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2017 Nanotechnology 28 265201

(http://iopscience.iop.org/0957-4484/28/26/265201)

IOP Publishing Nanotechnology
Nanotechnology 28 (2017) 265201 (6pp) https://doi.org/10.1088/1361-6528/aa7532

Reliable passivation of black phosphorus by thin hybrid coating

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Received 11 April 2017, revised 16 May 2017
Accepted for publication 26 May 2017
Published 8 June 2017

Abstract

Black phosphorus (BP) possesses several extraordinary physical properties, which include in-plane anisotropy, thickness dependent direct bandgap and high carrier mobility. These physical properties make BP highly desirable from the point of view of fundamental science and modern optoelectronics applications. The excitement about this material has always been accompanied by unreserved skepticism due to its extraordinary degradation under ambient conditions. Here we show ambient degradation of exfoliated BP can be effectively suppressed using thin layer of hybrid metal organic chemical vapor deposition coating of boron nitride (BN) followed by atomic layer deposition coating of Al_2O_3. We have extensively studied the time dependent surface, optical and electrical properties of BP encapsulated by BN and/or Al_2O_3 using nanoscale infrared imaging and *I–V* characterizations. Our results show hybrid thin layer (~5 nm) BN/Al_2O_3 coated BP exfoliated on SiO_2 substrate is protected from degradation in ambient for over 6 months, much longer than those coated only by BN or Al_2O_3 layers. Our theoretical modeling of the experimental degradation growth pattern shows that the influence of neighboring elements on the degradation of a given element is minimal for BP flakes with hybrid coating. Electrical characterization further confirms the effectiveness of BN/Al_2O_3 as encapsulation layer and gate dielectrics with minor changes after several weeks.

Keywords: black phosphorus, passivation, degradation, hybrid coating

1. Introduction

Since the first exfoliation of graphene [1], several two dimensional van der Waals materials have been identified and studied [2]. Aside from being excellent host of new physics, these materials promise various potential applications in modern optics and electronics. Among recently isolated layered materials, black phosphorus (BP) stands out as an important material with many unique physical properties such as tunable bandgap in the visible-near infrared wavelength region [3, 4] and in-plane anisotropy that promise novel applications in extensive areas such as field effect transistors (FET) [5], photodetectors [6], photoconductive switches [7].

A significant problem that limits applications of BP is its rapid degradation rate under ambient conditions. Over the last 2–3 years the scientific community has aggressively pursed to understand, avoid and protect the degradation problem in many innovative ways [8–12]. BP's susceptibility to degradation has been related to its unstable bonding structure arising from the free lone pairs of phosphorus atoms [8, 13]. The rate of oxidation of BP depends on oxygen concentration, light intensity and energy gap has also been investigated [14]. BP oxidation has also been proposed to be caused by a synergetic effect of water and oxygen where water drives the oxidation via the reaction with the surface oxide which then creates oxygen dissociations [15]. Various methods have been investigated by researchers to overcome or slow the degradation of BP with notable degree of success. These include organic coatings and organic covalent/non-covalent functionalization [11, 12, 16, 17], inorganic coatings [10, 12, 18–20]

and a combination of organic and inorganic coatings [21]. We recently studied the degradation of BP extensively by a combination of nanoscale imaging and theoretical modeling, and showed that thick (10 nm or more) Al_2O_3 coatings can protect BP from ambient degradation [22]. However, finding experimental approaches to reduce the degradation rate with thinner coatings is still a challenge. In this work, we show that a hybrid metal organic chemical vapor deposition (MOCVD) deposited <2 nm boron nitride (BN) layer followed by 3 nm Al_2O_3 grown using atomic layer deposition (ALD) can completely protect BP from degradation for over 6 months.

2. Results and discussion

BP flakes were transferred onto pre-cleaned Si and SiO_2 substrates using conventional mechanical exfoliation. Thin layer of boron nitride (BN) and/or Al_2O_3 were then deposited using MOCVD and ALD techniques respectively. Four BP samples were prepared with different coatings and substrates. (i) BP flakes on Si wafer covered by 1.6 nm thin BN layer, (ii) BP flakes on SiO_2 substrate coated with 1.6 nm BN layer, and (iii) BP flakes on SiO_2 substrate coated with 1.6 nm thick BN followed by 4 nm thick Al_2O_3. All samples were kept in ambient condition at 22 °C with relative humidity ∼40%. Topographic and near-field infrared images were taken using a commercial scattering type Scanning Near-Field Optical Microscopy (s-SNOM) microscope described in our earlier BP degradation studies [22]. s-SNOM provides topography and infrared near-field images of BP flakes allowing investigation of the degradation evolution and effectiveness of coatings. For revealing the electrical properties of these encapsulated BP layers, a p-channel metal-oxide field-effect transistor (pMOSFET) structure was fabricated using 8 nm BP flake with 200 nm channel length (L) and with BN/Al_2O_3 as gate dielectric. Details of pMOSFET device fabrication and electrical measurement procedures can be found in earlier publication [23].

Figure 1 shows topography and third harmonic near-field amplitude (A_3) images of eight BP flakes. Those are with thicknesses ∼30 nm (figures 1(a)–(c)), ∼8 nm (figures 1(d)–(f)), ∼5 nm (figure 1(g)) and ∼15 nm (figure 1(h)). To study the effect of substrates we exfoliated BP on Si and SiO_2 substrates. All exfoliated samples were passivated with either BN (figures 1(a), (b), (d) and (e)), hybrid BN-Al_2O_3 (figures 1(c) and (f)) or Al_2O_3 (figure 1(g) and (h)) coatings. We took successive images of all samples shown in figure 1 for over 6 months but only displayed certain selected images from each flake for comparison.

As shown in figures 1(a), (b), (d) and (e) 1.6 nm BN coating is robust and protects degradation in both the 8 and 30 nm thick flakes till about ∼at day 11 since exfoliation. After the 11th day, the 8 nm thick flake raptures the BN coating and begins to degrade forming bubbles that grow in size as a function of time. Whereas the 30 nm thick BP flake begins with small bubbles that enlarge with time after the 11th day. The rate of degradation is much slower in 30 nm thick BP flake compared to 8 nm flake of the same coating. BN coating keeps the BP flakes intact regardless of thickness for 11 days we monitored and the degradation afterwards proceeds at much slower rate compared to uncoated BP. We have shown two Al_2O_3 coated BP flakes of thickness 5 nm (figure 1(g)) and 15 nm (figure 1(h)). The Al_2O_3 coating layer for these two are 1 nm and 5 nm, respectively. The 5 nm flake coated with 1 nm Al_2O_3 degraded rapidly and ruptured by day 16. However, the 5 nm Al_2O_3 coating of 15 nm thick flake has decelerated the degradation process significantly, but sporadically evolved bubbles were prominent by day 65. A detailed account on the effect of Al_2O_3 coating of BP has been given in our previous article [22]. Other studies of BN-BP-BN sandwiched stable heterostructures have been reported before, however the degradation of BP was not monitored beyond a week to assess the effectiveness of the coating [10].

Hybrid BN (1.6 nm thick) plus Al_2O_3 (3 nm thick) coated BP flakes of thickness 8 and 30 nm are shown in figures 1(c) and (f). Over the time span of our measurement (over 6 months) the 30 nm BP flake did not show any sign of degradation. The thinner 8 nm double coated flake showed no degradation for over two weeks and starts to show minor degradation which increased very slowly till day 45 as shown in figure 1(f). Our results unequivocally show that hybrid BN (MOCVD) and Al_2O_3 (ALD) coating completely avoids degradation of BP flakes for thickness ∼30 nm for over 6 months and significantly slows down degradation for thinner (∼8 nm thick) BP flakes over a period of a month and half.

We have also investigated the effect of the substrate on which BP flakes are exfoliated on the degradation. Figure 2 shows the topography and near-field amplitude of two BP flakes (thickness 8 and 30 nm) exfoliated on Si and SiO_2 substrates and both covered by 1.6 nm BN. These images show that both the 8 and 30 nm thick flakes exfoliated on Si wafer show larger degraded area in a similar duration to those exfoliated on SiO_2. When the height of the tallest degradation 'bubble' on thicker flakes of these two samples are compared, it shows that the bubble height of the flake on SiO_2 is ∼50% smaller than that of the flake on the Si substrate. Both the area coverage and the volume of the degraded bubbles suggest that BP exfoliated on SiO_2 substrate degrades at a slower rate. These results further suggest that it is important to select not only coating material but also the substrate on which to exfoliate/grow BP to reduce degradation [10]. We also note the near-field contrast of BP on Si substrate is larger than that on SiO_2 due to the larger permittivity of Si ($\varepsilon_{Si} > \varepsilon_{BP} > \varepsilon_{SiO2}$).

We implemented a model developed in our previous work in [22] to understand the evolution of the degradation process of the samples investigated experimentally. In this model, the sample surface is divided in to $N \times N$ square elements were randomly defined to be in degraded or non-degraded state. For each of these elements the number of degraded neighbor elements, n; ($0 < n < 8$) were correlated to the degradation probability of the considered element. We considered two cases (i) inclusion, and (ii) exclusion of the influence of neighboring elements on the degradation of a given element. Experimental data in our previous study well fitted with model that considers case (i) where inclusion of

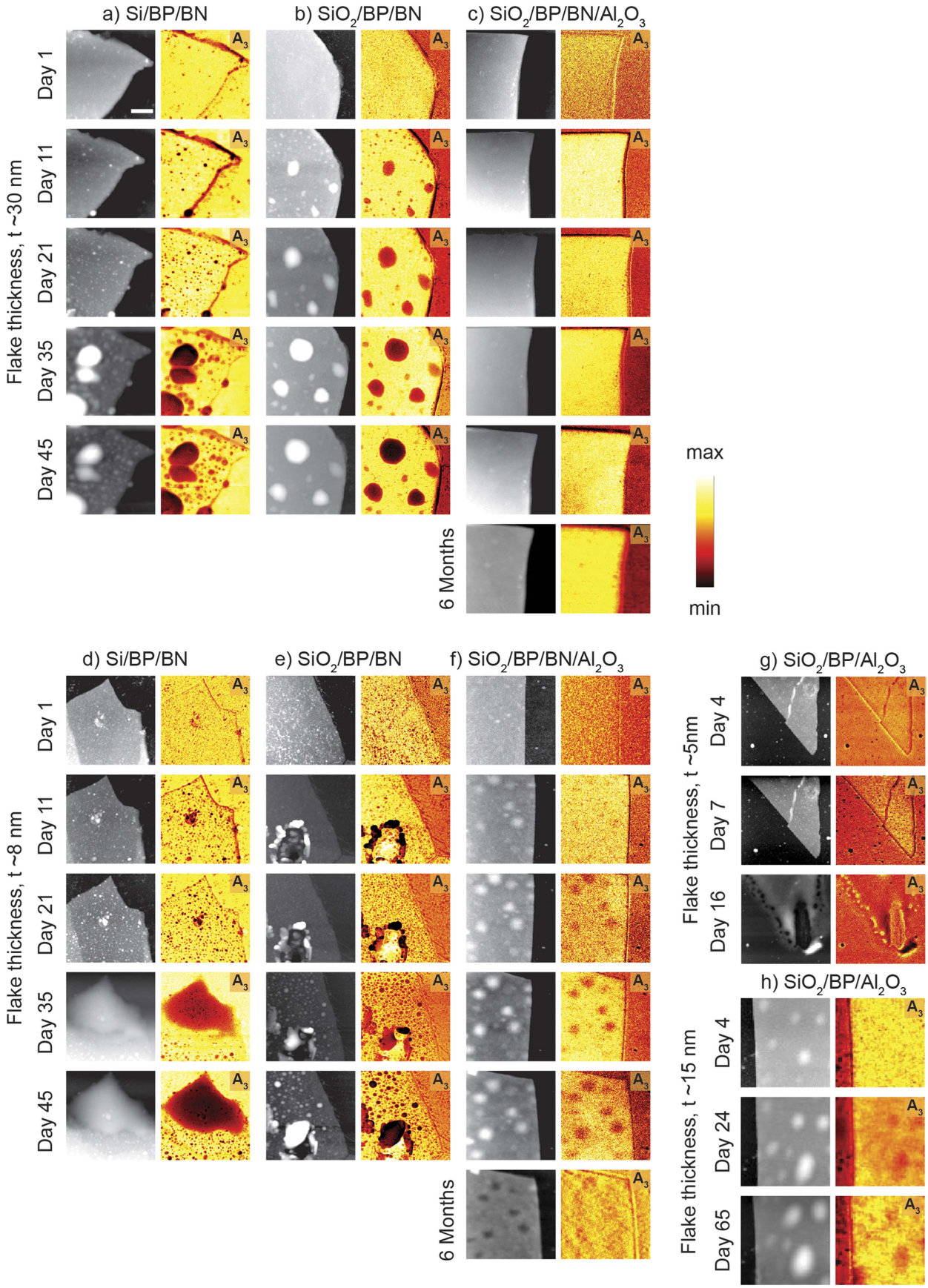

Figure 1. The topography (*grey-white*) and third harmonic near-field amplitude, A_3 (*red-yellow*) images of BP on Si (a) and (d) and SiO_2 (b), (c), (e), (f), (g) and (h) substrates. The flakes are encapsulated by BN (a), (b), (d) and (e), hybrid coating of BN-Al_2O_3 (c) and (f), and by Al_2O_3 (g) and (h) layers. Scale bar 500 nm.

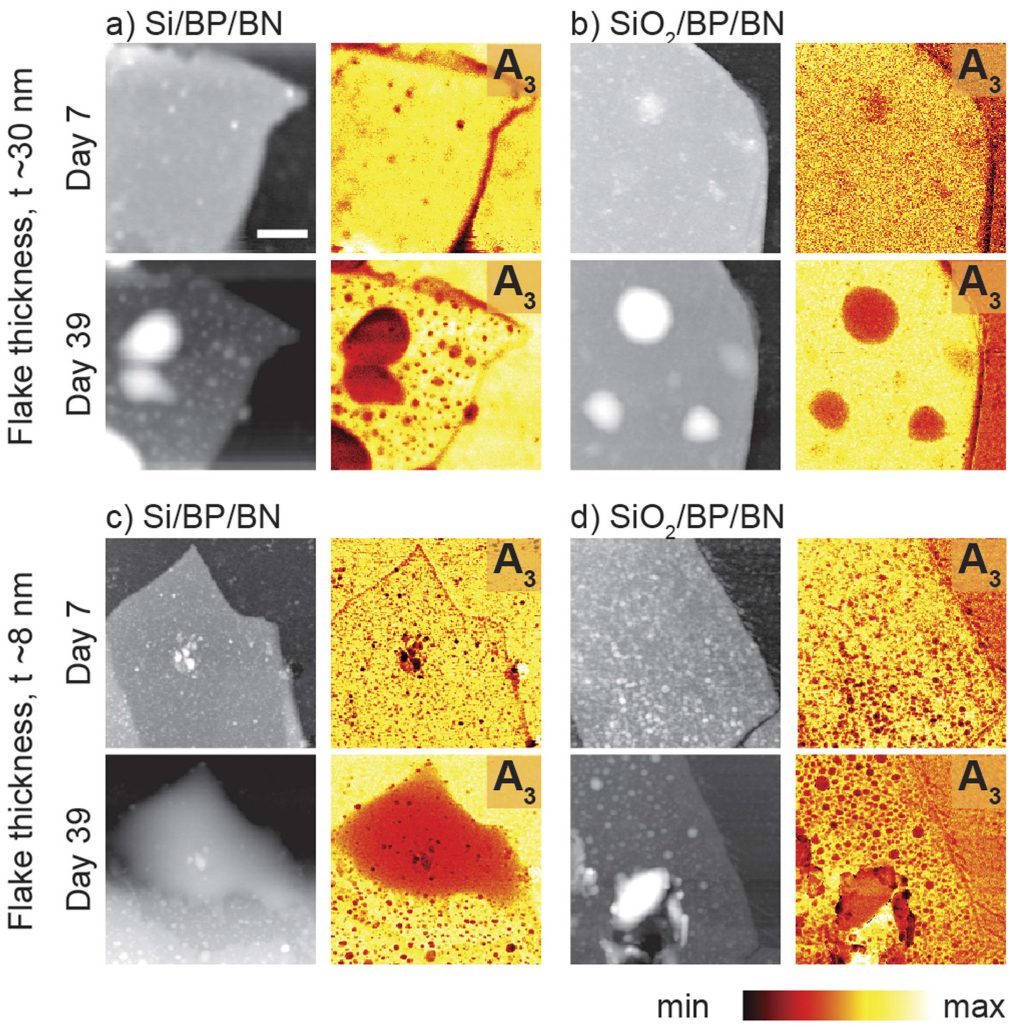

Figure 2. The topography (*grey-white*) and third harmonic near-field amplitude (*red-yellow*) images of the flakes of Si/BP/BN with thickness ~30 nm (a) and ~8 nm (c) and flakes of SiO_2/BP/BN with thickness ~30 nm (b) and ~8 nm (d) on day 7 and day 39. Scale bar 500 nm.

the influence of neighbors was a considerable factor [22]. In our present experiment we found that as the passivation becomes more robust such as using hybrid coating, the evolution of percent degradation as a function of time does not depend on the influence of neighbors as described further below.

In figure 3 we show in blue circles the degradation area percentage as function of time extracted from the experiments for each of the six flakes described in figure 1 and discussion thereof. The red lines in figure 2 show the fitting result of percent degradation of each flake, based on our theoretical model [22]. Of all the samples studied, both 8 and 30 nm thick BP flakes exfoliated on Si wafer and coated only with BN layer are the samples with highest rate of degradation. As shown in figures 2(a) and (d), for these samples the model that considers inclusion of influence of the neighboring elements on the degradation (case i) agrees well with the experimental data. However, for the flakes with slower degradation, fitting significantly failed to represent the experimental results when neighbor influence is considered in calculations. Surprisingly, when the neighbor influence is excluded in calculations the model fitted the experimental data in a very good agreement as shown in figures 2(b), (c) and (e) resulting in an almost-linear relationship between degradation area percentage and time. This behavior suggests that the neighbor influence on degradation of a given site is significantly suppressed in the SiO_2/BP/BN and SiO_2/BP/BN/Al_2O_3 samples. Moreover, according to the topography and near-field amplitude images shown in figure 1(f), and degradation % versus time in figure 2(f), the 30 nm flake on SiO_2 coated with BN and Al_2O_3 shows significantly protected from degradation. We also note thickness dependent degradation of BP has been explained recently by the decrease in bandgap with increasing layer thickness that leads to decrease in oxygen acceptance rate [17].

The output characteristics of the drain current (I_d) versus drain voltage (V_{ds}) of a BN/Al_2O_3 top-gate BP MOSFET the device are shown in figure 4(a). The highest drain current, $I_d = 800\ \mu A\ \mu m^{-1}$ was achieved at $V_d = -1.6$ V and gate voltage, $V_g = -4$ V. The low contact resistance and high hole mobility of BP lead to the high on-state drain current of this device. However, due to the narrow bandgap

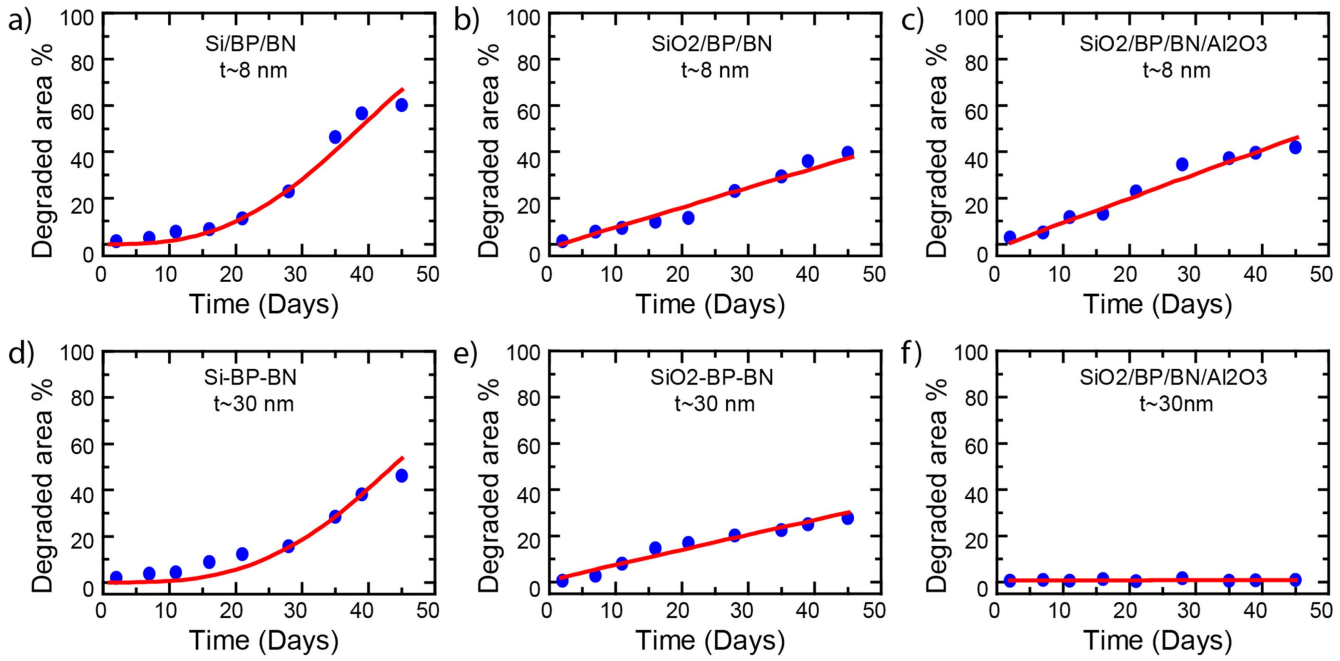

Figure 3. Evolution of degradation area percentage of six flakes shown in figure 1 over the duration of 45 *days* plotted (*blue dots*) together with the fitting (*red lines*) results.

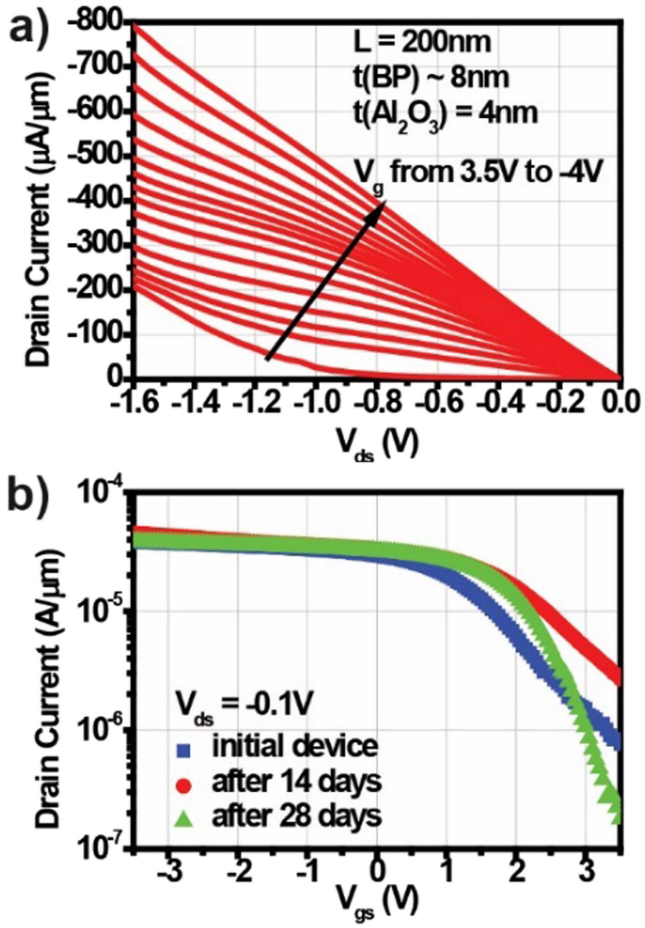

Figure 4. (a) Output characteristics of a BP MOSFET with BN/Al_2O_3 as bi-layer gate dielectric. The high electron transport from the drain contact at high V_{ds} leading to degradation of off-state of the device. (b) Time dependence of drain current, I_d versus V_{gs} of a BP MOSFET with Ni/Au as contact metals. The device has minor off-state changes after four week.

of BP, the electron Schottky barrier is low in general, in great contrast to transition metal dichalcogenides such as MoS_2, ambipolar effect degrades the off-state of the device, which leads to a significant current at large drain voltage. In order to study how the device performance changes with time, the I_d–V_{gs} transfer characteristics measurements were performed after fabrication, and after 14 and 28 days stored in nitrogen box, with $V_d = -0.1$ V. These time dependent I_d–V_{gs} curves are presented in figure 4(b). Even after 28 days, the device still worked with small changes at off-state such as a minor shift in threshold voltage observed on day 14 and day 28 curves. Without BN/Al_2O_3 encapsulation, the device is hard to survive over 24 h due to the strong chemical reaction of BP with moisture in ambient [14, 24]. The electrical characterizations are also consistent with the surface analysis described above.

In summary, based on both surface analysis and electrical measurements, we have shown that the surface stability of BP can be significantly improved by a hybrid ~5 nm coating of BN/Al_2O_3. Even after 6 months, no sign of surface degradation was observed on ~30 nm BP flake. The electrical properties of pMOSFET device structure with BN/Al_2O_3 as gate produced excellent drain current of 800 μA μm^{-1} promising the use of this technique for further development of BP based electrical devices.

Acknowledgments

The work was supported by a grant from the Air Force Office of Scientific Research (AFOSR) grant number FA9559-16-1-0172. SG and NA acknowledge support provided by National Science Foundation grant no. 1553251. The authors would

like to thank Mike Snure and Qing Paduano from AFRL, Wright-Patterson AFB providing us the high-quality of MOCVD BN films.

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