

Comparison of Hall Mobility and Carrier Density of Thin Black Phosphorus Exfoliated from Bulk Crystals Provided by Various Vendors

Katie Welch⁽¹⁾, Mahmudul Hasan Doha⁽¹⁾, Zachary P. Uttley⁽²⁾, Arash Fereidouni⁽¹⁾, Abayomi Omolewu⁽¹⁾, Jose Santos⁽²⁾, Magda El-Shenawee⁽²⁾ and Hugh O. H. Churchill⁽¹⁾

(1) Department of Physics, University of Arkansas, Fayetteville, AR, USA

(2) Department of Electrical Engineering, University of Arkansas, Fayetteville, AR, USA

Abstract—In this project, Hall bar devices with black phosphorus (BP) as the semiconductor layer were fabricated to measure the Hall mobility and carrier density of exfoliated BP flakes obtained from bulk crystals acquired from various commercial sources. Black phosphorus is proposed as an alternative material for terahertz photoconductive antennas (PCAs) from the standard GaAs or InGaAs PCAs that are currently available commercially [1]. Black phosphorus is an anisotropic material with a reported Hall mobility over three times greater than GaAs, but our preliminary testing of BP PCAs has shown dramatic differences of electrical properties between black phosphorus sourced from three different vendors. To determine the best quality black phosphorus source, Hall bar devices containing 40 nm BP flakes were used to measure the carrier mobility of the semiconductor. A Hall bar device is created by layering a 40nm BP flake underneath a hexagonal boron-nitride (hBN) flake, all on top of gold contacts in a Hall bar arrangement fabricated on a high-resistivity silicon substrate. The hBN acts as a passivation layer for the BP so that it may be safely removed from the glove box without damage. The Hall mobility of the material from different sources ranges from around 100 cm²/Vs to 1600 cm²/Vs, with only one source showing promising, high-mobility results. This study allows BP with optimized electrical properties to be incorporated into THz PCAs for characterization via THz time domain spectroscopy.

I. INTRODUCTION

Technology using THz frequencies is not as well developed as microwave and optical technologies, in part due to a lack of efficient, broadband, and compact sources of THz radiation [2]. Terahertz imaging applications use a short-pulse Ti:Sapphire or fiber laser at 780 nm that generates THz radiation in a bandwidth from 0.1-4 THz using an InGaAs or GaAs photoconductive antennas (PCAs) in a terahertz time-domain spectroscopy (TDS) system [1]. InGaAs or GaAs are normally used as the active material for THz generation due to its low electron density and high carrier mobility. More recently, black phosphorus has been introduced as a PCA material [3], which shows promising characteristics of strong absorption and high saturation velocity. Black phosphorus (BP) is an air-sensitive anisotropic material with strong absorption in the armchair direction for near infrared wavelengths that are easily accessible for laboratory purposes.

Similar to the typical PCA materials, black phosphorus has a low electron density ($\sim 10^{12}$) and high carrier mobility at room temperature for 2D samples (1500 cm²/Vs) [1]. However, previous fabrications of BP PCAs showed inconsistency of material properties with poor emission in the THz spectra. To investigate the effect of vendor selection on material quality, three different vendors of black phosphorus were used: Smart Elements (Smart), 2D Semiconductors (2DS), and HQ Graphene (HQ). To evaluate material quality from each vendor, BP Hall bar devices were fabricated and measured at room temperature to determine the average mobility and density.

II. METHODOLOGY

A. Experimental Methods

The bulk materials were stored in a nitrogen glove box to prevent degradation. Observations of the bulk crystals showed obvious physical differences: HQ BP exhibited layered, flake-like qualities in bulk, while Smart and 2DS were dense and uniform without layered characteristics. Hall bar devices with six contacts were fabricated inside the glovebox with the help of hermetic transfer cells [4]. BP flakes of ~ 40 nm thickness were created by heated two-dimensional exfoliations of each BP vendor. Atomic force microscopy was used to verify the thickness of each flake; the thickness was chosen to maximize absorption by creating an anti-reflective cavity for the BP when capped with 140 nm hexagonal boron nitride (hBN) [3].

A fully fabricated BP Hall bar is shown in Fig. 1. The Hall bar devices were fabricated using the previously acquired flakes through 2D exfoliations inside a N₂ glovebox. Each BP flake underwent differential reflectance anisotropy measurements, where the absorption of a BP flake in a hermetic transfer cell was measured with a polarized 650 nm laser. The intensity of the reflected beam was measured as a function of the laser polarization, which allows for a determination of the zigzag and armchair directions of the BP [3].

Hall bar devices were fabricated on high-resistivity silicon chips ($>10,000 \Omega\text{cm}$) with 300 nm of thermal oxide. Samples were patterned by electron beam lithography using PMMA A4 resist. After development, the chip was etched to a depth of 60 nm with 10% HF. The contacts were completed by metal evaporation of 5 nm Cr and 60 nm Au, leaving 5 nm of gold extending above the surface of the chip. Using a thin-film

polycarbonate (PC) stamp on PDMS, BP was transferred onto the Hall bar so that the armchair direction, with higher absorption than the zigzag direction, was aligned along the source/drain direction. A hBN flake larger than the BP flake was similarly transferred on top, completing the device so that it was fully passivated from air. At this point, the BP device can be removed from the glovebox safely and wire bonded for electrical measurements.

Once fully fabricated, the devices were loaded into a cryostat at room temperature to represent the typical environment for THz PCAs, and a magnet sweep of -7.5 T to 7.5 T allowed the mobility and density to be measured using standard lock-in techniques. While the thickness of hBN is important for PCAs due to absorption properties, arbitrary thicknesses were chosen here (100 nm - 300 nm) as the hBN only acts as a passivation layer for the BP in Hall bar devices.



Figure 1. Black phosphorus (gold-colored flake centered on the contacts) Hall bars passivated with hBN (nearly transparent in this image).

B. Data Analysis

The slope of V_{xy} versus magnetic field (B) is related to the Hall resistance, shown in (1), where I_{DS} is the source-to-drain current applied on the device. The hall resistance (R_H) is inversely proportional to the electron density (n) times the charge of an electron:

$$R_H = \frac{1}{ne} = \frac{\text{slope}}{I_{DS}} \quad (1)$$

The Hall mobility is dependent on the geometry of the fabricated Hall bar device (2), where L_{xx} is the V_{xx} separation distance (5 μm), W is the V_{xy} separation (4 μm), and V_{xx} is the voltage across the longitudinal probes at zero magnetic field:

$$\mu_H = \frac{L_{xx}}{W} R_H \frac{I_{DS}}{V_{xx}} \quad (2)$$

These expressions were used to extract the mobility and density of Hall bars fabricated with each type of BP.

III. RESULTS

Two devices using BP from each of the three vendors were created and measured, resulting in six Hall bar devices. Example Hall data for one device (second HQ device) are shown in Fig. 2. Mobility and density for each device are shown in Table I, with vendor HQ showing the highest mobility and lowest carrier density. Each device had similar geometry, but were measured with various values of I_{DS} ranging from 10 nA to 1 μA depending on the contact resistance and the 1 V compliance limit set on the current source.

TABLE I. RESULTS OF HALL BAR MEASUREMENT

Hall Bar Results	Black Phosphorus Vendor					
	Smart Elements		2D Semiconductors		HQ Graphene	
Density (cm^{-2})	2.4e14	2.5e14	7.5e13	1.6e13	6.5e11	1.2e13
Mobility (cm^2/Vs)	93	76	3	200	1615	529

Devices fabricated from vendors Smart and 2DS showed similar mobilities of less than 100 cm^2/Vs . Vendor HQ showed the best qualities for THz PCAs, averaging a little less than the expected 1500 cm^2/Vs , but significantly higher than the former two vendors.

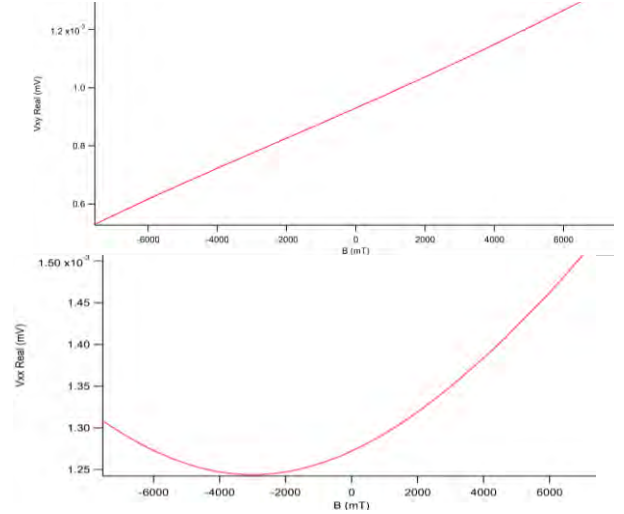


Figure 2. Hall Bar measurements of HQ Graphene BP.

IV. Conclusion

Only one vendor, HQ Graphene, showed sufficiently promising carrier density and mobility to continue fabrication of BP THz PCAs as a potential replacement for the current commercially available PCAs. The other two vendors, 2D Semiconductors and Smart Elements, showed similar bulk qualities as well as Hall bar properties, both of which were inadequate for THz PCAs. The results from this work will allow the continuation of BP PCAs with the vendor HQ Graphene, and further contribute to the works of [1, 2, 3].

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