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Effective photoconductivity of exfoliated black phosphorus for optoelectronic switching under 1.55 μm optical excitation

A. Penillard,^{1,a)} C. Tripon-Canseliet,¹ M. Rosticher,² I. Maksimovic,¹ Z. Liu,³ and E. Géron¹

¹Laboratoire de Physique et d'Etude des Matériaux, Ecole Supérieure de Physique et de Chimie Industrielle de la ville de Paris, UMR8213, 10 rue Vauquelin 75231 Paris Cedex 05, France

²Laboratoire Pierre Aigrain, Département de Physique de l'Ecole Normale Supérieure, 24 rue Lhomond 75231 Paris Cedex 05, France

³School of Materials Science and Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Republic of Singapore

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We present a microwave photoconductive switch based on exfoliated black phosphorus and strongly responding to a 1.55 μm optical excitation. According to its number of atomic layers, exfoliated black phosphorus presents unique properties for optoelectronic applications, like a tunable direct bandgap from 0.3 eV to 2 eV, strong mobilities, and strong conductivities. The switch shows a maximum ON/OFF ratio of 17 dB at 1 GHz, and 2.2 dB at 20 GHz under 1.55- μm laser excitation at 50 mW, never achieved with bidimensional materials. © 2016 AIP Publishing LLC.

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I. INTRODUCTION

A microwave photoconductive switch allows to optically control the magnitude and phase of microwave signals feeding active or passive devices and is also promising for terahertz optoelectronic applications due to the picosecond response to an optical excitation. In 1960, Smith *et al.*¹ succeeded in the first demonstration on Gallium Arsenide substrate photoconductivity implemented in a microwave switching device. From 1989, from the work done by Smith *et al.*, Low-Temperature Grown gallium arsenide (LTG-GaAs) substrate is commonly used to achieve picosecond response ultrafast applications.² Indeed, LT-GaAs material offers interesting carrier dynamic performances such as sub-picosecond lifetime and efficient mobility, preserving semi-insulating properties in terms of dark resistivity. However, the use of LT-GaAs is limited to maximum 0.8 μm optical wavelength operation because of its direct energy bandgap at 1.43 eV, which prohibits its use for common optical communication wavelength of 1.3 μm and 1.5 μm . A first attempt to overcome this limitation was the development of trap assisted two-photons absorption (TPA) in GaAs, but the photo-responsivity obtained was rather weak.³ The other solution is to engineer a new photoconductive material with suitable bandgap energy thanks to lattice matching of III-V compounds. Recently, a working microwave photoconductive switch at 1.55 μm based on GaNAsSb has been reported.⁴

A great interest has been lately initiated for 2D materials with a tunable bandgap. Amongst them, black Phosphorus (bP) appears as a very promising material for optoelectronic applications as its direct bandgap of 0.3 eV in bulk configuration is converted to a bandgap of 2 eV, assuming a 2D configuration by atomically thin layer.⁵ The electronic structure of bP from monolayer to bulk definition is determined by *ab*

initio DFT calculation⁶ and can be predicted according to the effective number of layer. Following this prediction and assuming a reported photo carrier lifetime around 100 ps,⁷ 2D layer stacking of bP becomes a promising material for the fabrication of photoconductive switch operating at common optical communication wavelengths. In this paper, we report the fabrication and the performances of different bP-based microwave photoconductive switches under 1.55 μm CW illumination, validating experimentally the energy bandgap dependency with 2D layer stacking number.

II. EXPERIMENT

In our experiment, the microwave photoconductive device is composed of two metallic electrodes with optimized profile design in coplanar technology deposited on a bP active material, reported on a high resistivity substrate. An optical illumination will control the photoconductive effect in the active material, enabling the transmission of a microwave signal (see Fig. 1), by the local generation of electron-hole pairs in the illuminated area (see Fig. 1).

bP layers were fabricated by scotch-tape exfoliation^{8–10} from a bulk bP substrate using blue scotch NITTO and a PDMS stamp at room temperature, in order to transfer the layers from the scotch to a Si/SiO₂ substrate. Processed bP layers were estimated to be around 1 nm, 12 nm, and 20 nm thick, by atomic force measurement (AFM). Linear tapered metal contact were fabricated using standard electron-beam lithography and evaporation of 10 nm of titanium, 150 nm of gold, and 50 nm of palladium (see Fig. 2). We choose palladium for the electrodes because the work function difference creates an ohmic contact on one of the electrode and a Schottky contact on the other. The electrode gaps were measured by scanning electron microscopy to be, respectively, 150 nm (for the 1 nm thick layer), 200 nm (for the 12 nm thick layer), and 680 nm (for the 20 nm thick layer). We also fabricated a microwave photoconductive switch on a Si/SiO₂

^{a)}Electronic mail: anne.penillard@espci.fr

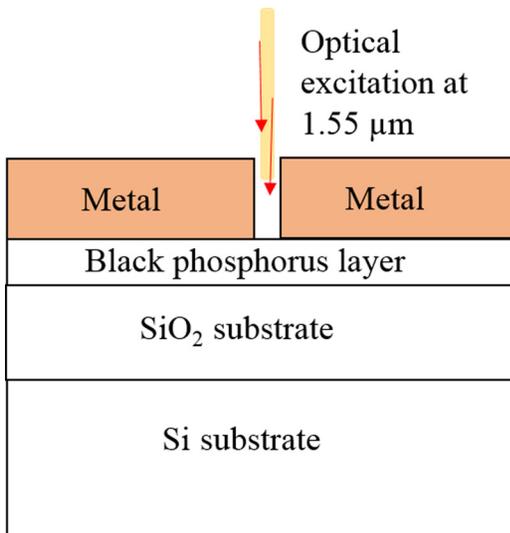


FIG. 1. Schematic diagram of the black phosphorus microwave photoconductive switch.

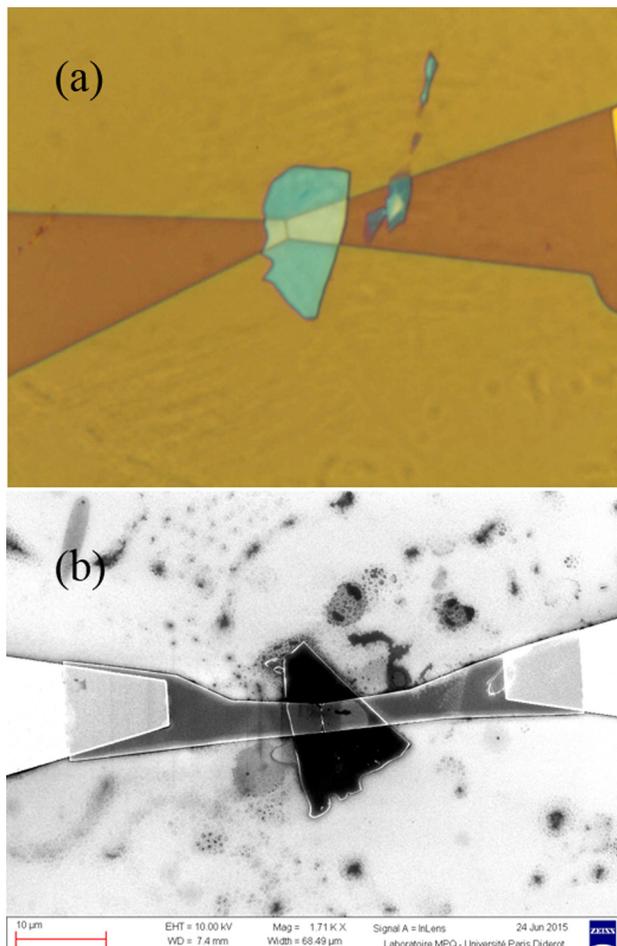


FIG. 2. (a) Optical image of an exfoliated black phosphorus layer in blue with two electrodes, before the evaporation of palladium. The electrode gap length is 100 nm. (b) Scanning electron microscope image of a black phosphorus based photoconductive switch. The exfoliated layer is in black, the two palladium electrodes in grey, and the gold waveguide in white.

substrate without any bP layers, in order to take into account the substrate response.

As 2D bP layers become very sensitive to their environment (air, humidity, light¹⁰), defects such as small droplets appear at the surface, degrading the material electronic properties with thickness (see Fig. 3). In order to prevent this degradation, the exfoliated bP is encapsulated with transparent polymethyl methacrylate (PMMA) and kept in dark between each step in the fabrication process.

III. RESULTS AND DISCUSSION

Microwave performances of bP layer-based devices are evaluated by measuring its ON/OFF ratio ($R_{ON/OFF}$) (1) versus frequency which determines its switching efficiency by illumination. S-Matrix coefficients of the device are measured with a 0.04–67 GHz Rhode & Schwartz Vectorial Network Analyzer under the two working states, after a SOLT calibration with a 101–190 CASCADE calibration kit, in a CPW probe test environment. Top optical excitation of the devices is assumed by a $2\ \mu\text{m}$ lensed fiber placed in a CASCADE Lightwave probe support and connected to a pulsed TOPTICA laser source operating at $1.55\ \mu\text{m}$. From measurements, by the determination of transmission coefficient (S_{21}), device microwave ON/OFF ratio is then directly extracted from the following equation:

$$R_{ON/OFF} = S_{21}(ON)/S_{21}(OFF) = R_{ON/OFF} e^{i\Delta\phi_{ON/OFF}}. \quad (1)$$

In dark conditions, observation of the device transfer function behavior in frequency from S_{21} parameter measurement in magnitude and phase confirms the quality of the developed technological process as a highpass filter characteristic is clearly identified. Corresponding Insertion Losses (IL) and Insertion Phase (IP) from 1 GHz to 60 GHz at values of 53.7 dB and 73.6° down to 21.8 dB and 18.3° are measured from 20 nm-thick bP-based sample to be compared to 54.3 dB and 86.8° down to 20.5 dB from Si-based only sample.

Figure 4 shows the evolution of the ON/OFF ratio according to the input microwave signal frequency, for

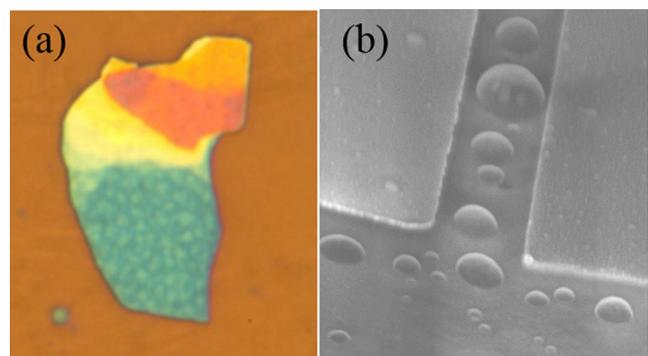


FIG. 3. Effects of the extreme sensitivity of the exfoliated bP to the environment. (a) Optical image of a bP flake several hours after exfoliation. Apparition of droplets at the surface. (b) Scanning electron microscope image of the surface of a black phosphorus layer at especially the gap between the two palladium electrodes one hour after exfoliation. Apparition of droplets at the surface of the black phosphorus.

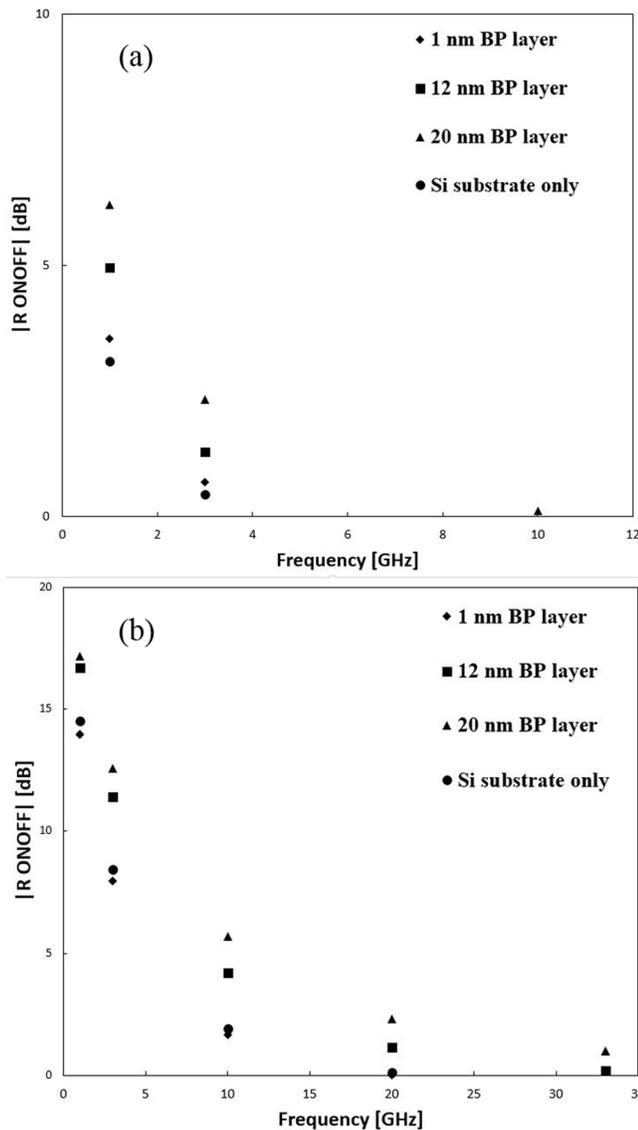


FIG. 4. Plot of the ON/OFF ratio of the black phosphorus based microwave photoconductive switches with a black phosphorus layers thickness of 1 nm, 12 nm, and 20 nm, and the ON/OFF ratio of a switch without black phosphorus (based on Si/SiO₂ substrate) versus frequency, (a) for a laser power of 20 mW and a wavelength of 1.55 μm and (b) for a laser power of 50 mW and a wavelength of 1.55 μm.

different mean optical power levels varying from 10 mW to 50 mW. In the case of one bP layer-based device, experimental results reveal ON/OFF ratio values lower than in the case of Si-substrate device, validating bP layer transparency with regard to thickness. Indeed, according to Cai & Al, the layer must be at least 2.5–3 nm thick to absorb an energy to a 1.55 μm optical wavelength excitation. For thicker layers, and under a 20 mW mean power illumination, microwave ON/OFF ratio decreases from 5 dB and 6 dB to zero for an input microwave signal frequency varying from 1 GHz to 10 GHz, for the 20 nm and 12 nm-thick-bP layer devices, respectively. These results demonstrate 2 dB ON/OFF ratio enhancement from Si-substrate device microwave response. Best experimental results are obtained under a 50 mW optical mean power, for which ON/OFF ratio reaches around 17.2 dB value for 1 GHz for the 20 nm and 16.7 dB for the

12 nm thick bP-layer based device. At higher frequencies, the ratio is always good with a 5.7 dB ratio at 10 GHz for the 20 nm, and a 2.3 dB ratio at 20 GHz.

As referred in previous publication, microwave devices are approximated at first order by an equivalent electrical circuit constituted by a series gap capacitance (C_g) and a total photoconductance (G_g)² defined by the following equation:

$$G_g = \Delta\sigma_{ph} \frac{W_{eff}}{L_g} \frac{1}{(1 - \alpha^2 L^2)} \left[\frac{1}{\alpha} - L \frac{\alpha L^2 + \nu_s \tau}{L + \nu_s \tau} \right], \quad (2)$$

with $\Delta\sigma_{ph} = \frac{e}{h\nu} (\mu_n + \mu_p) \eta \alpha \tau (1 - R) \frac{P_{opt}}{A}$, τ is the carrier lifetime, α is the absorption coefficient of the black phosphorus layer, L is the diffusion length, e is the electronic charge, h is the Planck's constant, ν_s is the surface recombination velocity, P_{opt} is the optical power, A is the effective illumination Area, μ_n and μ_p are the mobilities of electrons and holes, R is the surface reflection coefficient, η is the quantum efficiency of internal photoelectrical effect, and C_g is the capacitance. L_g is the gap length and W the electrode width.

In our case, and in an admittance representation, G_g can be expressed as the sum of bP layer (G_{bP}) and Si-substrate (G_{Si}) photoconductance. From this assumption and by a S-matrix to Y-matrix coefficients conversion, experimental photoconductivity of bP layers can be directly extracted under different optical power levels.

Determination of C_g parameter is also executed by identical analytic procedure, under dark environment only as illumination effect can be neglected. From measurement results, C_g value remains around 5 fF for each bP layer based device as predicted.

Fig. 5 shows the plot of the photoconductance versus frequency for the different samples. According to Cai and Al predictions of the bP electronic gap, we were able to predict the absorption coefficient of each bP layer. For the 1 nm bP layer, there is no absorption at 1.55 μm, since the bandgap is not big enough. This is consistent with the ON/OFF ratio

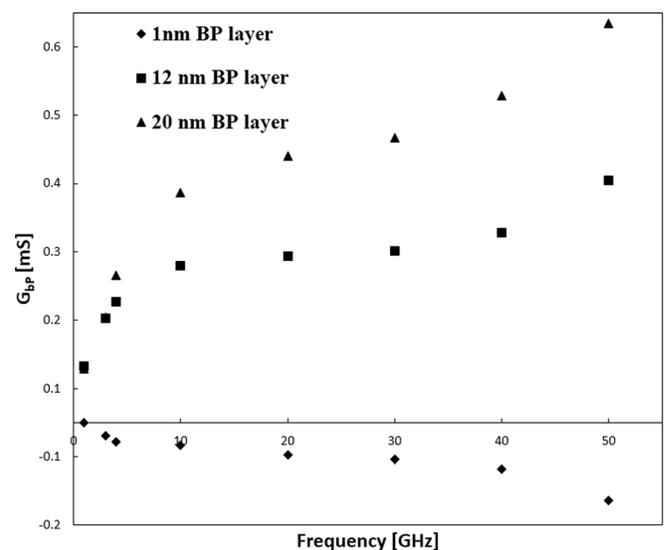


FIG. 5. Plot of the conductance of the BP based photoconductive switch with different layer thicknesses, for a laser power of 50 mW and a wavelength of 1.55 μm.

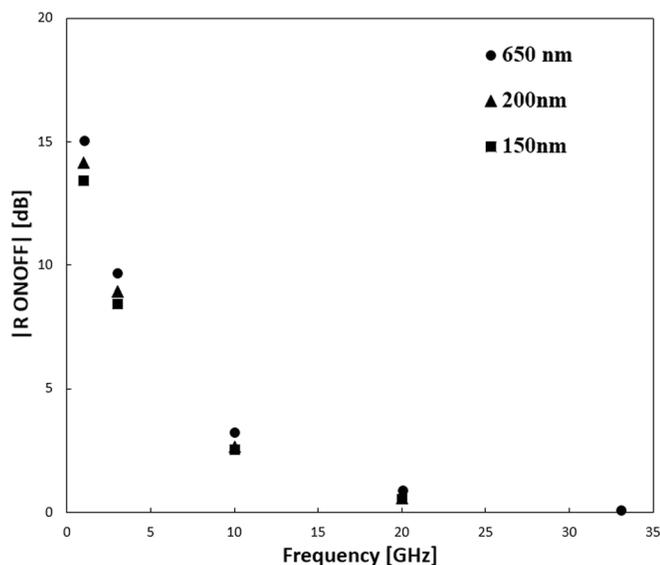


FIG. 6. Plot of the ON/OFF ratio of the silicium substrate based microwave photoconductive switches with electrode gaps of 150 nm, 200 nm, and 650 nm, for a laser power of 25.6 mW and a wavelength of 1.55 μm .

obtained and the negative conductance observed. For the 12 nm thick layer and the 20 nm thick one, the absorption coefficient are, respectively, $2.43 \times 10^4 \text{cm}^{-1}$ and $2.52 \times 10^4 \text{cm}^{-1}$ which was expected since the 20 nm bP layer's ON/OFF ratio and conductance are stronger than the 12 nm bP layer's ones.

In association with the 2D material conductivity change in frequency during ON state (G_{bP}) corresponding to photo-generated carrier densities approximated to 10^{17}cm^{-3} for a photoconductance of 0.5 mS, the device capacitance (C_g) shifts also with optical power level, from 13.8 fF to 23.5 fF at 1 GHz and from 4.7 fF to 6.4 fF at 10 GHz in the case of a 20 nm-thick bP-based sample and a 50 mW input power illumination. After a frequency of 30 GHz, this capacitance value recovers the corresponding OFF state value of 4 fF. This shifting behavior governs then the device cut-off frequency through C_g/G_{bP} ratio in addition with carrier lifetime still experimentally unknown today in phosphorene. Further time-domain and Hall effect experiments will be conducted to status on carrier's dynamics identification in this material. Experimental refractive index estimation is under process to predict light coupling efficiency to bP layers and to identify suitable substrate support for index matching which will optimize the device IL under illumination.

Finally, we also analyzed the standard response at 1.55 μm of the Si-substrate based photoconductive switch used as reference (see Fig. 6), demonstrating then an unusual

absorption, whereas Si material energy bandgap of 1.12 eV is indirect and corresponds to an absorption spectral band from 225 nm to 1100 nm. This response is attributed to a TPA process triggered by the pulsed-mode optical excitation, occurring in Si material with a theoretical β coefficient of 0.45cm GW^{-1} .¹⁰ These phenomena also explain microwave ON/OFF ratio values obtained in the case of the photoconductive switch with the 1 nm thick bP layer. These results are probably due to TPA inside Si substrate, after optical filtering effect of the bP ultrathin layer.

IV. CONCLUSION

A microwave photoconductive switch working at 1.55 μm wavelength optical excitation and based on exfoliated black phosphorus layer stacking has been demonstrated, with a microwave response up to 35 GHz at 50 mW. Future works will be focused on electrode design optimization to 2D material surface area in order to analyze bP layer anisotropy in microwave domain. A dedicated analysis on encapsulation techniques will be also done in order to enhance device protection to environment and therefore enhance its performances.

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