Sensors & Actuators: B. Chemical 273 (2018) 358–364

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Flexible integrated black phosphorus sensor arrays for high performance ion sensing

Peng Li[a,*], Dongzhi Zhang[b,*], Junfeng Wu[b], Yuhua Cao[b], Zhenling Wu[b]

[a] State Key Laboratory of Precision Measurement Technology and Instruments, Department of Precision Instruments, Tsinghua University, Beijing 100084, China
[b] College of Information and Control Engineering, China University of Petroleum (East China), Qingdao 266580, China

ARTICLE INFO

Keywords:
BP
Flexible
Wearable
Sensor
Integration
Mercury (II) ions

ABSTRACT

The extraordinary properties of black phosphorus (BP) make it an attracting candidate for next-generation chemical sensors. BP is strain-sensitive due to piezoresistive effect, but the impact of strain on BP chemical sensing performance is still unknown which is critical to flexible devices. Additionally, BP sensor integration is highly desired because of the complexity of real samples, but it remains only theoretically explored. Here, we developed flexible integrated BP sensor arrays (FIBA) functionalized with ionophore, which demonstrated excellent mechanical flexibility (strain limits of 1%) and stability (bending 500 times). Small strain variation (from 0.33% to −0.16%) resulted in 175% enhancement of sensitivity due to Schottky barrier modulation. Rapid (4 s) label-free detection of 1 μg/L Hg^{2+} was achieved, within the permissible limit of the guideline for drinking water quality provided by the World Health Organization (WHO). The low-cost simple-structured FIBA realized multiplexed detection of Hg^{2+}, Cd^{2+}, Pb^{2+}, and Na^{+} at trace concentration with excellent selectivity. FIBA also exhibited the ability of monitoring target ions in real samples (Cd^{2+} in tap water and Na^{+} in human sweat). These results demonstrate that FIBA is a promising candidate for wide range of vital signs or environment monitoring.

1. Introduction

Flexible/wearable sensors enable real-time continuously monitoring of wearer's physiological state or environment [1], which has attracted tremendous interest. Among various flexible sensing materials, black phosphorus (BP) is considered to be a promising candidate. BP is a layered 2D semiconductor that is able to reach one-atomic-layer thickness by mechanical exfoliation[2] or chemical vapor deposition [3]. It is one of the most attractive graphene analogues, because mono- and multi-layer BP show both larger current on/off ratio (1×10^3 to 1×10^5) [2,4–6], than that of graphene transistors [7–9] and higher carrier mobility (1000 $cm^2\ V^{-1}s^{-1}$) [10–12] than that of transitional metal dichalcogenides (TMDs) field-effect transistors (FETs), including MoS_2 [13–15]. Compared with graphene which band gap is 0 [16], the natural band gap in BP results in stronger modulation on current produced by analyte adsorption, fundamentally improving the chemical sensitivity [17]. Besides, the molecule adsorption energies of BP are larger than those of graphene and MoS_2 [18]. As a consequence, BP is able to detect various types of analytes in ultralow concentration situations by monitoring the conductance/resistance shift caused by the adsorption of target molecules [19]. Additionally, BP has good mechanical flexibility. It can sustain tensile strain levels up to 30% [20], and avoid inelastic relaxation because of the high elastic strain limit. These unique features, together with its low noise level [21], extremely large surface-to-volume ratio [22], and facile preparation [23], make BP an ideal sensing material for high-performance flexible sensors.

However, to the best of our knowledge, flexible BP ion sensor remains unexplored. Flexible/wearable devices are subject to strain of daily wear and physical exercise [24], and the strain is reported to have different impact on the performance of different wearable sensors [25,26]. Recent theoretical [27] and experimental results [28] demonstrate that the strain induced band gap modulation of BP gives rise to piezoresistive effect, in which a significant change in conductivity can be observed during mechanical deformation. Therefore, it is of key importance to reveal the influence of strain on the chemical sensing performance of BP, which is critical to flexible/wearable devices. Additionally, previously reported BP sensors can only detect one type of ion/molecule at a time [17,19]. Given the complexity of real samples, simultaneous and multiplexed screening of target analyte is crucial and requires integration to ensure the accuracy of sensing. As such, the integration of BP sensors is highly desired but remains only theoretically explored.

In this paper, we demonstrated flexible integrated BP chemical sensor arrays (FIBA) functionalized with ionophore which only allows

* Corresponding authors.

https://doi.org/10.1016/j.snb.2018.06.077
Received 22 November 2017; Received in revised form 1 June 2018; Accepted 15 June 2018
Available online 18 June 2018

certain type of ions to selectively permeate through it. We systematically investigated the impact of strain/stress on the sensing performance and the underling mechanism of flexible BP sensors. Multiplexed detection of Hg^{2+}, Cd^{2+}, Pb^{2+}, and Na^{+}, at trace concentration was achieved with excellent selectivity. The FIBA also demonstrated the ability of monitoring target ions in real samples. Compared with other wearable sensor technology, FIBA has the advantages of low cost, simple structure, and high performance. Our results show the prominent advantages of BP as a flexible sensing material.

2. Experimental details

2.1. Materials

Bulk BP was received from XFNANO. Cadmium, mercury, lead, and sodium ionophores, tetrahydrofuran (THF), dibuty butylphosphonate, sodium tetraphenylborate, Poly(vinyl chloride), (10-Hydroxydecyl)butyrate, Potassium tetrakis (4-chlorophenyl) borate, 2-Nitrophenyl octylether, and bis(2-ethylehexyl) sebacate were all received from Sigma-Aldrich Inc.

2.2. BP synthesis

Multi-layer BP flakes were mechanically exfoliated by scotch tape from bulk BP and transferred onto the surface of polydimethylsiloxane (PDMS) stamp. Mechanical exfoliation method was chosen because it can provide high quality 2D materials [29]. Thin BP flake was initially selected by optical microscope, and then it was transferred onto a 1 × 1 cm flexible poly(ethylene terephthalate) (PET) substrate from PDMS stamp (Fig. 1a). We used micromanipulator to control the position of BP flake on PET with accuracy of 1 μm approximately. The above synthesis and transferring process were repeated 4 times to form well organized BP arrays.

2.3. AFM and Raman characterization

After BP synthesis, we accurately identified the thicknesses of these thin flakes by tapping mode atomic force microscopy (AFM). The driving parameters of an AFM cantilever were chosen to place the oscillator in the net attractive regime during tapping mode imaging, as monitored via the phase signal. The quality of BP flakes was characterized by Witec Alpha300R Confocal Raman microscope with excitation laser wavelength of 514 nm. The power of laser was 1 mW in order to avoid sample damage, and the laser spot was 1 μm in diameter, approximately.

2.4. FIBA fabrication

FIBA were fabricated after BP synthesis and transferring process. We defined the source (S) and drain (D) metal electrodes by photolithography, followed by Ti and Au sputtering (typically 10 nm and 50 nm, respectively), and metal lift-off process (Fig. 1b). The distance between S and D electrodes was 5 μm. According to previous reports, ions/molecules can be adsorbed directly onto unprotected electrodes, resulting in change of metal work function and contact resistance [30]. Additionally, unprotected atomically thin-layered BP films degrade rapidly in ambient environment due to oxidation and layer by layer etching [21]. Therefore, we passivated the sensor with dielectric layer of 30 nm HfO_2 (Fig. 1c). The thickness of HfO_2 was precisely controlled during sputtering. Sequentially, 5 μL cadmium, mercury, lead, and sodium ionophore solution were drop casted onto corresponding BP sensors. Mercury membrane cocktail is a mixture of mercury ionophore (4.5 wt%), dibutyl butylphosphonate (37.9 wt%), sodium tetraphenylborate (0.8 wt%), and Poly(vinyl chloride) (56.8 wt%) [31]. Cadmium membrane cocktail consisted of cadmium ionophore (1 wt%), (10-Hydroxydecyl)butyrate (65 wt%), and Poly(vinyl chloride) (34 wt %) [19]. Lead membrane cocktail consisted of lead ionophore (1 wt%), Potassium tetrakis (4-chlorophenyl) borate (0.35 wt%), 2-Nitrophenyl octylether (65.65 wt%), and Poly (vinyl chloride) (33 wt%) [32]. Sodium membrane cocktail consisted of sodium ionophore (1 wt%), sodium tetraphenylborate (0.55 wt%), bis(2-ethylehexyl) sebacate (65.45 wt%), and Poly(vinyl chloride) (33 wt%) [33]. 100 mg of the membrane cocktail was dissolved in 500 μl of THF. Sensors were then kept in air at room temperature for 10–15 min to let the solvent, THF, completely evaporate and form a solid ionophore layer on BP surface (Fig. 1d). After this process, the FIBA was ready for ion sensing.

3. Results and discussions

3.1. BP and sensor characterization

We investigated the thickness and quality of these thin flakes by AFM and Raman microscopy. Fig. 2a is the AFM height profile derived from a multilayer BP flake on PET substrate, demonstrating a thickness of 47 nm approximately. AFM topographic image (inset of Fig. 2a) illustrates that the size of BP flake is over 10 μm. Raman spectrum shows three prominent characteristic peaks (Fig. 2b) which are Raman shifts attributed to the A_g^1, B_{2g} and A_g^2 phonon modes of pristine BP[12]. The B_{2g} (~ 440 cm^{-1}) and A_g^2 (~ 466 cm^{-1}) peaks correspond to P atoms vibrate within the plane, whereas A_g^1 (~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 BP crystal. Fig. 2c is the photo of FIBA which size is 1 × 1 cm, and Fig. 2d is the scanning electron microscope (SEM) image of one of the as-fabricated BP sensors.

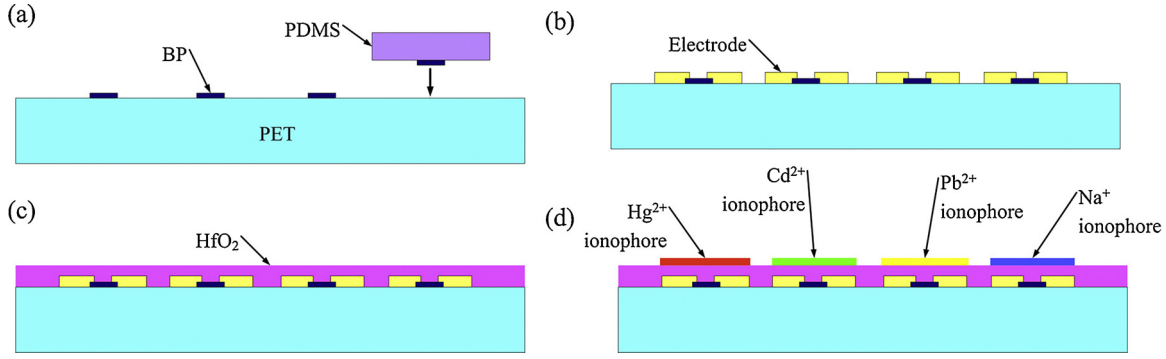

Fig. 1. FIBA fabrication processes. (a) Multilayer BP flakes were mechanically exfoliated and transferred onto PDMS stamp. Thin BP flakes were selected and transferred onto PET substrate from PDMS by micromanipulator. (b) The S and D electrodes were fabricated by Ti/Au deposition and lift-off process. (c) The sensors were passivated with dielectric layer. (d) The BP sensors were functionalized with ionophores to improve the selectivity.