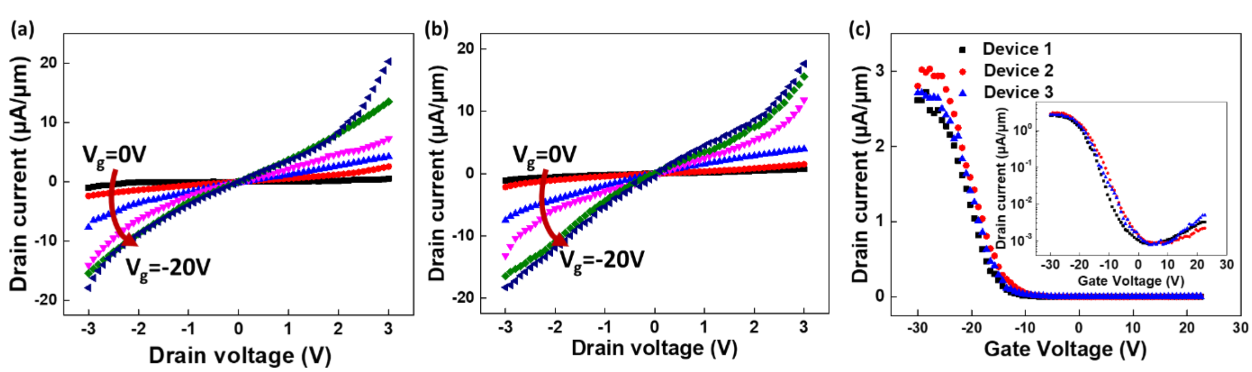

Fig. R2 (a) and (b) I_{ds} -V_{ds} curves of two BP FET samples with 75 µm channel length at V_g= 0 V, -1 V, -3 V, -5 V, -10 V, and -20 V. (c) Transfer characteristics of BP FET with 75 µm channel length in linear scale with -0.1 V drain voltage. Inset: in logarithmic scale.

2.The authors should clarify the condition of the I_{ds} -V_{ds} curves under different passivation conditions of BP FET arrays presented in Fig. 4c whether the BP film is before or after wet-transfer process.

Answers: Thanks for the reviewer's good comments. The results presented in Fig. 4c were evaluated using the FETs constructed with BP thin films after wet-transfer process.

Page 8, line 22 in the revised version: "We also examined the I_{ds} -V_{ds} characteristics of BP FETs on SiO_2/Si substrate with and without coating the EVA polymer in ambient conditions overnight to reveal the passivation effect of the polymer. The passivated and unpassivated BP FET devices were subjected to the identical circumstances for same time period. By comparing the results presented in Fig. 4c, the application of a polymer coating as a passivation strategy is proven to be highly effective in preserving the performance of FETs that are fabricated using wet-transferred BP."

3.Furthermore, it is suggested that the authors include a comparison of the effect of passivation on the electrical transfer properties of as-grown BP on mica substrate and wet-transferred BP on SiO_2/Si substrate under the same conditions.

Answers: Thank you for the comments from the reviewer.

In response to the reviewer's suggestion, we also examined the I_{ds} -V_{ds} characteristics of BP FETs on mica substrate with and without coating the EVA polymer under the same conditions as described in the manuscript to reveal the passivation effect of the polymer. The results presented in Fig. R3 and Fig. 4c of the manuscript both confirm that the effect of polymer coating as passivation is a highly effective approach for maintaining the performance of FETs fabricated with the as-grown BP thin films.

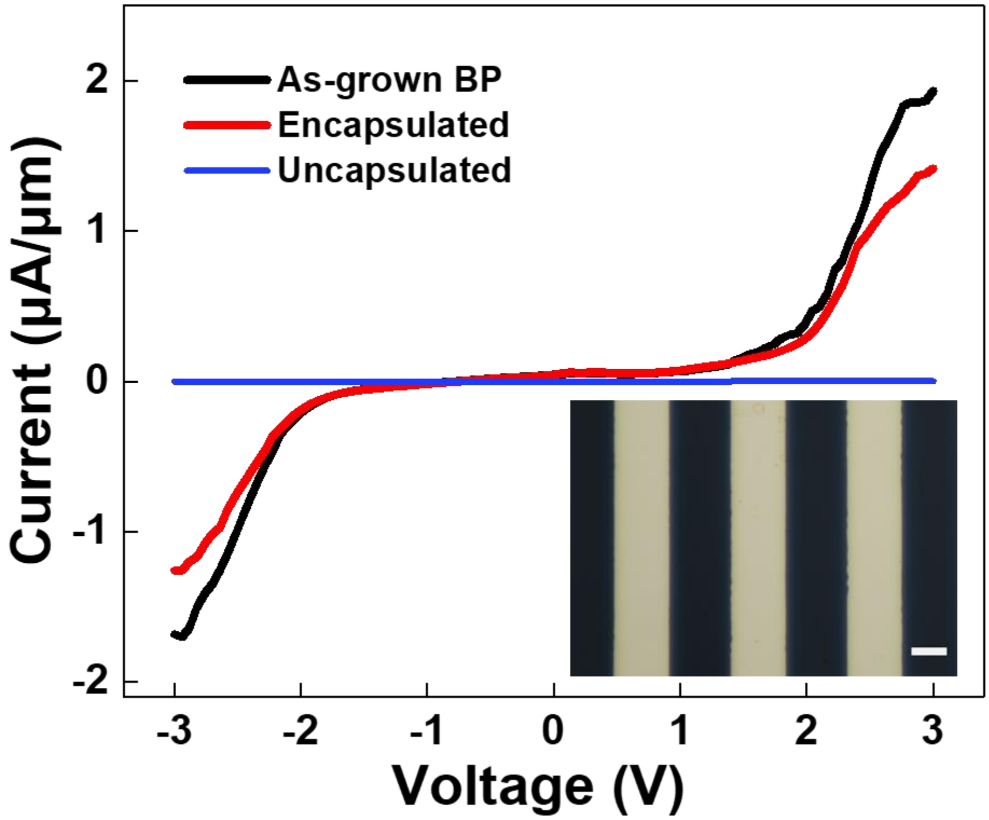

Fig. R3 I_{ds} -V_{ds} curves under different passivation conditions. Inset: Optical microscope image of BP FET arrays on mica substrate with scale bar of 50 µm.

4.The authors stated that EVA swelled when immersed in IPA solvent, and no obvious changes was observed when immersed in EG solvent. However, Fig. S2 shows noticeable variations in the initial thickness of EVA before immersion, with approximately 1.03 µm and 0.21 µm, respectively. Is it possible that the initial thickness of the EVA polymer could impact its extent of swelling in different solvents?

Answers: Thanks a lot for the question from the reviewer.

We have investigated the swelling behavior of EVA polymer films in EG and solvents, ensuring that the films were of comparable thickness (refer to Fig. R4). Our findings indicate that the EVA polymer's thickness remained almost unchanged after immersion in EG (4% of thickness difference), whereas a noticeable welling effect was observed when the polymer was immersed in IPA (55% of thickness difference). The additional data has also been included in the updated supporting information as Fig. S2.

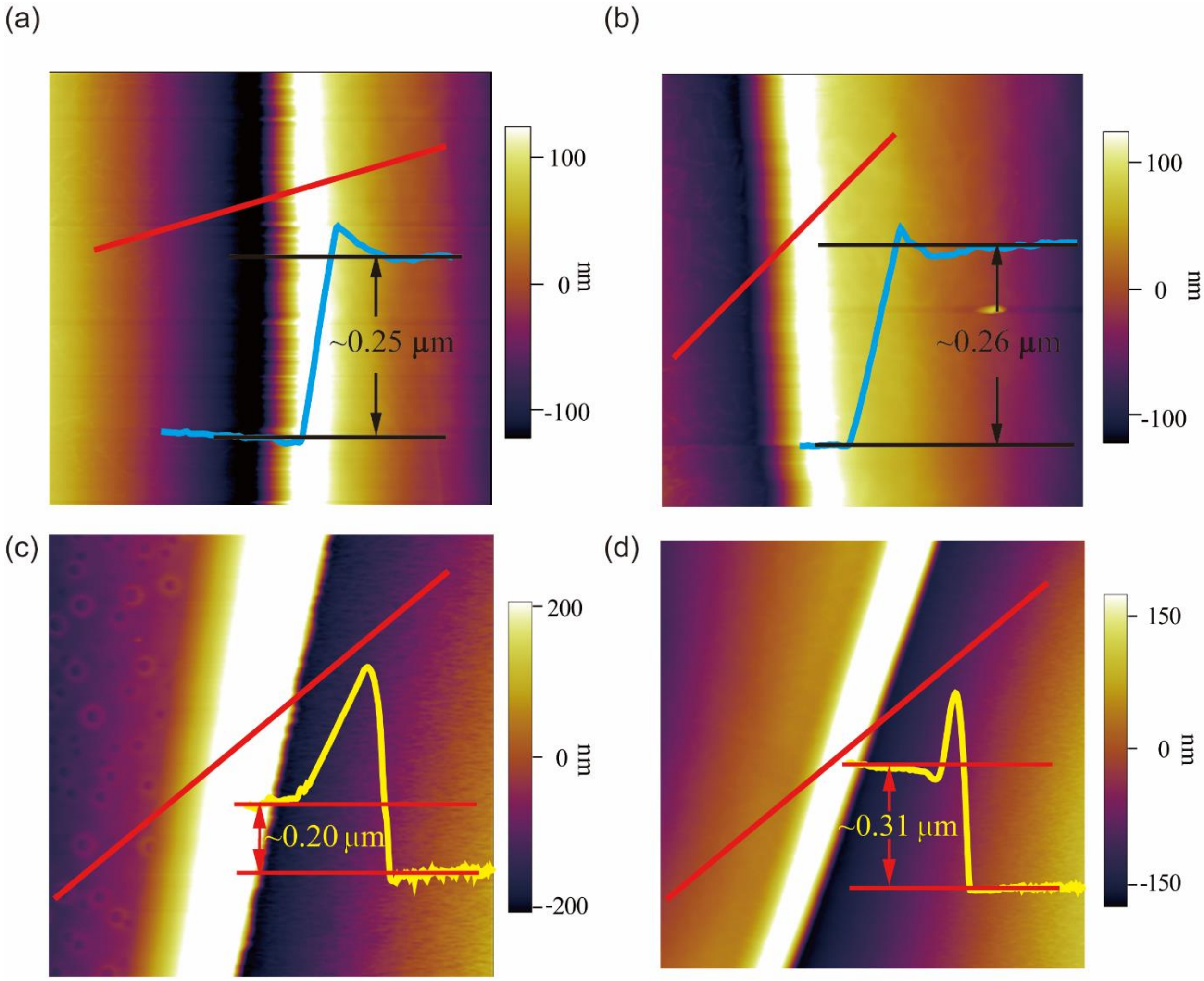

Fig. R4 AFM topography and height analysis of the EVA polymer (a) before and (b) after immersion in EG solvent. Similar analysis of the EVA polymer (c) before and (d) after immersion in IPA solvent.

5.The units and description should be included in Table. S1.

Answers: Thanks for the reviewer's careful reading.

The units and description have been added to the table.

In the revised version: "Table S1 Surface energies of EG and glycerol utilized for the contact angle measurements (mN/m)

Tested liquid	Total (Dispersion+Polarity)	Dispersion coefficient	Polarity coefficient
EG	48	33.9	14.1
Glycerol	64	36.3	27.7

6.The authors successfully demonstrated the transfer of BP thin films and suggested that this transfer strategy could be expanded to other as-grown 2D materials. Considering the importance of universality, it is suggested the author to demonstrate and expand this transfer approach to other on-substrate 2D materials.

Answers: Thanks a lot for the reviewer's insightful comments.

In response to the reviewer's suggestion, we expanded our method to the transfer of CVD-grown MoS_2 samples. Figure S5 of the revised supporting information demonstrates that MoS_2 film can be successfully transferred, resulting in a clean and high-quality surface without any detectable fractures.

In the revised version: "

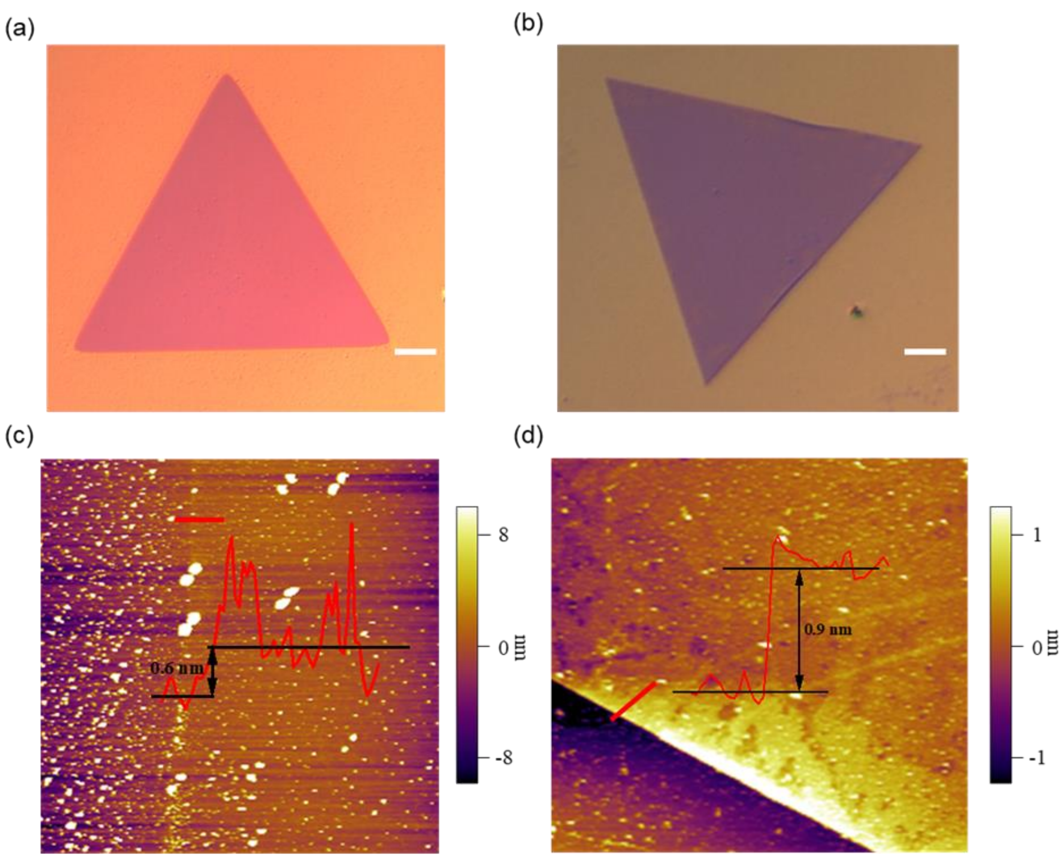

Fig. S5 Microscopic image of (a) as-grown MoS_2 and (b) wet-transferred MoS_2. AFM images and height profiles of (c) direct grown and (d) wet-transferred MoS_2 thin films.”

7.There are some typos on Fig. 4d, ‘Before removing the polyer.’.

Answers: Thanks so much for the reviewer’s careful check. The typo has been revised and the manuscript were carefully proofread.

In the revised version: “

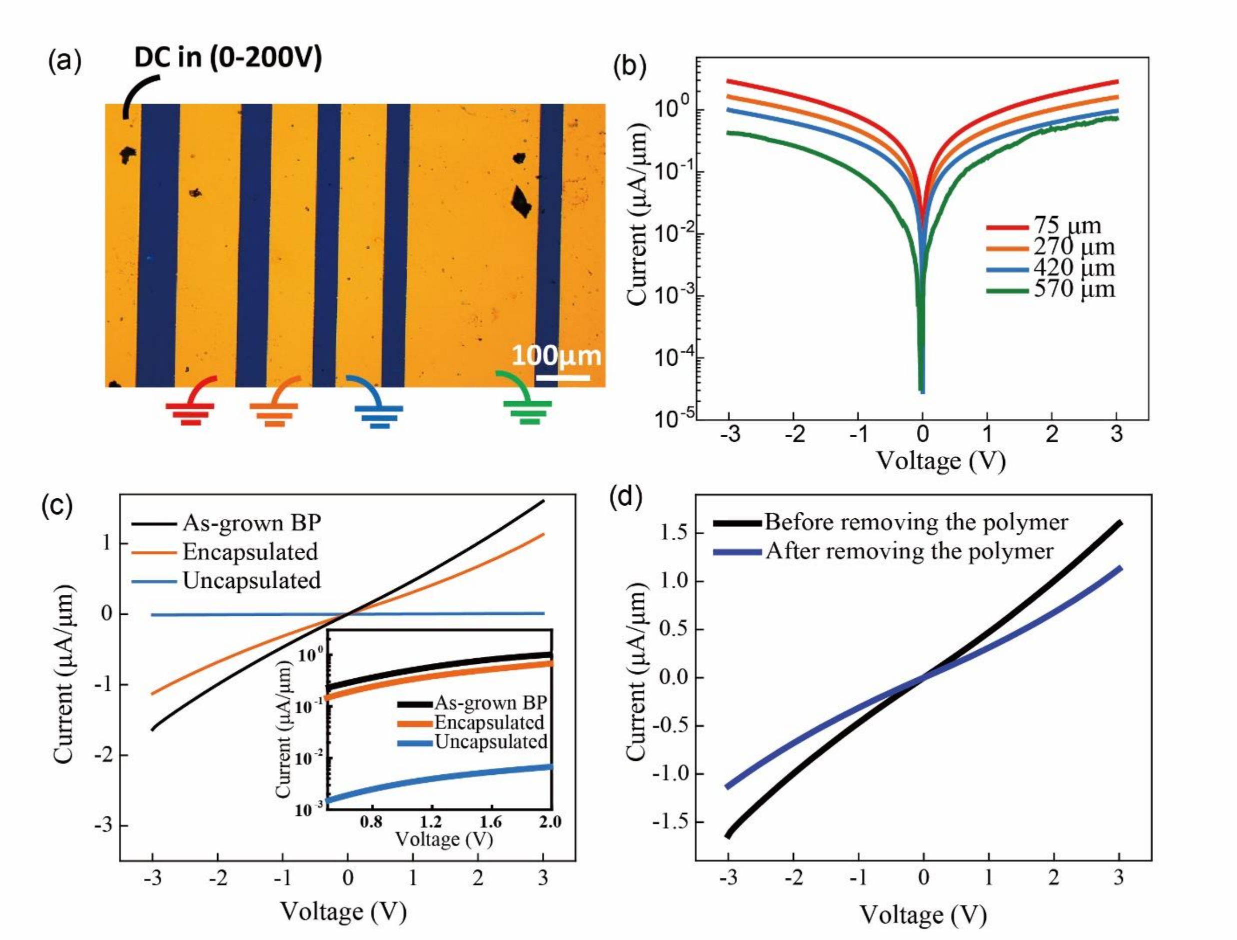

Fig. 4 (a) Optical microscope image of BP FET arrays with different channel lengths on SiO_2/Si substrate. (b) I_{ds} -V_{ds} curves of the BP FET with 75 µm (red), 270 µm (orange), 420 µm (blue) and 570 µm (green) channel lengths. (c) I_{ds} -V_{ds} curves under different passivation conditions in linear and logarithmic (inset) scale. (d) I_{ds} -V_{ds} curves before and after removing the EVA polymer. ”

Reviewer #3 (Remarks to the Author):

This manuscript reports on a wet transfer approach to prepare centimeter-scale black phosphorus (BP) mono-layered crystalline films on silicon substrates for fabrication of field-effect transistors (FET) arrays. Detailed characterization indicated that as-transferred BP films possess uniform morphology and crystallinity, enabling the fabrication of large-scale bottom-gated FET arrays with high carrier mobility and current on/off ratios, although the values are smaller than that in reported literature (Nat. Mater. 22, 717-724 (2023)). The results are interesting and convincing for further development of scalable integration of 2D materials into electronic device applications. Before its further consideration, the following issues need to be addressed:

Thanks for the reviewer's positive feedback. In the revised manuscript, we have taken great care to address all the comments provided by the reviewer.

1. Although the authors have developed a wet transfer approach for their PLD grown BP films to apply them to device applications, the previous reported direct preparation of subcentimetre-scale BP films on SiO_2/Si substrate (Nat. Mater. 22, 717-724 (2023)) should be properly acknowledged in the introduction part.

Answers: Thanks for the valuable suggestion from the reviewer. In the introduction, we have acknowledged the reported work on the direct preparation of subcentimetre-scale BP films on SiO_2/Si substrates.

Page 3, line 5 in the revised version: "…To address this limitation, Chen et al. reported the synthesis of subcentimetre-size single-crystal BP films with thickness around 290 nm on SiO_2/Si substrates, and demonstrated back-gate FETs with excellent device performance.[22] Our group also achieved results in fabricating ultrathin centimetre-scale BP on mica substrates through pulsed laser deposition (PLD).[23] Nonetheless, the as-prepared BP is primarily deposited on mica substrate, which is not typical for electronic device fabrication in the current silicon-dominated semiconducting industry. Therefore, it is important to discover an effective transfer process that integrates our BP thin films with complementary metal–oxide–semiconductor (CMOS)-compatible substrates, while persevering their high crystallinity and outstanding properties."

2. When benchmark the device performance, the values in the literature of Nat. Mater. 22, 717-724 (2023) should be included.

Answers: Thanks so much for the reviewer's suggestion. The values in the literature of Nat. Mater. 22, 717-724 (2023) have been added to Table 1 for comparison.

In the revised version: "

Table 1 Comparison of thin-film FETs constructed with same material (BP) or similar preparation methods (wet transfer)

Material	Preparation method	Substrate	Thickness (nm)	Dimensions (μm)	On/off ratio	Field-effect mobility ($cm^2V^{-1}s^{-1}$)	Ref.
BP	PLD + wet transfer	SiO_2/Si	~5	10^4	3.6×10^3	295	This work
BP	PLD	Mica	5	10^4	$\sim5\times10^3$	213	23
BP	CVD	SiO_2/Si	290	10^3	$\sim10^5$	6500	22
BP	Mechanical exfoliation	SiO_2/Si	~10	5	$\sim10^4$	~100	32
BP	Liquid exfoliation	SiO_2/Si	12	0.8	$\sim10^3$	0.58	33
MoS_2	CVD + wet transfer	SiO_2/Si	0.91	~20	10^6–10^7	35	34
MoS_2	CVD + wet transfer	SiO_2/Si	0.7	~40	10^8–10^9	7.6	35
MoS_2	CVD + wet transfer	SiO_2/Si	10	10^3	10^5	4.5	36

3. The channel lengths of the BP devices are too long (>70 μm) to extract the size effect of the BP films, which weakens the advantages of 2D BP channel over that of silicon when scaling down to nanometer limit. A shorter channel length (Such as 1 μm or shorter) in BP devices is required.

Answers: Thank you for the reviewer's valuable comments.

In response to the reviewer's advice, we have fabricated BP FETs with a channel width of 1 μm, and the microscopic image of the device array is shown in Fig. R5a. Fig. R5b depicts the well-behaved I_{ds}–V_{ds} output characteristics of the FET constructed using a BP thin film with a thickness of around 5 nm. The transfer characteristic is presented in Fig. R5c, while the field-effect mobility and on/off ratio of the BP FET was determined to be 312 $cm^2\ V^{-1}\ s^{-1}$ and 7.8×10^3, respectively. This improved performance observed in BP FETs with a shorter channel length can be attributed to the fact that the back-gate electric field can more effectively modulate the charge carriers across the entire channel region. Also, in devices with longer channel, defects or non-uniformities in the BP film have a greater chance of propagating and affecting the entire channel and degrade the overall performance. In contrast, a shorter channel results in fewer potential defect sites, limiting the distance over which these defects can propagate and reducing their overall impact on device performance. The electrical characterization of the BP FET arrays with 1 µm channel length was added in the revised supporting information as Fig. S6.

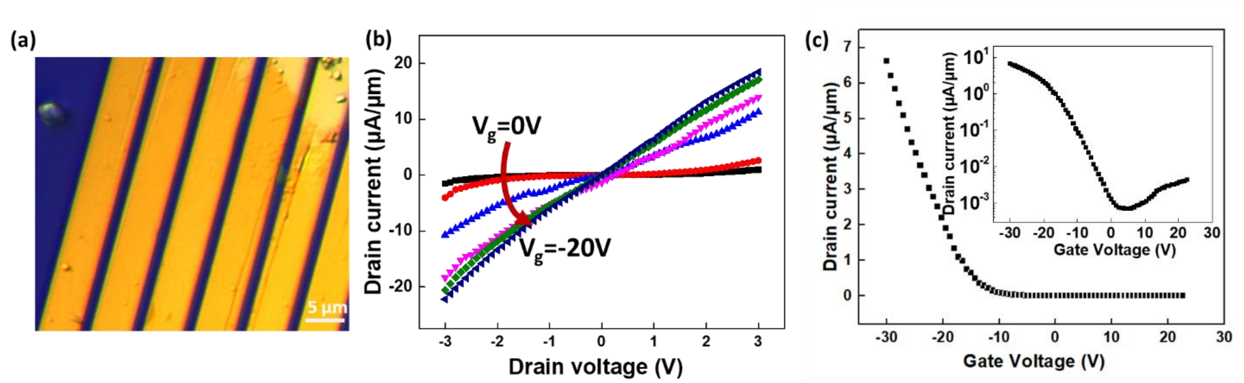

Fig. R5 (a) Optical microscope image of BP FET arrays with 1 µm channel length on SiO_2/Si substrate. (b) I_{ds} -V_{ds} curves of the BP FET at V_g= 0 V, -1 V, -3 V, -5 V, -10 V, and -20 V. (c) Transfer characteristics of BP FET with 1 µm channel length in linear scale with -0.1 V drain voltage. Inset: in logarithmic scale.

Reviewer comments:

Reviewer #1

(Remarks to the Author)
All the concerns/comments are considered carefully, and the authors have modified the manuscript accordingly. The modifications indeed improved the manuscript's quality and readability. The findings are appropriately represented and easily understandable. I recommend the current version of the manuscript for publication.

Reviewer #2

(Remarks to the Author)
The author has revised the article according to the requirements and made great improvements. This manuscript can be accepted.

Reviewer #3

(Remarks to the Author)
In the revised manuscript, the authors have addressed all the issues and now I support the publish of this manuscript.