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# Lithography-free fabrication of field effect transistor channels with randomly contact-printed black phosphorus flakes

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ABSTRACT

Black phosphorus (BP) has distinctive properties of tunable direct band gap as a semiconductor material, and both high carrier mobility and on/off switching performance for electronic devices, but has a significant drawback of material degradation in ambient atmosphere. Also, unlike graphene or $MoS_2$, BP is only synthesized in bulk shapes limiting the fabrication of thin film-based devices. We demonstrated a contact printing process for BP field effect transistors (FET) with the steps of mechanical exfoliation of BP flakes and their randomized stamping in dry-transfer regime. The contact printing featured by fast, continuous and solvent-free process on the pre-patterned electrodes guarantees high process efficiency providing immunity against the chemical degradation of BP layers. With asymmetric *I-V* characteristics, the resultant BP-channelized FET shows the electrical properties of on/off current ratio, hole mobility, and subthreshold swing as $> 10^2$, $\sim 130\ cm^2/Vs$, and $\sim 4.6$ V/dec, respectively.

## 1. Introduction

Since black phosphorus (BP) was rediscovered in 2-dimensional (2D) form, the research interest on BP has been increased exponentially quite recently [1]. BP is the most stable among the phosphorus allotropes, is constructed with puckered structure, and has thickness-dependent tunable direct band gap which varies from 0.3 eV (bulk) to 2 eV (monolayer) bridging the spectral gap between graphene and transition metal dichalcogenides (TMDs) [2,3]. In electric applications, most importantly, BP-based field effect transistor (FET) is demonstrated for both high on/off current ratio ($I_{ON}/I_{OFF}$) and experimental field effect hole mobility ($\mu_{FE}$) displaying $\sim 10^5$ and near $1000\ cm^2/Vs$ at room temperature, respectively [3–5]. These distinguishing properties suppose BP as a promising candidate for nanoelectronics and nanophotonics applications for future high-speed data management [2]. Since bulk BP was firstly obtained from Bridgman in 1914, synthesis of BP with a route of vapor growth has been limited up to now [2]. Therefore, in order for the 2D BP, the bulk BP is usually thinned by applying secondary process, exfoliation. Both mechanical and liquid-phase exfoliation schemes have been proposed [2–4,6–8]. Mechanical exfoliation requires a scotch tape or poly(dimethylsiloxane) (PDMS) for the BP transfer onto a wafer to fabricate electrical devices, and additional process steps such as 'flake-searching' through a microscope and lithography for lift-off are essentially required to finalize the FET fabrication [9,10]. Liquid phase exfoliation is suggested in wet process regime to make up the drawbacks shown by the conventional stamping method. However, the efficiency of the process is still low due to the uncontrollable flake size, shape and position for demonstrating BP-based devices. Moreover, the conventional device preparation process suffers from the significant exposures duration of BP to ambient atmosphere. This is very critical to BP that is chemically degraded by oxygen in ambient atmosphere. Also the oxygen gets sufficient activation energy from even light to penetrate into the BP lattice forming phosphorus trioxide so that the degradation is accelerated [11]. Unfortunately, the degradation problem of BP was still not fully solved yet [12]. Since the electrical characteristics of the devices rely on surface degradation of the BP crystal, a fabrication process under minimum exposure to ambient oxygen and light is highly required.

We developed a process for BP-based FETs employing random contact printing of the controlled flakes on a substrate with pre-patterned metal electrodes. The process has advantages not in only terms of solvent and lithography-free but also continuous and simple fabrication with a dramatically reduced process duration for the immunity of BP flakes against the deleterious degradation, thereby guaranteeing a

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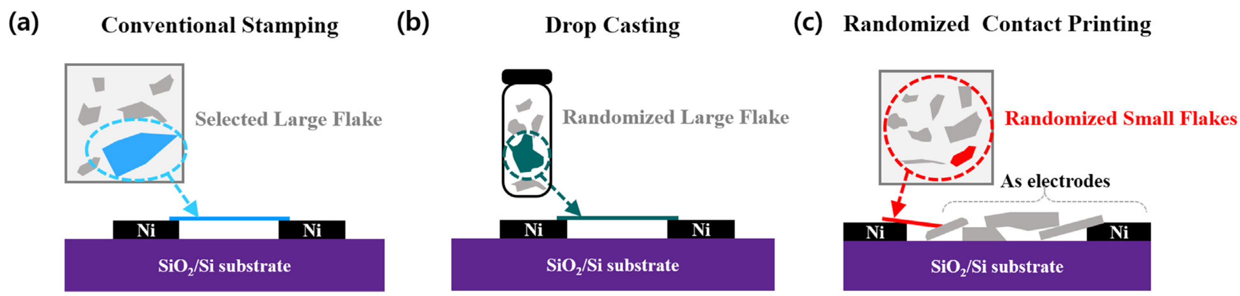


**Fig. 1.** Schematic illustration of (a) conventional stamping, (b) drop casting, and (c) randomized contact printing.

good chance for additional passivation processes to achieve the long-term stability of BP devices. $I_{ON}/I_{OFF}$, $\mu_{FE}$, and subthreshold swing (SS) measured from the resultant BP-based FET showed > $10^2$, ~ 130 $cm^2$/Vs, and ~ 4.6 V/dec, respectively.

## 2. Experiments

### 2.1. Fabrication of BP-based FETs and their characterization

Fig. 1 explains the fabrication processes of BP-based FETs fabrication including a conventional stamping (Fig. 1(a)), a drop casting (Fig. 1(b)) and our randomized contact printing (Fig. 1(c)). The key process issues of each fabrication method are displayed in the Table 1. Also, the processes are compared in terms of the device performance, process efficiency, and surface modification. Due to the flake-searching step, the conventional stamping by mechanical exfoliation has extremely low process efficiency even though the resultant device has the best performance. Drop casting includes liquid phase sonication and centrifugation such that the liquid phase fabrication predominantly enables unintended surface modification. On the other hand, our randomized contact printing process has pre-patterning electrodes and flake thickness and density control processes without any flake-searching or liquid phase, which provides high process efficiency. Especially, the proposed process is designed for a mass production of the electronic devices with tolerable performance.

Fig. 2 illustrates the developed FET fabrication procedure using contact printing the BP flakes onto the substrate with the pre-patterned nickel (Ni) electrodes. Fig. 2(a) shows an aligned metal mask on the substrate with which the pre-patterned 20-nm Ni electrodes onto a $SiO_2$/Si substrate was formed by e-beam evaporation (see Fig. 2(b)). Fig. 2(c) and (d) show the mechanical BP exfoliation process using PDMS stamping for the initial thickness and density control of the BP flakes. PDMS stamp was fabricated by mixing Sylgard 184 A and curing agent 184B with the ratio of 10:1. After degassing it for 30 min, the mixture was hardened at 70 °C for about 20 min on the wafer. The thickness of PDMS layer was about 0.1 ~ 0.2 mm confirmed by the alpha-step measurement. The PDMS surface hardened on the wafer was used to exfoliate and transfer BP flakes. Fig. 2(e) shows the BP transfer onto the substrate with pre-patterned Ni electrodes using the PDMS stamp that has the BP flakes with initially controlled thickness and density distribution. The transferred BP flakes were checked to form a successful channel between electrodes through optical microscope (OM). The size of the electrode is 1 mm × 1 mm and the distance between the electrodes is 30 μ m. Since the channel formation with the BP flakes between the electrodes relies on the statistical possibility, when the density of the BP flakes is too high, extra stamping should be applied to reduce the density to form the optimized BP channels as illustrated in Fig. 2(f). Polyimide (PI) tape with the thickness of 110 μ m was used for the additional control of BP flakes. Except pre-patterning electrodes, whole process duration was shorter than 30 min that is significant to minimize the BP degradation before the passivation. As the final step, the resultant BP FETs were passivated by poly (methyl methacrylate) (PMMA) to avoid the extra-degradation [6,13]. The formed BP channels were confirmed by current-voltage (*I-V*) measurement. Raman scattering spectra were analyzed via a confocal Raman spectroscope (Renishaw instruments) with a 532 nm laser. BP crystallinity was confirmed using X-ray diffraction (XRD, Dmax2500/PC). BP thickness was characterized by Atomic force measurement (AFM, Park System XE-100). *I-V* characteristics of the BP-based FET were analyzed using a semiconductor parameter analyzer (Agilent 4155B).

## 3. Results and discussion

### 3.1. BP characterization

In order to analyze the exfoliated BP flakes, Raman, XRD, and AFM were employed. Fig. 3(a) shows Raman spectra of the BP flakes. Typical Raman characteristic peaks of BP are shown as $A_g^1$(360–365 $cm^{-1}$), $B_{2g}$(~440 $cm^{-1}$), and $A_g^2$(460–470 $cm^{-1}$) that correspond to Raman active modes including out-of-plane vibration mode for $A_g^1$, and in-plane vibration modes for $B_{2g}$, and $A_g^2$ [14,15]. Fig. 3(b) shows the XRD analysis of the exfoliated BP measured with the condition of incident angle = 0.5°, scanning range in 2θ = 5 ~ 60°, and scanning step = 0.2°. The XRD peaks that correspond to BP's typical miller indices of (020), (040), and (060) were located at 2θ = 17°, 34.2°, and 51.7° [16,17]. Since the XRD was measured with the low density of randomly exfoliated BP flakes on the thick Si wafer, the BP peak intensity is relatively low compared to the high Si peak intensity. After optimizing the BP flake with the thickness and density control process for 10 nm, the flakes were analyzed with AFM with the flake number of over 200 and the scan size was 40 × 40 $\mu m^2$. The thickness histogram is presented in Fig. 3(c) and the measured thickness range is from 4 to 150 nm and each bars represents the ranged of 5 nm starting from 4 nm. It was found that the flakes of 10 nm thick were dominant. The corresponding flakes of height profiles and scanned AFM images of various BP flakes

**Table 1**
Comparison of the fabrication processes for 2D nanomaterial-based FETs.

| | Conventional Stamping | Drop Casting | Randomized Contact Printing |
|---|---|---|---|
| Key Process Issues | – Flake-searching<br>– Lithography | – Sonication and Centrifugation<br>– Solvent evaporation | – Pre-patterning electrodes<br>– Flake density control |
| Device Performance | High | Tolerable | Tolerable |
| Process Efficiency | Extremely low | Low | High |
| Surface Modification | Low | High | Low |