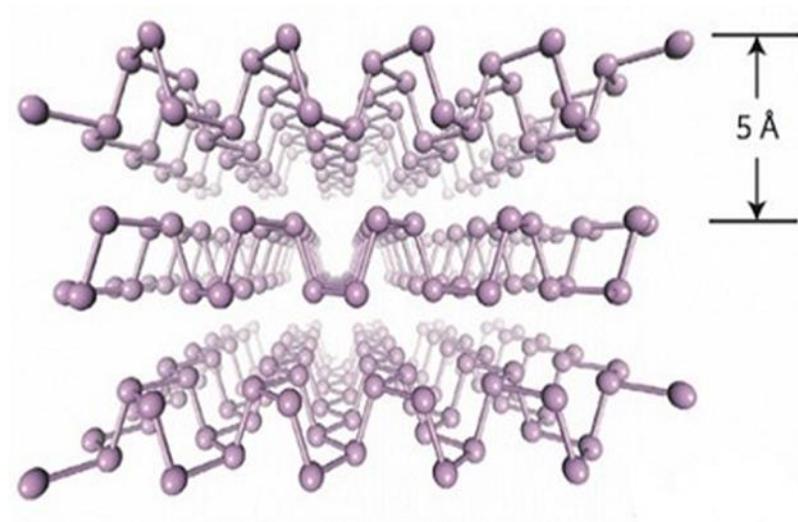# Identifying the crystal orientation of the black phosphorus

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I. Introduction

Black phosphorus is a new member of 2D materials family. It has several noticeable properties, for instance, the direct bandgap and anisotropic in-plane structure.


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All the anisotropy is due to the plucked structure of monolayer BP. There are two special in-plane directions, say, zigzag direction and armchair direction. When making electronic or optical-electronic devices the first step is to identify the crystal orientation.

There are many ways to identify the crystal orientation, among which utilizing the anisotropy of the Raman spectrum is a relatively quick and easy method. When Yuanbo's graduate students first explored this material they rotated the sample manually and collected the Raman spectrum data, which was arduous, time-consuming and imprecise. So I helped to upgraded the Raman spectrum in the laboratory to be an angle resolved Raman spectrometer. Comparing with the published data of angular dependent BP Raman spectrum (for example 10.1021/acsnano.5b00698 and 10.1002/anie.201410108) one can then identify the crystal direction.

II. Device setup
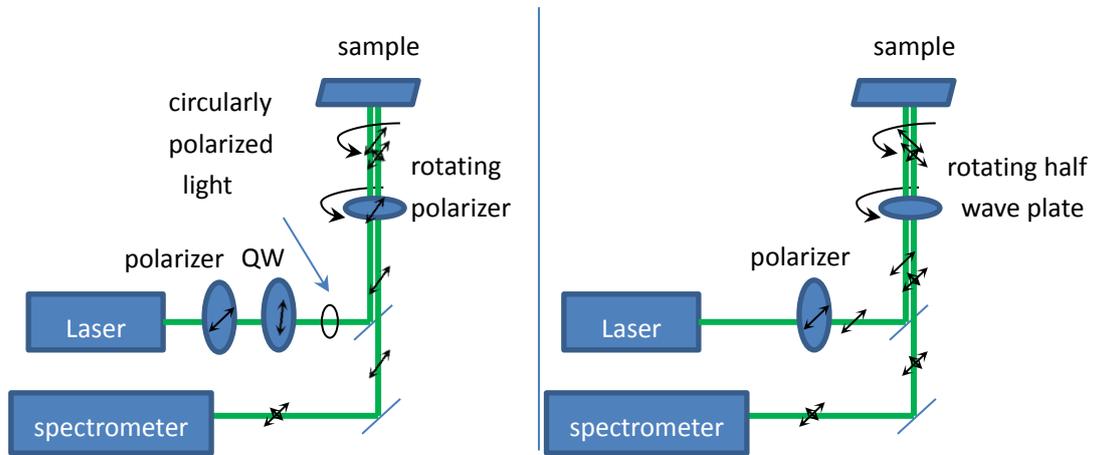
I first tried to use a polarizer and a half quarter plate to create a circularly polarized light and then use a rotatable polarizer to create the linearly polarized light to act with the sample. However in practical we found this configuration has several problems

i) Circularly polarized light is difficult both to produce and to maintain. The angle between the fast axis of the quarter wave plate and the polarization direction of the first polarizer should be exactly 45 °. Besides, the circularly polarized light would be reflected by a beam splitter, after which the polarization is not well-defined.

ii) Due to the back scattering geometry of our device, both the incident beam and the scattered beam would pass the polarizer, we can only get incomplete information about the spectrum.

iii) The polarization of the beam analyzed by the spectrometer is changing. Errors may be introduced due to the angle dependent response of the spectrometer.

I used the 520 cm^{-1} peak of silicon to calibrate the system. The result is as follows:
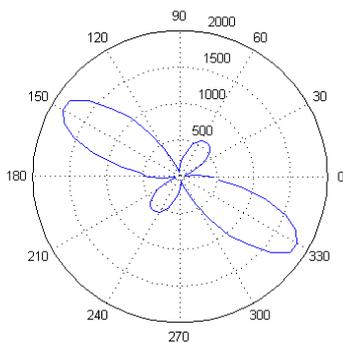
The spectrum of the black phosphorus was also taken, but the result was not satisfying.
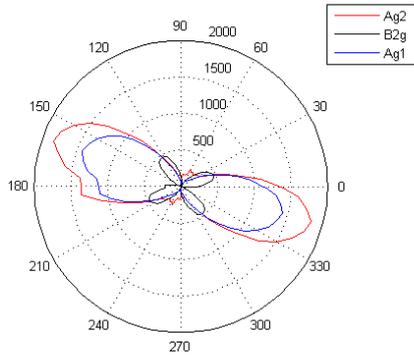
So I took the opportunity to consult Prof. Feng Wang when he was visiting the laboratory. Following his suggestion, I used one polarizer and a rotatable half wave plate to substitute the polarizer in the older setup.

The direction of the polarizer is set to be parallel to the beam splitter, so after reflection its polarization is still well-defined.

Compared with the former one, this configuration has two advantages

i) Using the HWP to change the polarization direction will give you a more stable intensity as well as changeable polarization direction;

ii) The polarization of the beam entering the spectrum won't change. For that when incident beam passed the HWP, the polarization direction changed for 2θ (assume the angle between the axis of the polarizer and the fast axis of the HWP is θ). And when the scattered beam passed, a -2θ rotation was induced. That is to say the HWP will change the polarization back before the beam enter the spectrometer, so nothing should be worried about the possible anisotropy of the spectrometer's response.

One may also notice there is a discrepancy between 175 and 180 in the data of black phosphorus. This is a glitch often met with, which is believed to originate from the imprecision of the rotation stage. I tried to make the rotation stage rotate by one cycle but sometimes it will stop before having finished one. This will be explained in the appendix which talks about the technique details of my setup.

III. Calibration and Data acquisition

First, to ensure that the system works, I used the most common material in the lab– a piece of silicon wafer – to test it. The curve in the polar plot is the intensity of 520 cm^{-1} peak verses the direction of the polarized light (when the beam polarized at horizontal direction in the picture the angle is marker as 0 or 180°). To make sure that the anisotropic result does attribute to the anisotropic structure of the sample rather than the intensity difference of the incident beam, I rotated the sample for about 45 degrees. We can observe that the curve in the polar plot also rotates about 45 degrees, so we can get the conclusion that the system can resolve the crystal direction.

In order to verify further that the intensity would not change when the HWP is rotating, I used a piece of graphite to calibrate the system. Graphite has a honeycomb lattice structure. The symmetry group of single atom layer is D_{6h} which means its lattice structure has more symmetric operations than that of single layer black phosphorus, so we expect the angle resolved Raman spectrum to be more isotropic. The experimental data supported our speculation, we can see the curve in the polar plot of the intensity of G peak is nearly a circle, and this fact does not change after we rotated the sample.
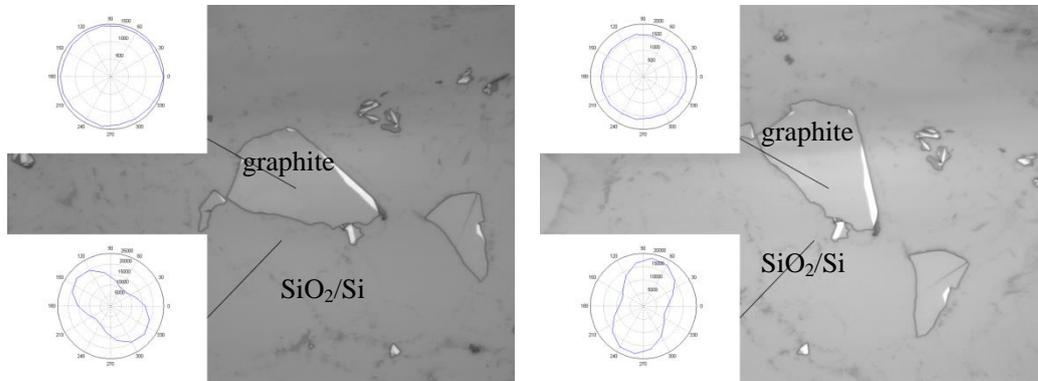
After verifying the feasibility of the system, I used it to test black phosphorus samples. Typically, in the low wave number region of the Raman spectrum of black phosphorus is as follows, we can find three Raman peaks centered at about 362cm^{-1}, 440cm^{-1} and 467cm^{-1},which are corresponding to A^1_g, B$_{2g}$ and A^2_g vibration modes respectively.
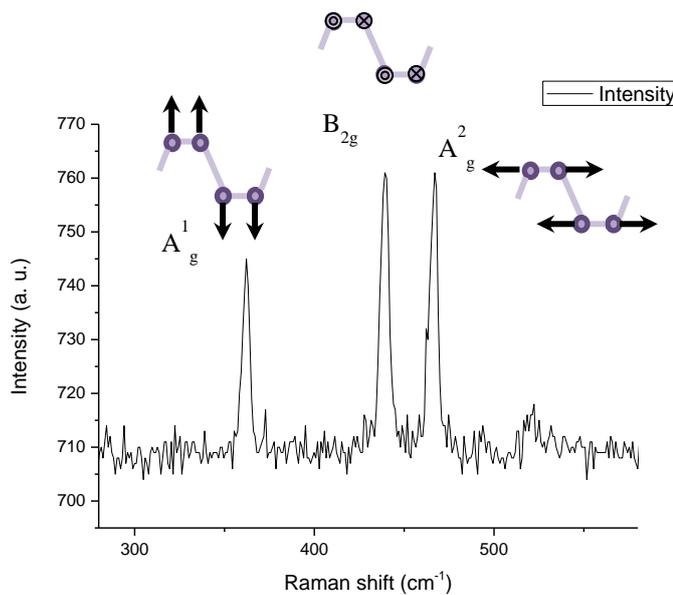
I used polarized light in different directions to excite the sample and take the spectrum of the light reflected from the sample. After doing fitting I got the area beneath each of the three characteristic Raman peaks, and plot them in polar coordinate.
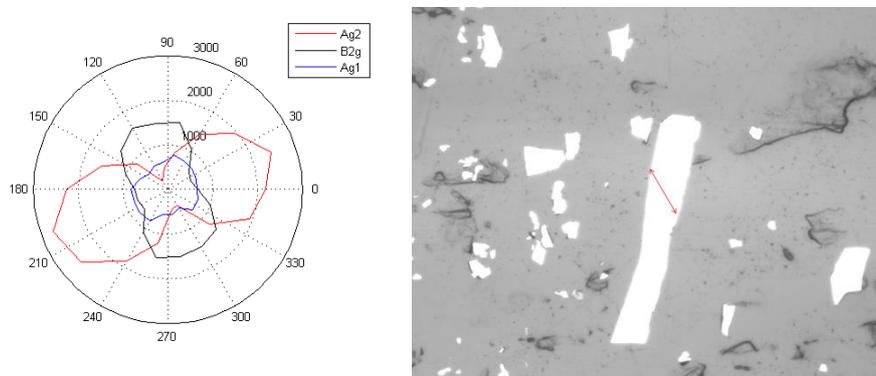
According to the published paper (DOI: 10.1021/acsnano.5b00698) When the intensity of the A_{2g} reaches its minimum, the direction of the incident polarized light is along the zigzag direction. Since I always make the light initially polarized along the horizontal direction in the microscope photo every time before measuring, the direction in the polar plot can be directly matched with that in the optical photo. I then mark the zigzag direction with red double arrow on the optical photo. Thus we have finished to calibrate the axis direction. Next we need to verify it through electric transport measurement.

One thing remains to confuse me is that according to the reference mentioned before (DOI: 10.1021/acsnano.5b00698), A^1_g and A^2_g peaks will be anisotropic while the peak of B_{2g} mode is isotropic, however what the result I got shows the A^2_g and B_{2g} peaks are anisotropic but A^1_g peak seems to be isotropic. I have checked it carefully several times and I think my result is more reasonable because the symmetry of the vibration mode determines the symmetry of the Raman peak. Form the direction along the normal of the phosphorus atom plane only A^1_g vibration mode is isotropic.