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A great interest has been lately initiated in the optoelectronics field for 2D materials with a tunable bandgap. Being able to choose the bandgap of a material is a huge progress in optoelectronics, since it would permit to overcome the limitation imposed by the graphene lack of energy bandgap, but also the restriction imposed by already used semiconductor whose bandgap are fixed and cannot apply for IR-NIR applications. From DFT simulations predictions, Black Phosphorus (bP) becomes a bidimensional semiconducting material with a direct tunable energy bandgap from 0.3 eV to 2 eV by controlling number of layers. This material also has a picosecond carrier response and exceptional mobilities under external excitation. Hence black phosphorus is a promising 2D material candidate for photoconductive switching under a NIR optical excitation as in telecommunication wavelength range of 1.55 µm. In this paper, material electromagnetic properties analysis is described in a large frequency band from optical to microwave measurements executed on different samples allowing energy bandgap and work function dependency to fabrication techniques, anisotropy and multiscale optoelectronic device realization by switch contact engineering and material passivation or encapsulation. Material implementation in microwave devices opens the route to new broadband electronic functionalities triggered by optics, thanks to light/matter extreme confinement degree. In this paper we present fabrication method of bP based microwave photoconductive switch, with a focus on black phosphorus Raman characterization, and obtained performances.

Keywords: Black phosphorus, 2D materials, phosphorene, photoconductive switch, IR-NIR, microwave

Lately, research have been focusing on finding new suitable materials with good performance for optoelectronic applications, in terms of mobilities, optical bandgap and response. A wide range of material is being studied, from graphene to III-V coumpounds, and transition metal dichalcogenide heterostructure. Amongst them, black Phosphorus (bP) is worth being highlighted as its direct bandgap of 0.3 eV in bulk configuration progressively evolves to a bandgap of 2 eV when reduced down to a 2D configuration. Its tunable bandgap makes it very useful for applications at a common telecomm wavelength. Ab initio DFT calculation predicted the evolution of the bP electronic structure according to the number of layer[1], until a bulk state. Moreover, bP is p-typed and has a reported carrier lifetime of 100 ps[2] more or less, and a high carrier mobility[1] up to 1000 $cm^2V^{-1}s^{-1}$. At last, bP atomic structure was explored by diverse techniques like annular dark-field imaging in a scanning transmission electron microscope (ADF-STEM)[4], angle-resolved photoemission spectroscopy (ARPES)[3]. It has an orthorhombic structure and its atomic layers are linked by weak Van der Waals interaction, hence atomically-thin layers of black phosphorus can be easily obtained with mechanical exfoliation, making optoelectronic devices fabrication very accessible[5,6].

Nowadays, a strong interest has been put on the use of optical signal in the infrared (1.3 µm and 1.5 µm) to trigger electronic devices, allowing ultrafast application in the radiohertz to terahertz domain. Within these devices, attention has been drawn on microwave photoconductive switches for the control of microwave signals through the magnitude and the phase. In 1960, the first photoconductive switch was fabricated by Auston & Al[7]. Almost 30 years later, the development of LT-GaAs by Smith & Al [8] allowed the design of new switches[9], achieving efficient mobility and carrier

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dynamic, a picosecond response and subpicoseconde lifetime and great properties in term of dark resistivity. However these switches were limited by the LT-GaAs band gap of 1.5 eV, preventing any application at the telecom wavelengths of 1.3 µm and 1.5 µm. To outrun this limitation, some researchers developed nonlinear effect in GaAs with two photons absorption but without a great response as a result. Then, recently, a working microwave photoconductive switch at 1.55 µm based on a III-V compounds, GaNAsSb, has been reported[10], leading a new path to material engineering thanks to lattice matching. Focus is also put on few-layer bP for efficient photoconductive switching at 1.55µm for its energy bandgap tunability by process. In this paper, we report material characterization of several bP layer stacking together with the fabrication and performances of different bP-based microwave photoconductive switches under 1.55 µm laser beam oscillation, validating experimentally the energy bandgap dependency with 2D sheet thickness (see figure 1).

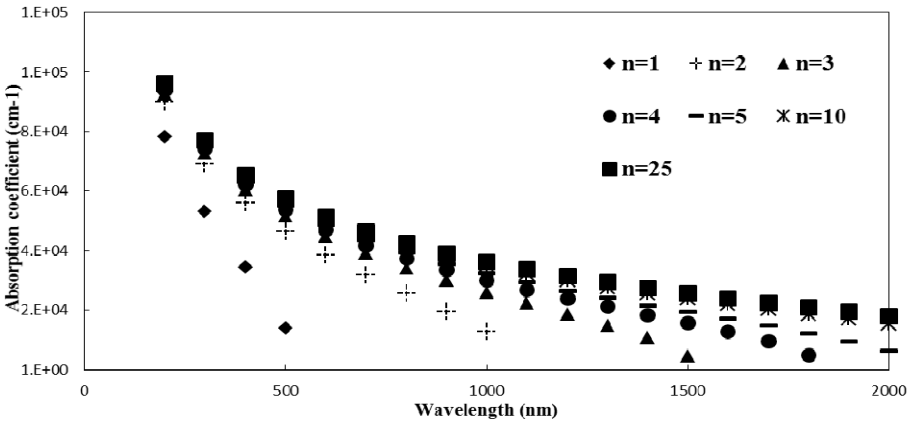

Figure 1 Absorption coefficient of the bP according to wavelength and the number of layers

1. EXFOLIATION AND CHARACTERIZATION OF BP

Black phosphorus layer were fabricated in a clean room by scotch-tape exfoliation from a bulk bP using a blue scotch Nitto and a PDMS stamp at room temperature and ambient air. The layers were transferred on a Si/SiO_2 substrate and a sapphire substrate both heated during 5 minutes at 110°C beforehand to enhance adhesion between the PDMS and the substrate[6]. Processed bP layers were estimated to be around 1 nm to 60nm thick, by atomic force measurement (AFM).

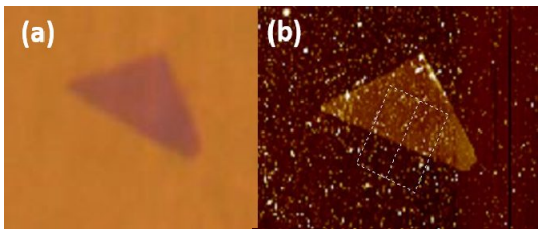

Figure 2 (a) optical image of a bP exfoliated layer (b) AFM measure of the same bP layer: 2-3nm thick

Raman spectroscopy was used on several bP sheets to study and characterize the atomic structure. bP exhibits an orthorhombic structure leading to a very high anisotropy in term of carrier mobilities, optical response, and conductivities. This anisotropy is the result of birefringence coupled with a strong angular dependency making the determination of crystallographic orientation a crucial factor in the design of electronic and optoelectronic devices. The two main crystallographic orientation in bP sheets are armchair (x) and zigzag (y) (see Figure 3) and can be easily determined with Raman spectroscopy. Indeed several studies[11] show the intensity dependency of the A_g^2, B_{2g} and A_g^1 modes with the bP orientation. According to them, the maximum intensity for the A_g^2 phonon is obtained when the laser beam polarization is aligned with the zig zag direction, and along the armchair direction for the B_{2g} phonon. Moreover, according to some experiments, the maximum conductivities and mobilities are achieved along either the armchair direction (x)[12], or the zigzag direction (y)[13].

We performed different Raman spectroscopy analysis at 532 nm on several bP sheets with different thickness (from ML to 58 nm), and different substrates (Si/SiO_2 and Sapphire). First, we studied the evolution of the A_g^1 intensity normalized with the substrate Raman mode (Silicium) according to the sample thickness (see Figure 4.). As predicted, we observe a linear evolution. Indeed the A_g^1 phonon is perpendicular to the substrate surface, hence its intensity is not subject of orientation but becomes more intense with the bP layer thickness.

Second we studied the angular dependency of A_g^2 and B_{2g} in different bP layers. Figure 5.(a) shows this angular evolution for a 20 nm thick bP layer rotated every 15° until 180° with an incoming light polarized along 0° axis. Figure 5.(b) present another angular dependency for a 10nm thick bP layer but with a smaller rotation step (between 5 and 10°) angle and a laser beam polarization along 0° also. We observe a strong periodicity for the two phonons, around 90° between local maximums. The shift between the 2 phonons maxima fluctuates between 20° and 45° (verified on 10 samples of bP). In Figure 5, two different Raman spectroscopy setups were used, each with the same laser wavelength (532nm) but with different powers (2.7 mW for the 20nm thick and 0.675 mW for the 10nm thick). Between the two measurements, the laser power was reduced to prevent any damage on the bP layer and preserve it for optoelectronic devices fabrication. This variation explains the difference in Raman intensities for the two bP thin-films. We observe the same angular dependency for A_g^2 and B_{2g} in bP sample with two thickness but the same sheet (Figure 6). In those samples, the angular periodicity for A_g^2 is about 180°. Recent studies demonstrated a difference in bP layer stacking, which might be the origin of these Raman spectra differences. For all the spectra, B_{2g} as a 90° periodicity, consistent to the 45° angle with the x or y axis.

The study of the bP response to the Raman spectroscopy allows us to determine the crystallographic orientation: for example, in Figure 5, the first graphs shows that the maximum of intensity of the A_g^2 phonon, corresponding to the zigzag direction, is at 65° from the 0° angle, considering the 0° angle align with the x polarization from the laser beam. For the 10nm thick bP, the maximum intensity is reached when the layer is rotate by 105° from the 0° axis, and so is the zigzag direction. Moreover, Liu & Al[5] proved experimentally the angular dependency of the drain current and the transductance of several transistor with a 45° angle variation and build on a 10nm-thick bP layer. These results suggest strongly a similar anisotropic behavior for the mobilities. Unfortunately, no Raman measurement was conducted on this sheet of bP, making its orientation unknown, but its strong resemblance to the Raman angular dependence we obtained (Figure 5), suggests a maximum of mobilities reached once again along the armchair or the zigzag direction. In conclusion, knowing the structure of the bP allows us to design optoelectronic switches on bP layer with the best electrodes orientation and hence to enhance the performances.

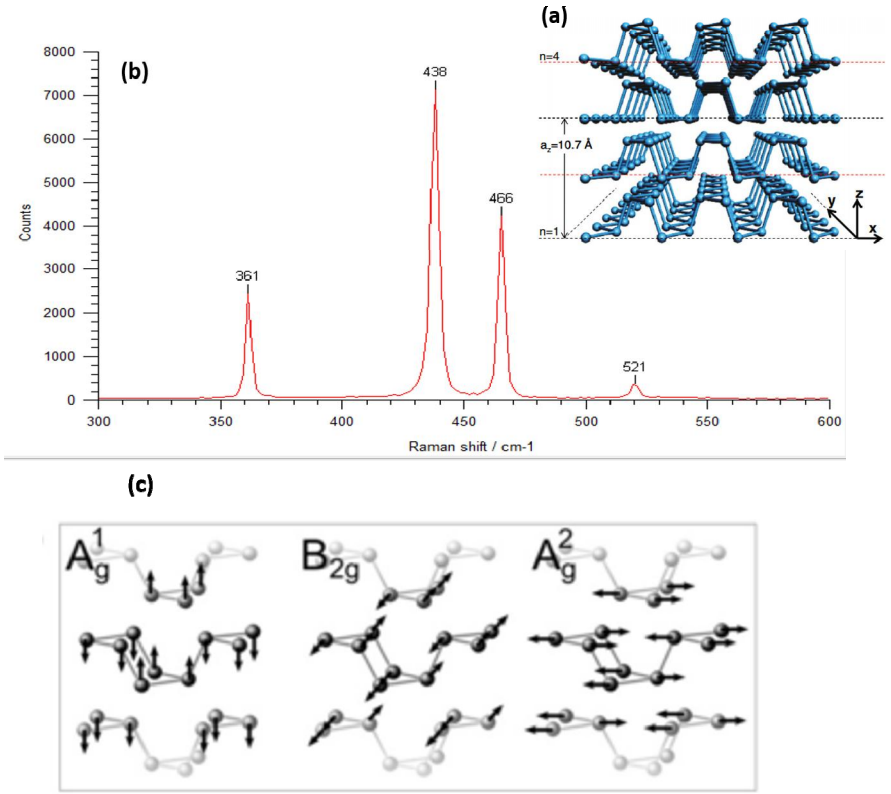

Figure 3 (a) atomic structure of n=4 layer of bP. (b) Typical Raman spectra of the black phosphorus, the 361, 438, 466, 521 peak correspond respectively to A_g^1, B_{2g}, A_g^2 and the silicium substrate. (c) Three Raman modes in the bP and their vibrations directions.

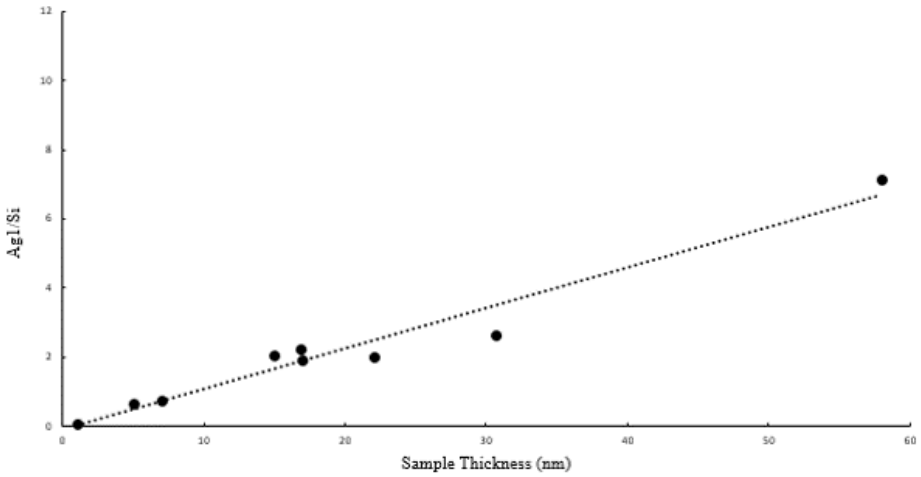

Figure 4 Evolution of the Ag1/Silicium Raman intensity with thickness

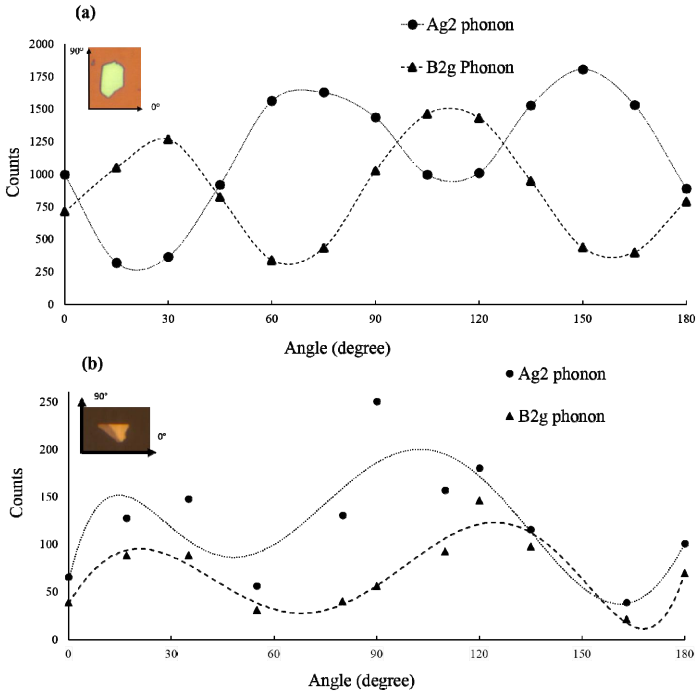

Figure 5 (a) Angular dependency of the A_g^2 and B_{2g} phonons for a 20 nm thick bP layer at 532 nm. (b) Angular dependency of the A_g^2 and B_{2g} phonons for a 10 nm thick bP layer at 532 nm.

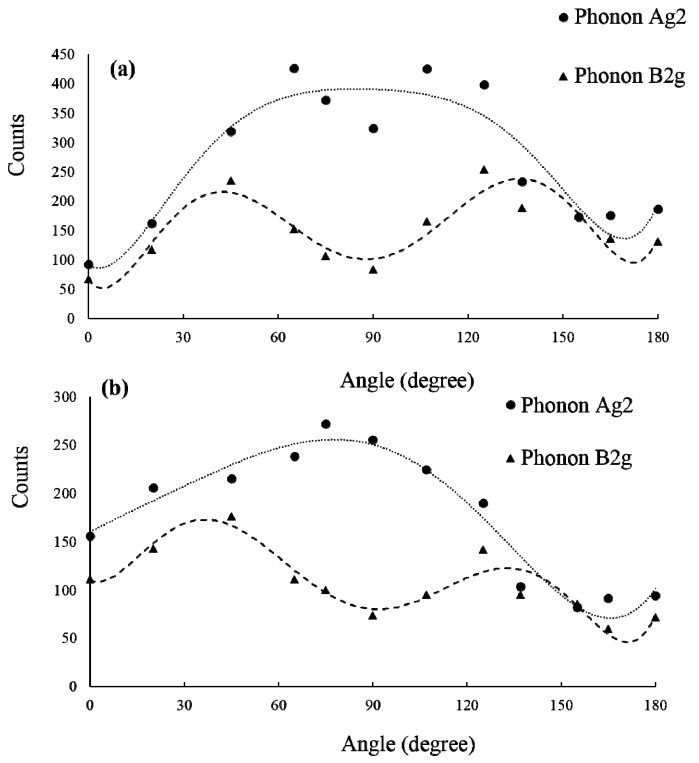

Figure 6 Angular evolution of the Ag1 and Ag2 phonons for the same sheet of bP but with different thicknesses: (a) 15 nm (b) 46 nm

2. BP SENSITIVITY TO ENVIRONMENT

When exfoliated down to few layers, black phosphorus becomes very sensitive to its environment and especially to water molecules in the air. Indeed bP is strongly hydrophilic. When exposed to an ambient air for several hours, bP is etched layer by layer[14]: small droplets appear at the surface of the layer, degrading the electronic properties and at long term completely destroying the layer (Figure 7). A recent publication from Ziletti & Al [15] advances oxygene as a trigger for bP degradation. Moreover, during degradation, bP becomes strongly p-doped.
This major issue needs to be overcome in order to build viable bP based components for example by encapsulating the bP layer to isolate it from the air. Atomic layer deposition (ALD) of Al_2O_3 is a common solution, but not a long term one since the O_2 in the Al_2O_3 can damage the bP. Other groups also tried to encapsulate the bP with boron nitride, but the technique needs improvement. In our case, we need to encapsulate the bP with a transparent, nonmetallic layer, to take advantage of its optical response. ALD could be a good solution but a faster, less expensive one is to recover the device with a thin layer of transparent polymethyl methacrylate (PMMA). PMMA is a transparent resin and is also easily removed or added. Moreover PMMA Raman spectra is very different from the bP one, making possible Raman measurement with the PMMA protective layer.

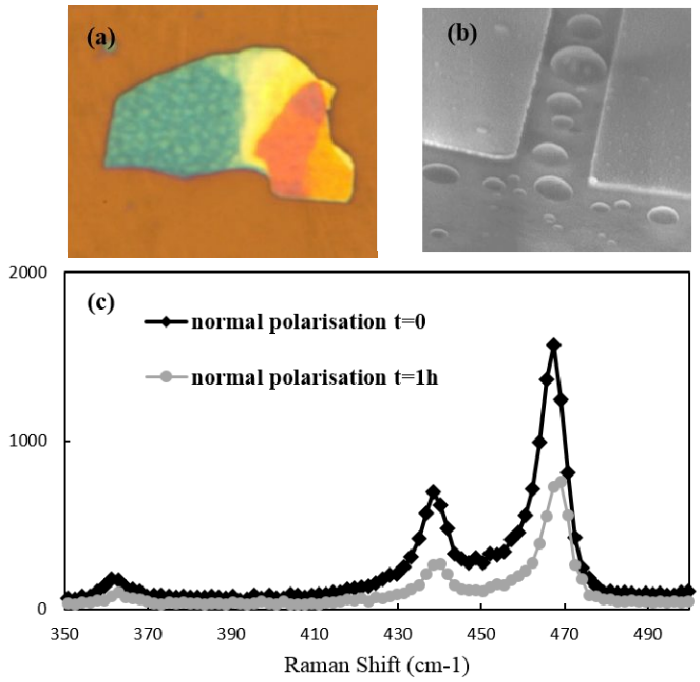

Figure 7 (a) Optical image of exfoliated bP. Observation of droplets at its surface. (b) SEM image of the droplets at the surface of the black phosphorus, and between two electrodes. (c) Raman spectroscopy (532nm, normal polarization) of a 2nm thick bP layer just after exfoliation and one hour after exfoliation.

3. TOWARDS MICROWAVE PHOTOCONDUCTIVE SWITCHES

The determination of suitable exfoliated bP flakes and their orientation is the first step for optical switches engineering. Then we deposit two metallic electrodes following an optimized planar design on bP active material, reported on a high resistivity substrate (Figure 8. (a).) An optical excitation at 1.55 µm illuminate the area between the two electrode, generating locally hole-electrons pairs. The electron-hole pair allow the transmission and the control of a microwave signal in a large frequency range (from 10 MHz to 50 GHz). To obtain a photoresponse to a 1.55 µm optical excitation, the bandgap of the layer must be 0.8 eV or less, and so the layer must be at least 1.5 nm thick (around 3 atomic sheets).

The absorption coefficient grows bigger with the thickness. Moreover, the best mobilities (up to $1000cm^2V^{-1}s^{-1}$) are obtained around 10 nm layer thick[3]. Under 10nm, the mobilities reduce with the thickness of the layer stacking.
In a previous article[2], we described several microwave photoconductive switches build on 1nm, 12nm and 20nm thick bP-layer, on a Si/SiO2 substrate. We obtained a response up to 35 GHz at 50mW for an 1.55µm incoming signal. We then fabricated others microwave photoconductive switches by mechanical exfoliation on a Si/SiO2 substrate, with an optimized electrode design to enhance the performance. Indeed the first microwave photoconductive switch had two palladium electrodes creating an ohmic contact on one side, and a Shottky contact on the other, following the device polarization and the difference in work function. For the new devices, we chose to evaporate gold for one electrode and aluminum for the other, in order to create ohmic contact for electron and hole at both interfaces (Figure 8 (a)). Hence, palladium and aluminum conductivities are good. The gap between the two electrodes is 650nm, in agreement with performances obtain previously on microwave photoconductive switches with different gap length[16]. The gold waveguide and the Pd/Al electrode were processed by a three-step e-beam lithography followed by metal evaporation in a clean room. As 2D bP layers are very sensitive to their environment, the exfoliated bP was encapsulated with PMMA and kept in dark between each step in the fabrication process. At the end, the bP was encapsulated with atomic layer deposition of Al_2O_3.

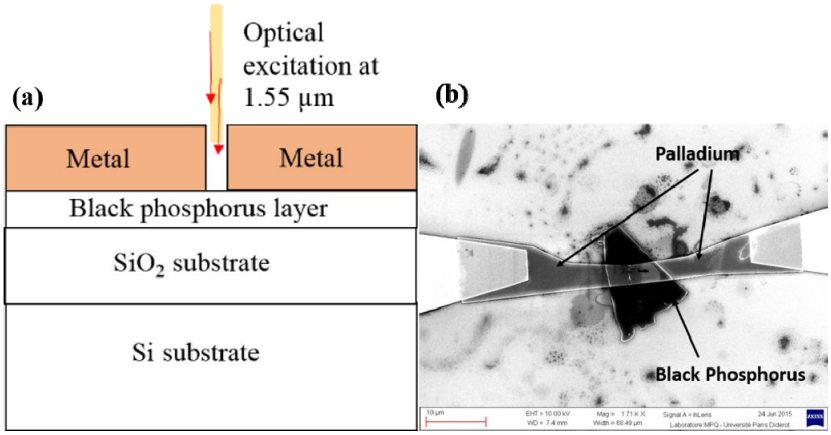

Figure 8 (a) Schematic bP-based photoconductive switch on a Si/SiO2 substrate. (b) SEM image of a microwave photonductive switch.

The performance of the microwave photoconductive switch is evaluated by measuring its ON/OFF ratio ($\mathbf{R}_{ON/OFF}$)with and without optical illumination at the gap. The S parameter (S_{21}) were extracted using a 0.04-67 GHz Rohde & Schwarz Vectorial Network Analyzer under the two working states, after a SOLT calibration with a 101-190 CASCADE calibration kit, in a probe test environment. We used an LEA photonics CW infrared laser (1.55 µm) in order to avoid any two photons absorption in the Si/SiO_2 substrate[16]. Figure 9 displays the results for a microwave photoconductive switch based on a 23 nm thick at different laser powers, from 10mW to 62mW. We observed a response up to 50 GHz with a 1 dB ON/OFF ratio. At lower frequencies (10GHz), the ON/OFF ratio is up to 5dB. As expected, the ON/OFF ratio expands with the input laser power, but it is crucial to choose carefully the maximum input power in order to prevent degradation on the layer by the laser beam. The electrode orientation in this switch is random, and the aluminum electrode quality is rather bad, which certainly lower the performances. Another microwave photoconductive switch was built with a square design in order to explore the anisotropy of the bP (Figure 10 (a)). The switch allows us to measure ON/OFF ratio in two directions, parallel and perpendicular, but chosen randomly. The ON/OFF ratios obtained (Figure 10 (c)) are consistent with the 90° periodicity we observed in the first Raman measurement. Unfortunately the ON/OFF ratio are rather weak. This is probably due to the poor quality of the aluminum electrode (Figure 10 (b)).

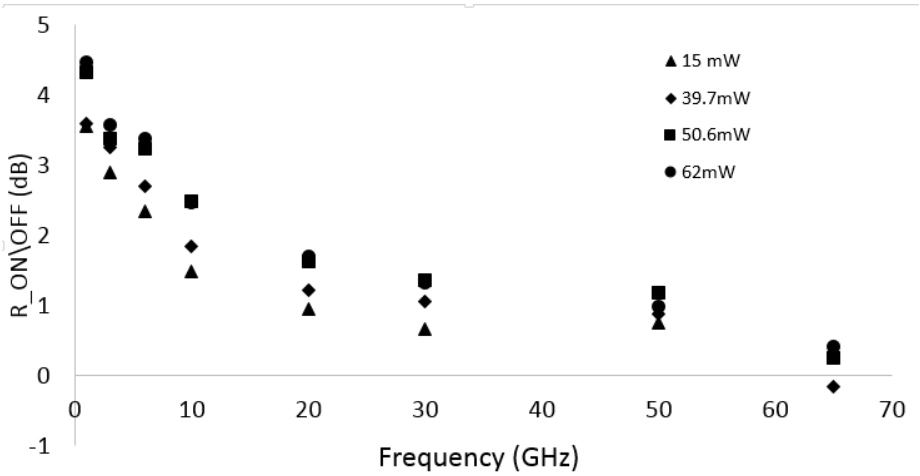

Figure 9 ON/OFF ratio of a microwave photoconductive switch based on a 23nm thick bP layer from 0 to 65 GHz, at different optical powers, from 10mW to 62mW.

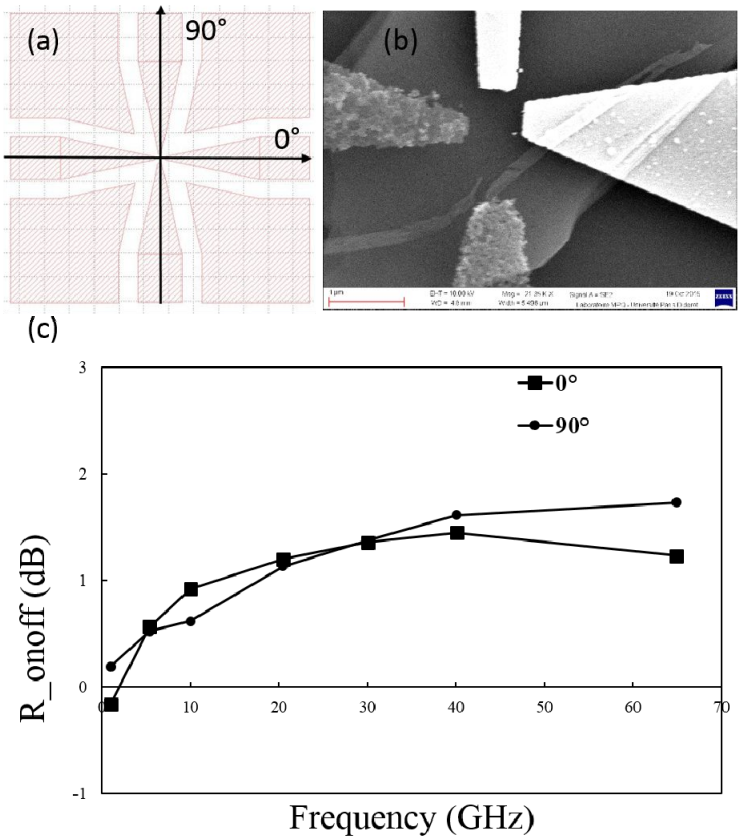

Figure 10 (a) Rectangular microwave photoconductive switch (b) Scanning electron microscopy of the Al/Pd electrodes based on a 50 nm thick bP layer (c) ON/OFF ratio obtained according to the frequency for two directions with 90° between them.

In conclusion, several distinct techniques can be used to study bP electronic structure and explore its optical and electronic properties. Amongst them, Raman spectroscopy appears as one of the fastest and less damaging to identify bP crystallographic orientation and thickness, by the study of A_g^2 (or B_{2g}) and A_g^1 phonons. After a Raman characterization of several bP layers to identify crystallographic orientations in the bP, we demonstrated functioning microwave photoconductive switches based on black phosphorus, up to 50GHz for a 50 mW 1.55 µm incoming optical signal.

Further work must be performed in order to truly understand the link between the structural organization in black phosphorus and the mobilities and conductivities. Indeed new publications detailing different possibilities of layer stacking have been released, opening a new path to understand the anisotropy in the bP. Further work must also be performed on bP synthesis to control the thickness, size and quality of the bP sheets, making bP components realizable at a larger scale.

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