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Short Communication

Effective passivation of black phosphorus transistor against ambient degradation by an ultra-thin tin oxide film

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Recently, two-dimensional (2D) layered semiconducting materials have been considered as promising channel materials to construct aggressively-scaled transistors owing to their excellent electrostatics and remained high carrier mobility even at atomic thickness [1,2]. Among all of the emerging 2D semiconductors, black phosphorus (BP) exhibits high comprehensive electrical properties if considering both of band-gap and carrier mobility [3–7]. Specifically, BP presents higher room temperature carrier mobility (approximately 1,000 $\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$) than transition metal sulfides (TMDs), and a larger band gap (from 0.3 to 1.5 eV) than graphene, as well as a relative good stability in air [8]. In addition, layered BP is anisotropic in the plane and has different properties in the armchair and zigzag direction [9,10], which potentially bring some additional advantages in devices. As a result, BP has drawn amount of attentions for constructing high-performance and short channel field-effect transistors (FETs) with high speed or excellent scaling down behavior [11–15]. However, the stability of layered BP in the atmosphere is the key problem for the actual applications in electronics. For the layered BP exposed to air, oxygen will be adsorbed on the surface and converted to oxygen ionize under the influence of light, and oxygen ionizes will react with BP and produce phosphoric oxide, which reacts with H_2O in the air [16,17]. The above process is repeated to cause the ambition degradation of the BP, and then leads to severe instability in BP devices [18–20]. Therefore, the effective surface passivation of BP is necessary to suppress the degradation of a BP device during the fabricating process and even after fabrication. Various surface passivation methods have been developed to protect BPs, including chemical modifications and physical coverings [21–28]. Among these reported schemes, some are easy to alter or even degrade the electrical properties of BP [24], others require expensive and inefficient process such as atomic layer deposition (ALD) growth [25]. Transferred films including h-BN, graphene and MoS_2 are also used to cover the BP sample as a passivation layer [27], but are not a scalable method, which is necessary for the actual applications of BP based electronics. Therefore, a simple, scalable and effective passivation method, which meanwhile maintains the material performance, is still in urgent need for the BP devices.

In this work, we demonstrate a simple but effective passivation method for exfoliated BP FETs against ambient degradation through covering a thin tin oxide film. We fabricate back-gated FETs based on exfoliated few layer BP flakes and then form a tin oxide film, which is formed through an electron-beam evaporating a tin film (1 nm thickness) followed by a natural oxidation in air. The tin oxide passivation layer allows the BP FETs to maintain the original performance for a long time in ambient.

Few layer BP flakes were prepared through mechanical exfoliation on marked (with patterned metal film) silicon substrate covered with 300 nm thermal-grown SiO_2. The samples were then soaked in acetone for 2 h to achieve clean surface for the following device fabrication. The location of BP flakes was determined with an optical microscope, and the thin ones large enough were chosen to build FETs. The source and drain contacts were fabricated through an electron-beam-lithography (EBL), an electron-beam evaporation (EBE) of Ti/Au film (5/40 nm) followed by a standard lift off process. A typical as-fabricated back-gated BP FET is shown in Fig. 1a, in which the BP flake presents a thickness of approximately 7 nm (approximately 12 layers) as indicated by the atomic force microscopic (AFM) measurement as in Fig. 1b. It is worth mentioning that an ultra-thin tin oxide layer is used to cover and passivate BP FET here. The tin oxide layer is simply formed through EBE growth of a tin film (1 nm) at a low deposition rate (0.3 $\text{Å}\ \text{s}^{-1}$), and a following natural oxidation in air. AFM image in Fig. 1c illuminates that the uniform and continuous tin oxide film has been

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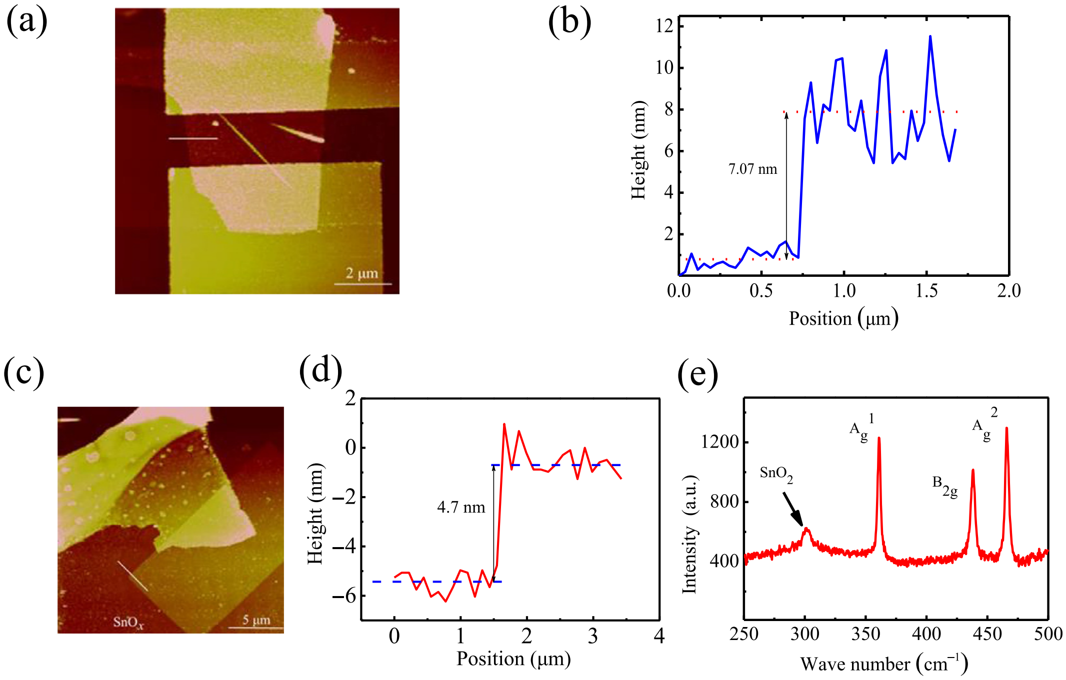

Fig. 1. (Color online) Characterization of exfoliated BP flakes and tin oxide film. (a) AFM image of a layered BP FET. (b) Height measurement of the BP along the white line in (a). (c) AFM image of the patterned SnO_2 film on SiO_2/Si substrate and BP. (d) Height measurement of the SnO_2 along the white line in (c). (e) Typical Raman spectrum of layered BP covered with SnO_2. The wavelength of excitation laser is 488 nm. The measurement was carried out after exposing the sample in air for five days.

formed on BP surface and Si/SiO_2 substrate, and the height measurement (Fig. 1d) shows that the thickness of the tin oxide is approximately 4.7 nm. Fig. 1e shows the Raman spectrum of a layered BP sample covered with tin oxide film, which presents three Raman modes including in-plane vibrational modes A_g^2, B_{2g} with vibration direction perpendicular to each other, and an out-plane vibrational mode A_g^1. It is consistent with the Raman spectrum of few layered BPs reported in Refs. [12,18,29]. In addition, the resonance peak at approximately 300 cm^{-1} (Fig. 1e) is corresponding to the SnO_2 [30], and then further verifies the existence of tin oxide film on BP.

The finished BP FET with tin oxide passivation layer is shown as the schematic view in Fig. 2a, and a typical as-fabricated device is shown in the scanning electron microscope (SEM) image in Fig. 2b. Through measuring in air, the back-gated BP transistor without passivation presents typical p-type field-effect properties (Fig. 2c, dot curve) with a current on/off ratio as high as 10^4 and a current density of 4 $\mu A\ \mu m^{-1}$ under the bias (V_{ds}) of −0.5 V. According to the standard field-effect model, the retrieved field-effect hole mobility from the transfer curve in Fig. 2c is approximately 116 $cm^2\ V^{-1}\ s^{-1}$, which is comparable to room temperature hole mobility in many reported BP FETs with the similar thickness [5,12,26]. It should be noted that obvious current vibrations appear in the transfer curves, which indicates the instability of pure BP FETs in air. The FET was then passivated by SnO_2, and its transfer characteristics were measured in air and shown in Fig. 2c (solid curve). The BP FET with SnO_2 passivation keeps the p-type transfer characteristic with maintained current on/off ratio of 10^4 and hole mobility of 104 $cm^2\ V^{-1}\ s^{-1}$, which indicates that the passivation layer does not obviously degrade the performance of BP channel. Furthermore, the transfer curve becomes smooth and the n-branch in ambipolar behavior is lightly suppressed after passivation. To intuitively demonstrate the effect of SnO_2 passivation for BP FETs, we measured the transfer curves of two BP FETs (with/without passivation) on one chip which were exposed in air for 15 days as shown in Fig. 2d. After exposure in air for 15 days, the pure BP FET (without passivation) is nonconducting at any back-gate voltage, which indicates the BP channel is completely destroyed by H_2O/O_2 in air as reported by many previous works [20,26]. While the SnO_2-passivation BP FET maintains the typical p-type transfer characteristics without visible performance degradation even after exposure in air for 15 days, which reflects that the SnO_2 passivation can provide long-term stability for layered BP materials. The main reason for effective passivation is that continuous SnO_2 film is an effective barrier to water vapor penetration [30]. As is well known, it was the oxygenated H_2O in ambient to destroy structure of BP and then lead to permanent degradation [20]. The surface of layered BP firstly reacts with oxygen in the air, and the formed PO_x will react with water to form corrosive phosphoric acid. Therefore the layered BP will be continuously destroyed by the combined action of O_2 and H_2O in air [20–26]. The coverage of SnO_2 film on BP will prevent water vapor in air penetrating, and the penetrated pure O_2 cannot destroy the BP structure on and on. Therefore, the passivation of SnO_2 can protect the BP FETs effectively. In fact, the SnO_2 thin films were widely used as passivation layer in dye-sensitized solar cells, perovskite solar cells and other transistors [31,32]. In fact, there is a little performance change as the passivated BP FET is exposed in air (Fig. 2e). The V_{th} drift negatively after 10 h exposure is mainly due to that O_2 in air penetrates SnO_2 film and reaches the surface of BP. As a donor impurity for BP, O atoms on BP surface leads to V_{th} negative drift in BP FET. In addition, O atoms can also oxidize BP slowly, and then the top layers of BP have been oxidized by O_2 for the longer time (15 days here). The FET based on thinned BP layer presents reduced current and suppressed ambipolar transfer curve as shown in Fig. 2e.

We also measure the performance evolution in air of BP FETs with/without SnO_2 passivation as shown in Fig. 3, in which four kinds of electrical parameters including on-current (I_{on}), hole mobility, current on/off ratio (I_{on}/I_{off}) and subthreshold swing (SS) are monitored with time. For the BP FET without passivation, all of the four parameters (I_{on}, hole mobility, I_{on}/I_{off} and SS) severely

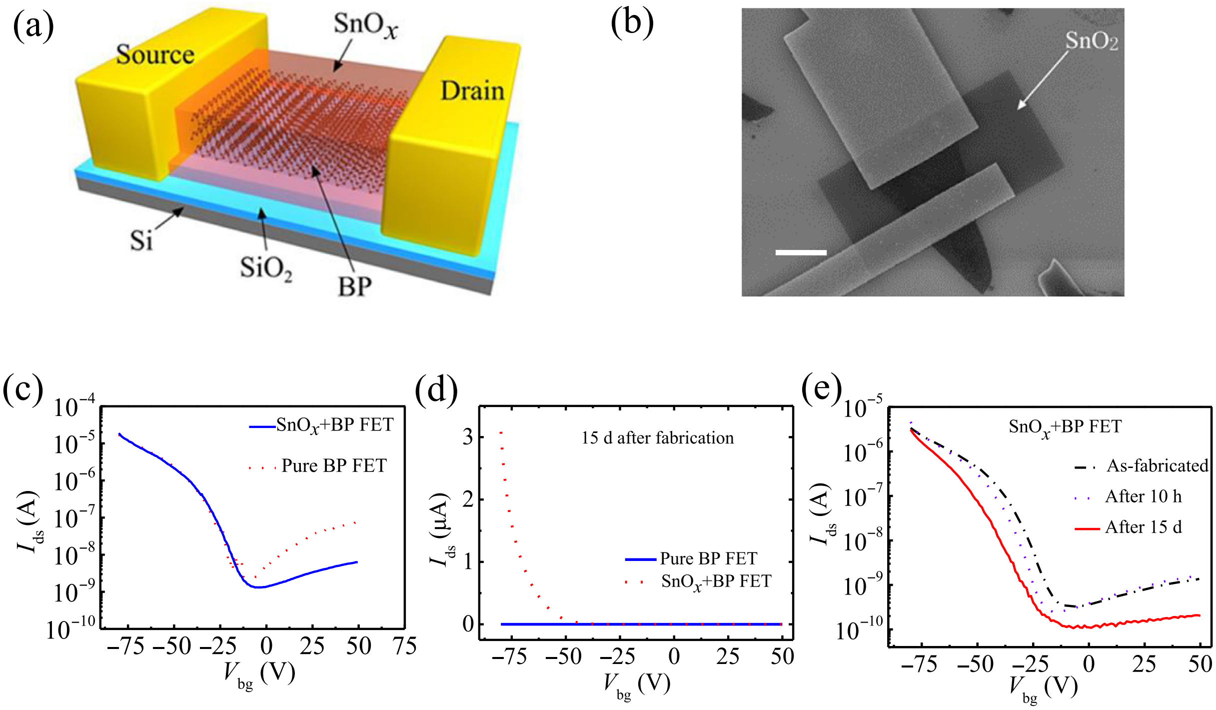

Fig. 2. (Color online) Structure and electrical characterization of BP FETs with/without SnO_2 passivation. All of the devices were measured in air. (a) Three-dimensional schematic view of BPFET with SnO_2 passivation. (b) SEM image of an as-fabricated BP FET covered with a patterned SnO_2 film. The scale bar is 2 μm. (c) Transfer curves of the BP FETs without/with SnO_2 film passivation measured in air, V_{ds} = −0.5 V. The BP FETs present channel length of 1.75 μm and width of 4.6 μm. **(d)** Transfer curves of BP FETs with/without passivation after exposure in air for 15 days, V_{ds} = −0.1 V. (e) Transfer curves of the passivated BP FET at different time, including as fabricated, 10 h and 15 days later, V_{ds} = −0.1 V.

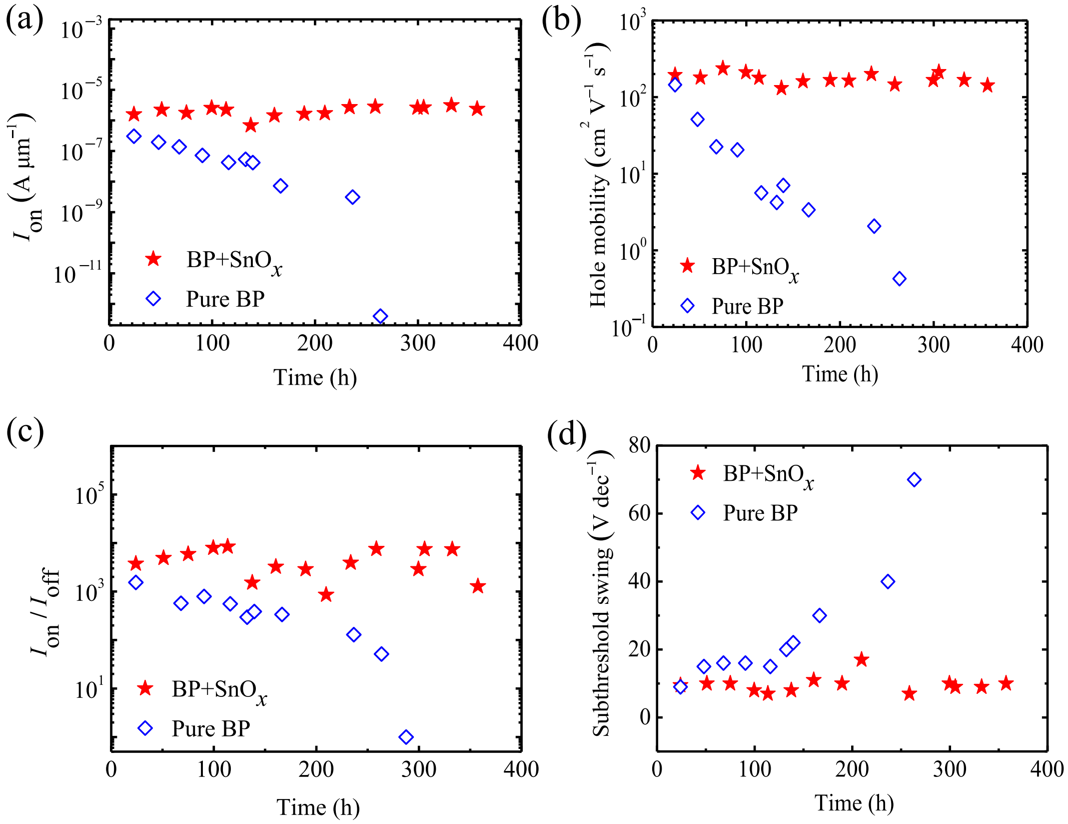

Fig. 3. (Color online) Ambient performance evolution of BP FETs with/without SnO_2 passivation. (a) On-current density I_{on} (at V_{ds} = −0.1 V and V_{bg} = −80 V) versus ambient exposure time. (b) Time-dependent hole mobility (peak field-effect mobility at V_{ds} = −0.1 V). (c) Time-dependent current on/off ratio. (d) Subthreshold swing SS of two kinds of BP FETs versus ambient exposure time.

degrade with time, indicating the comprehensive performance degradation for BP FETs exposed in air. In fact, the un-passivated BP device should be failed after exposed in air for 200 h as shown in Fig. 3a to d, and eventually becomes completely non-conducting for 15 days as shown in Fig. 2e. The SnO_2 passivated BP FET exhibits excellent ambient stability as benchmarked by the four key metrics. Specifically, during exposing the passivation BP FET to air for as long as 15 days, the I_{on} maintains as approximately 2 μA μm^{-1} (at V_{ds} = –0.1 V), and hole mobility keeps at approximately 200 cm^2 V^{-1} s^{-1}. In addition, there are almost invisible changes on current on/off ratio and SS with time for at least 15 days. In fact, some devices survive in air for two months, but the performance should unevenly degrade. The SnO_2 can form stable and smooth interface (Fig. 2b) on BP, and retain the high performance of the BP FET. Therefore, SnO_2 passivation method can be considered as an effective and scalable method for BP FETs.

As a conclusion, we demonstrate a simple and effective passivation method for exfoliated BP FETs against ambient degradation. Specifically, back-gated FETs are fabricated based on exfoliated few layer BP flakes and then covered by a tin oxide film formed through an electron-beam evaporating a tin film followed by a natural oxidation in air. The SnO_2 film forms a water vapor barrier on BP to prevent the combined action of O_2 and water vapor in air from continuously destroying BP, and then protects the BP channel. The tin oxide passivation layer allows the BP FETs to keep typical p-type properties, and maintain hole mobility of approximately 200 cm^2 V^{-1} s^{-1} and high on–off current ratio of approximately 10^4 for over half a month in air.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

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Author contributions

Z. Z. and Z. P. proposed and supervised the project. D. W. prepared BP samples, fabricated transistors and performed measurements. D. W., Z.Z. and Z.P. analyzed the data and co-wrote the manuscript. All authors discussed the results and commented on the manuscript.

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