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Ultra-sensitive suspended atomically thin-layered black phosphorus mercury sensors

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ABSTRACT

The extraordinary properties of black phosphorus (BP) make it a promising candidate for next-generation transistor chemical sensors. However, BP films reported so far are supported on substrate, and substrate scattering drastically deteriorates its electrical properties. Consequentially, the potential sensing capability of intrinsic BP is highly underestimated and its sensing mechanism is masked. Additionally, the optimum sensing regime of BP remains unexplored. This article is the first demonstration of suspended BP sensor operated in subthreshold regime. BP exhibited significant enhancement of sensitivity for ultra-low-concentration mercury detection in the absence of substrate, and the sensitivity reached maximum in subthreshold regime. Without substrate scattering, the suspended BP device demonstrated 10 times lower 1/f noise which contributed to better signal-to-noise ratio. Therefore, rapid label-free trace detection of Hg^{2+} was achieved with detection limit of 0.01 ppb, lower than the world health organization (WHO) tolerance level (1 ppb). The time constant for ion detection extracted was 3 s. Additionally, experimental results revealed that good stability, repeatability, and selectivity were achieved. BP sensors also demonstrated the ability of detecting mercury ions in environment water samples. The underling sensing mechanism of intrinsic BP was ascribed to the carrier density variation resulted from surface charge gating effect, so suspended BP in subthreshold regime with optimum gating effect demonstrated the best sensitivity. Our results show the prominent advantages of intrinsic BP as a sensing material.

1. Introduction

Mercury is a widespread, highly toxic pollutant which can be accumulated along the food chain and have adverse effects on human health. According to world health organization (WHO), mercury concentration higher than 1 ppb can cause severe health problems (Tan et al., 2016), such as brain damage, kidney failure, immune system disruption, DNA damage, birth defects, and cancer. Therefore, detection of trace concentration of mercury in food, drinking water, and human body is essential. The most reliable methods for the determination of mercury ions include atomic absorption spectroscopy (AAS) (Xie et al., 2008), X-ray fluorescence (XRF) (Ravisankar et al., 2015), inductively coupled plasma-mass spectroscopy (ICP-MS) (Rui and Hao, 2012), inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Cong and Cai, 2010), and surface plasmon resonance sensing (SPR) (Rithesh et al., 2016). These laboratory-based approaches exhibit high performances. However, time-consuming sample pretreatment (labeling process), bulky and sophisticated optical detection system, and high cost prohibit them from wide application (Lagalante, 1999; Moradi et al., 2015).

Chemical sensors based on field-effect transistors (FETs) can overcome the obstacles of previous detection approaches. They are capable of realizing rapid label-free detection with low cost, low power consumption, and can be miniaturized for portable sensors (Ohno et al., 2009). Among various FET channels, black phosphorus (BP) is considered to be a promising candidate. BP, a layered material in which atomic-thin layers are stacked together by van der Waals interactions (Li et al., 2014, 2017; Chen et al., 2017a, 2017b), has drawn significant attention in both fundamental and applied research fields. Mono- and few-layer BP demonstrate both larger current on/off ratio (10^3–10^5) (Saito and Iwasa, 2015; Koenig et al., 2014; Zheng et al., 2017) than that of graphene transistors (Schwierz, 2010; Yan et al., 2014), and higher carrier mobility (1000 $cm^2 V^{-1} s^{-1}$) (Du et al., 2014; Ling et al., 2015; Prakash et al., 2017) than that of two dimensional transitional metal dichalcogenides field-effect transistors (FETs), including MoS_2 (Kim et al., 2012; Radisavljevic et al., 2011). Additionally, molecule adsorption energies of BP are larger than those of graphene and MoS_2 (Kou et al., 2014). These extraordinary properties, together with its

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extremely large surface-to-volume ratio, ultra low noise level, and facile preparation, make BP a promising nanomaterial for chemical sensing. BP FETs are predicted to be highly sensitive for the rapid label-free detection of ions/molecules in extremely low concentration situations by monitoring the resistance shift caused by the adsorption of target analytes (Kou et al., 2014). However, underlying this prediction is the assumption that BP is minimally affected by the interactions with the environment. The environment, especially the substrate, can affect such ultrathin films significantly (BP films reported so far are anchored on SiO_2 supporting substrate). Scattering due to dangling bonds on substrate surface largely reduces the carrier mobility of BP film and drastically deteriorates its electrical properties (Doganov et al., 2015). Consequentially, not only the potential sensing capability of BP is highly underestimated, but also the sensing mechanism of intrinsic BP is masked. Moreover, the ions/molecules detected cannot be absorbed on the bottom side of FET channel, which reduces the sensing area of BP film by half and thus significantly reduces its sensitivity. Besides, research has been focused on the linear regime of BP FET sensors (Chen et al., 2017a, 2017b), whereas, to the best of our knowledge, other regimes remain unexplored. Therefore, it is of key importance to reveal the sensing performance of pristine BP operated in optimum regime.

In this paper, we investigated the outstanding and fundamental questions about BP chemical sensor, its optimum sensing behavior and intrinsic sensing mechanism, by studying suspended BP FETs operated in subthreshold regime. Thus the substrate scattering can be avoided and the sensing area of BP can be fully utilized. We systematically explored their performance for trace Hg^{2+} detection. Free-standing BP mercury sensors gated into subthreshold regime demonstrated ultra-high sensitivity which was almost two-order of magnitude larger than that of non-suspended BP in linear regime. The proposed BP sensors were able to realize rapid (3 s) label-free detection of Hg^{2+} down to 0.01 ppb, and superb selectivity was achieved by functionalizing BP surface with mercury ionophore. BP also demonstrated the ability of detecting mercury ions from real water samples. Our results suggest the high potential of intrinsic BP for ion sensing.

2. Materials and methods

2.1. Materials

Bulk black phosphorus was received from XF Nano Inc. Mercury standard solution for ICP, mercury ionophore, sodium acetate, dibuty butylphosphonate, sodium tetraphenylborate, poly (vinyl chloride) (PVC), and tetrahydrofuran (THF) were all received from Sigma-Aldrich Inc.

2.2. BP synthesis and sensor fabrication

Few-layer BP flakes were mechanically exfoliated by scotch tape based method (Novoselov et al., 2004) and transferred onto low resistance silicon substrate covered with a layer of 300 nm thick SiO_2 (Fig. 1a). BP flakes of thickness less than 50 nm were initially chosen by optical contrast identification approach (Novoselov et al., 2004). Their thicknesses were then accurately identified by atomic force microscopy (AFM) operated in tapping mode. The spring constant and tip radius of AFM probe were 79 N/m and 50 nm, respectively. The quality of BP flakes derived was characterized by Witec Alpha300R Confocal Raman microscope with excitation laser wavelength of 514 nm and the power of the laser below 6 mW to avoid sample damage.

After BP synthesis, FET sensors based on suspended few-layer BP channel with an electrolyte-gate electrode were fabricated. We defined the gate (G), source (S), and drain (D) metal electrode by photolithography, followed by Cr and Au (typically 10 nm and 80 nm, respectively) sputtering, and metal lift-off process (Fig. 1b). The gap between source and drain electrodes was 2 μm. According to previous reports, ions/molecules can be adsorbed directly onto unprotected electrodes, resulting in variation of metal work function and contact resistance (Abe et al., 2008). As such, the source and drain electrode were passivated with dielectric layer. Sequentially, 1:6 buffered oxidize etchant (BOE) was applied to etch SiO_2 sacrificial layer beneath BP and release the free-standing structure (Fig. 1c), followed by critical point drying to avoid stiction problem. After this process, the BP FET sensors were ready for ion detection.

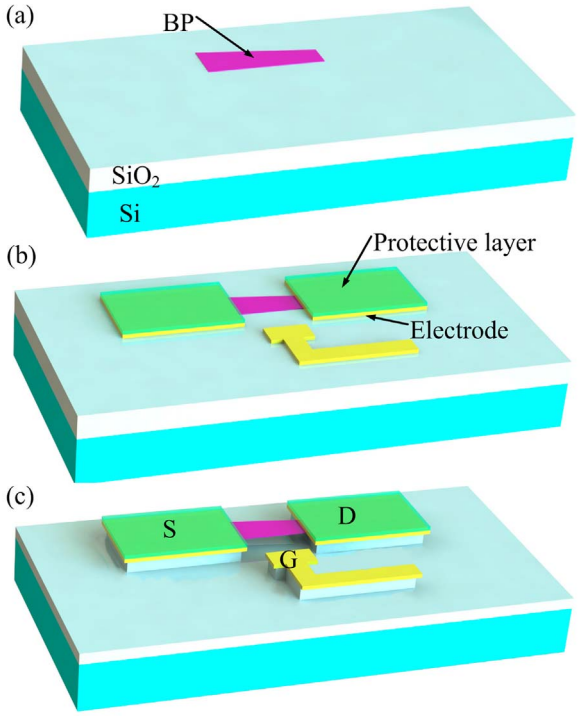

Fig. 1. BP FET sensor fabrication process. (a) A few-layer BP flake is mechanically exfoliated by scotch tape and transferred onto SiO_2/Si substrate. (b) Gate (G), source (S), and drain (D) metal electrodes are defined by photolithography, followed by Cr and Au sputtering, and metal lift-off process. S and D are covered with dielectric layer (protective layer). (c) BOE is applied to etch SiO_2 layer beneath BP, followed by critical point drying to avoid stiction.

3. Results and discussions

3.1. BP and sensor characterization

Fig. 2a is the AFM tapping mode topographic image of a few-layer BP flakes, which length is over 4 μm and is large enough to fabricate FET sensors. AFM height profile extracted from Fig. 2a demonstrates a thickness of 16 nm (Fig. 2b). Raman spectra of mechanical exfoliated flakes show three characteristic peaks (Fig. 2c), which are the Raman shifts attributed to the A^1_g, B_{2g} and A^2_g phonon modes of pristine BP (Zhu et al., 2015). The B_{2g} (~ 440 cm^{-1}) and A^2_g (~ 466 cm^{-1}) peaks correspond to atoms vibrate within the plane, whereas A^1_g (~ 362 cm^{-1}) peak corresponds to the out-of-plane vibration. These sharp phonon modes confirm that the material studied in this work is high quality atomically thin-layered BP crystal. Fig. 2d is the scanning electron microscope (SEM) image of an as-fabricated device with suspended BP channel. AFM topographic image (Fig. 2e) illustrates that the distance between BP channel and substrate is 250 nm, approximately.

The electrical properties of the suspended BP devices were investigated by semiconductor parameter analyzer (B1500A, Agilent Inc.) at room temperature. The results obtained from a typical device exhibited good linear relation between source-drain current I_{DS} and V_{DS}