

# Long-term stability study of graphene-passivated black phosphorus under air exposure



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## ABSTRACT

We use the graphene as a passivation layer to protect the black phosphorus from chemical reaction with air. Flakes of the black phosphorus crystal are covered by  $N = 1, 2,$  and  $3$  layers of CVD graphene and the Raman phonon modes are measured after the samples are exposed to air. For the double and triple layer passivation ( $N = 2, 3$ ) the Raman phonon peaks are maintained as long as  $\sim 100$  h (4 days) before the phonon intensity is reduced to 90% of the initial strength,  $I/I_0 = 0.9$ , demonstrating that the black phosphorus is strongly protected in contrast to the rapid degradation of the bare and single-layer covered black phosphorus. The long term stability achieved by multi-layer graphene passivation makes it possible to perform various electronic and optical experiments aimed for device application of this direct-gap van der Waals semiconductor with high electronic and thermal mobility under ambient environment.

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## 1. Introduction

Black phosphorus (BP) has emerged recently as an important van der Waals semiconductor due to the unique properties. Few-layer BP exhibits a direct energy gap in the electron band structure which is lacked in the gapless graphene [1,2]. The band gap can be varied from 0.3 eV (bulk) to 2 eV (monolayer) by increasing the sample thickness, i.e. the number of the phosphorus planes. Transport studies revealed high room temperature mobility  $\sim 1000 \text{ cm}^2\text{V}^{-1} \text{ s}^{-1}$  and large on/off current ratio in the BP-based electronic device. BP has the corrugated in-plane lattice structure which leads to interesting anisotropic behaviors in the electrical and optical responses [3]. For mono-layer BP sample, high thermal transport efficiency and high electronic mobility are predicted theoretically [4,5]. Indeed, BP holds promise for broad 2D semiconductor device application. However, BP becomes chemically unstable when exposed to air. In ambient environment the P-atoms react quickly with  $\text{O}_2$  and/or  $\text{H}_2\text{O}$  resulting in the loss of the intrinsic properties [6–9]. To overcome this weakness various ways of surface passivation have been demonstrated including, among others, the ALD deposition of  $\text{Al}_2\text{O}_3$  thin film, mechanical transfer of

boron nitride (BN) flake, and double capping of dielectric/fluoropolymer films [10–12]. However they either had to rely on UHV condition for the deposition of the passivation material ( $\text{Al}_2\text{O}_3$ ) or was restricted to very small area of protection ( $10 \mu\text{m}$  by  $10 \mu\text{m}$ ) due to the nature of BN flake. Search for new passivation method applicable in ambient condition and capable of large-area coverage is strongly desired for practical application of BP. In this work we use graphene for the BP-passivation. Graphene is considered as an efficient protection material due to the compact lattice structure and chemical stability [13]. For instance monolayer CVD graphene deposited on metal templates such as Cu, Ni and Ru can protect them from the oxidation. The protection however lasted not forever but only for some limited period of time after the sample is exposed to air [14–16]. Here we transfer CVD graphene sheet on BP flakes and measure the micro-Raman spectrum to monitor how the Raman phonon of BP is changed over time. We can deposit not only one but multiple layers of graphene by repeating the transfer. We show from the phonon measurement that the multiple-coverage by graphene strongly enhances the protection power and consequently BP is conserved for longer time in air.

## 2. Experiment

We prepared few-layer BP samples by exfoliating thin flakes from the bulk crystal (99.998%, Smart Elements) on  $\text{SiO}_2$  (270 nm)/

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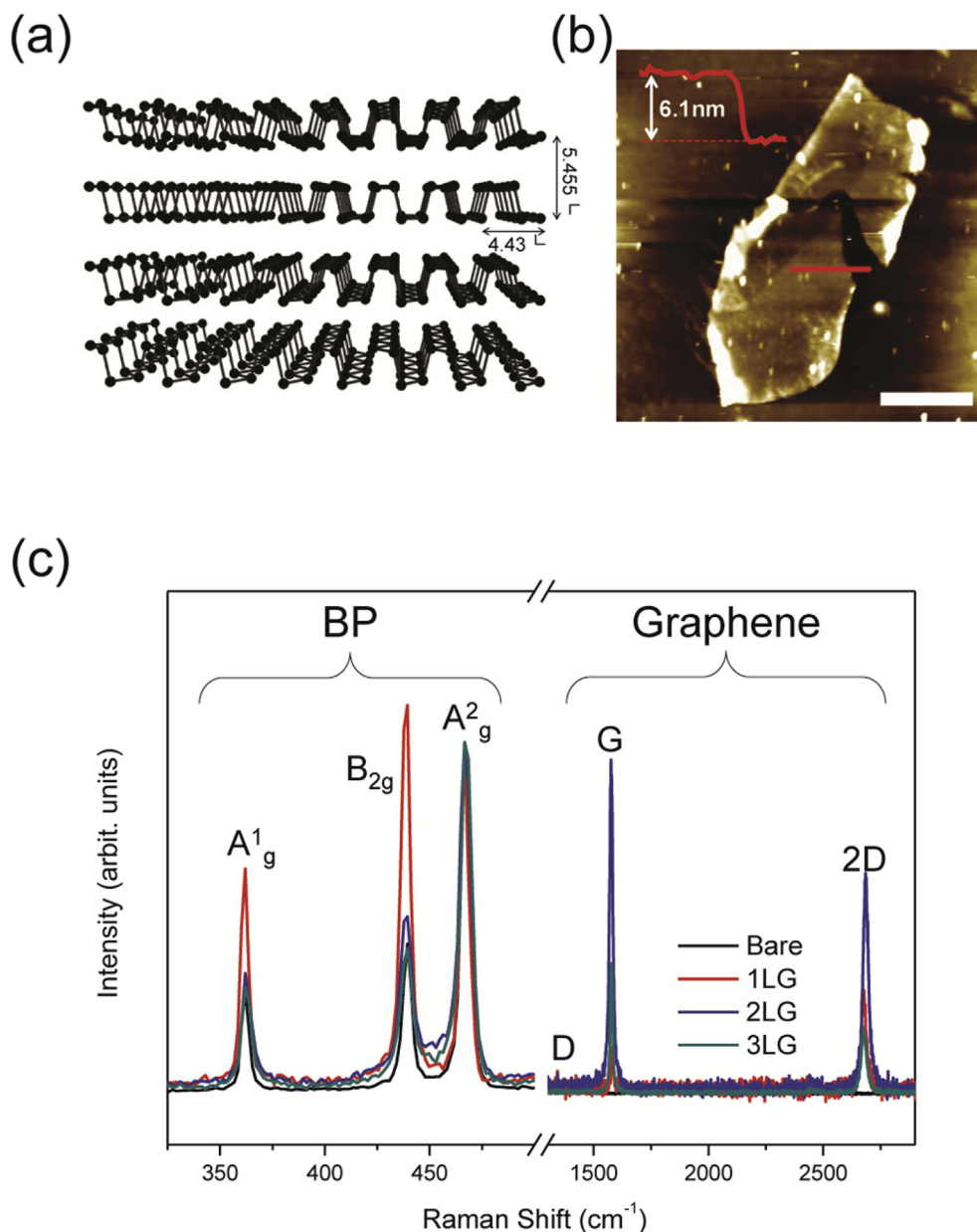
E-mail address: [echoi@uos.ac.kr](mailto:echoi@uos.ac.kr) (E.J. Choi).

Si substrate using the 3M magic tape and blue Nitto tapes. The sample thickness and surface morphology were measured using atomic force microscopy. For the graphene passivation we first synthesized graphene on Cu-templates using chemical vapor deposition (CVD) method [17]. High purity 25  $\mu\text{m}$  thick Cu-foil (Alfa-Aesar, 99.999%) was annealed at 1000  $^{\circ}\text{C}$  under low pressure hydrogen environment for 20 min. Subsequently, the chemical vapor deposition was performed using methane (15 sccm) and hydrogen (10 sccm) flow at the same temperature. Graphene sheet was detached by etching the Cu-foil and transferred it onto BP through water-free PDMS stamp technique [18]. By repeating the transfer we prepared a series of BP covered with one, two, and three layers of graphene, G/BP, G/G/BP, and G/G/G/BP. We expose them to air and measure time dependent change of BP using optical microscope imaging and Raman spectroscopy. Optical images were

taken using a commercial optical microscope set to an 1000-fold image magnification. A micro-Raman spectrometer (Renishaw, inVia micro Raman) equipped with 514 nm wavelength excitation laser (0.2 mW output power) was used for Raman phonon measurement. The size of the beam spot was adjusted to 1.4  $\mu\text{m}$  in diameter for the measurement. We continued the measurements at regular interval up to 22 days.

### 3. Result and discussion

Fig. 1 (a) shows the 3-dimensional crystal structure of BP consisting of corrugated phosphorene planes. Fig. 1 (b) shows atomic force microscopy (AFM) topography image of BP flake ( $\sim 3 \times 8.5 \mu\text{m}$ ) exfoliated on  $\text{SiO}_2$  substrate. The height profile scanned along the red line reveals thickness of the flake to be 6.1 nm which



**Fig. 1.** (a) Crystal structure of black phosphorus. (b) AFM topography image of exfoliated BP flake. Height profile measured along the red line is shown in the inset. Scale bar is 2.5  $\mu\text{m}$ . (c) Raman spectrum of the four BP samples. The Raman peaks represent the phonon modes from BP and from graphene. The peak intensity is normalized by A<sub>2g</sub> mode of BP. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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