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Imaging Mueller Matrix Ellipsometry for the Characterization of Micro-Structured Anisotropic Thin-Film Samples

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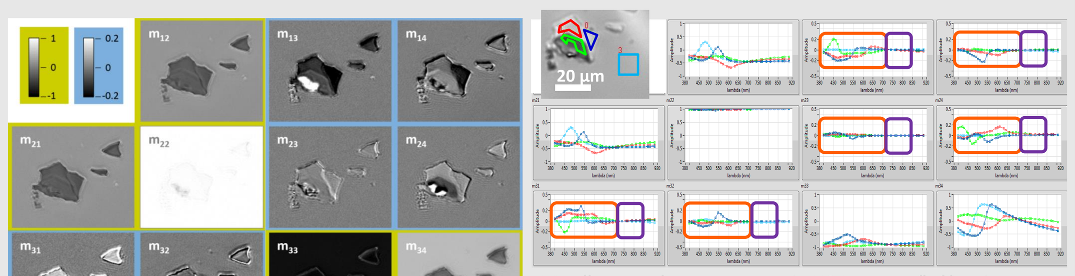
Introduction

Thin-film layers of black phosphorus - the most stable allotrope of the element phosphorus - is a promising material for future semiconductor electronics based on novel 2D-materials. Ultra-thin films or even monolayers of black phosphorus (b-P) may be fabricated by mechanical exfoliation (similar to graphene). 2D-b-P is of particular interest for semiconductor electronics as it features a widely tunable bandgap via the layer thickness (from ~2 eV for monolayers down to 0.3 eV for bulk material). Thus, it closes the energy gap between the other known 2D-materials graphene (zero bandgap) and transition-metal dichalcogenides (bandgap typically 1-2 eV) such as MoS_2.[1]

Regarding its optical properties, b-P stands out from other 2D-materials as well because its crystal structure causes an in-plane optical anisotropy in the visible range of the electromagnetic spectrum. However, the ellipsometric characterization of exfoliated flakes of b-P is extremely challenging as flake sizes are typically on the order of some 10µm, and the thickness often varies within a single flake.

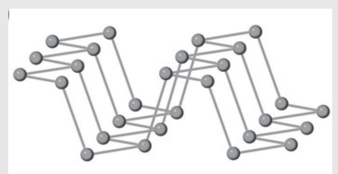
In this work, for the first time we report the ellipsometric characterization of micro-structured b-P-flakes by means of spectroscopic Imaging Mueller Matrix Ellipsometry (IMME). It features much higher x-y-resolution compared to conventional ellipsometers since for IMME this resolution is not limited by the size of the illuminating spot. By using IMME with a microscope objective lens, the measurement of anisotropic refractive indices and the orientation of the optical axes becomes feasible even on microstructured thin-film samples such as b-P-flakes.



Mueller-matrix map at λ=501 nm (left), λ-spectra obtained from spectroscopic mapping and evaluation of highlighted regions (top). Sample: b-P multilayer flake.

Sample description

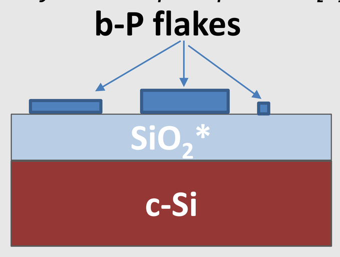
Black phosphorus:
- black phosphorus consists of sheets of phosphorus atoms forming a puckered honeycomb lattice
- Interlayer-bonds are weak (Van-der-Waals bonding)
- mechanical exfoliation produces thin-film flakes or even monolayers



Crystal structure of single-layer black phosphorus. [2]

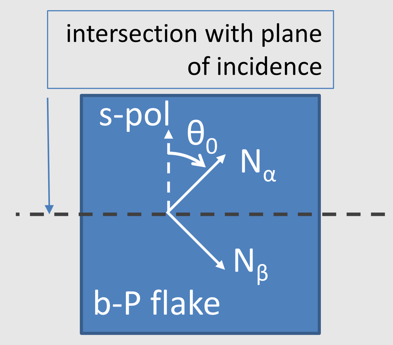
Sample fabrication:
- thin-film flakes of black phosphorus were prepared by mechanical exfoliation (peeling off) from bulk material applying a polydimethylsiloxane (PDMS) stamp [2]
- transfer of flakes onto a SiO2:Si-substrate by pressing PDMS stamp onto the substrate followed by a slow peel-off

The samples were prepared by Aday J. Molina-Mendoza and Dr. Andres Castellanos-Gomez.



**SiO_2 layer thickness 292 nm (obtained from spectroscopic IMME measurements)*

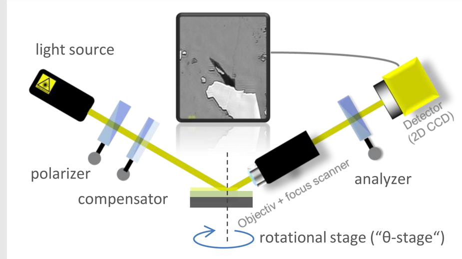
Ellipsometric modeling:
- describe b-P as orthorhombic, biaxial layer
- Parameter:
  - complex refractive indices for in-plane and out of plane components of index ellipsoid
  - orientation of in-plane principal axes (=offset of rotational positioning stage)
- Remark: b-P layer thickness will be determined independently (c. AFM-measurements)



Orientation of in-plane optical axes relative to s-polarization in ellipsometric measurement

Imaging MM Ellipsometry

Imaging Ellipsometry
- combination of ellipsometry and microscopy
- illuminating side: monochromatic illumination (collimated or slightly focused, no mircospot required)
- detecting side: microscope objective lens in detection beam path images sample onto camera (CCD, CMOS)



Setup of an imaging ellipsometer including objective, CCD-Camera, and polarizing optical elements

For an introduction to our technology please visit our technology page

Used setup
- imaging ellipsometer in PCSA-configuration (*nanofilm_ep4*, Accurion)
- objective lens: 50x magnification
- automated x-y-θ-sample stage
- light source: super-continuum laser (*SuperK extreme EXR-20*, NKT photonics) with accusto-optic tunable filter (*SuperK select*, NKT photonics), λ=460-700 nm)

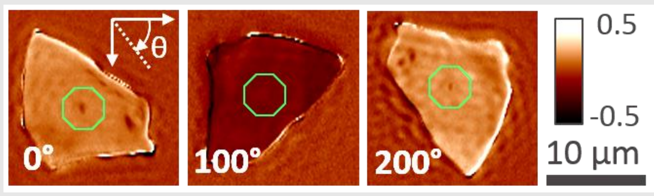
Spectroscopic Imaging Ellipsometer nanofilm_ep4

Imaging Mueller Matrix Ellipsometry (IMME):
- operation in rotating compensator mode
- measurement of 3x4-Mueller Matrix images (maps of the first 3 rows of normalized MM, normalization m_{11}=1)

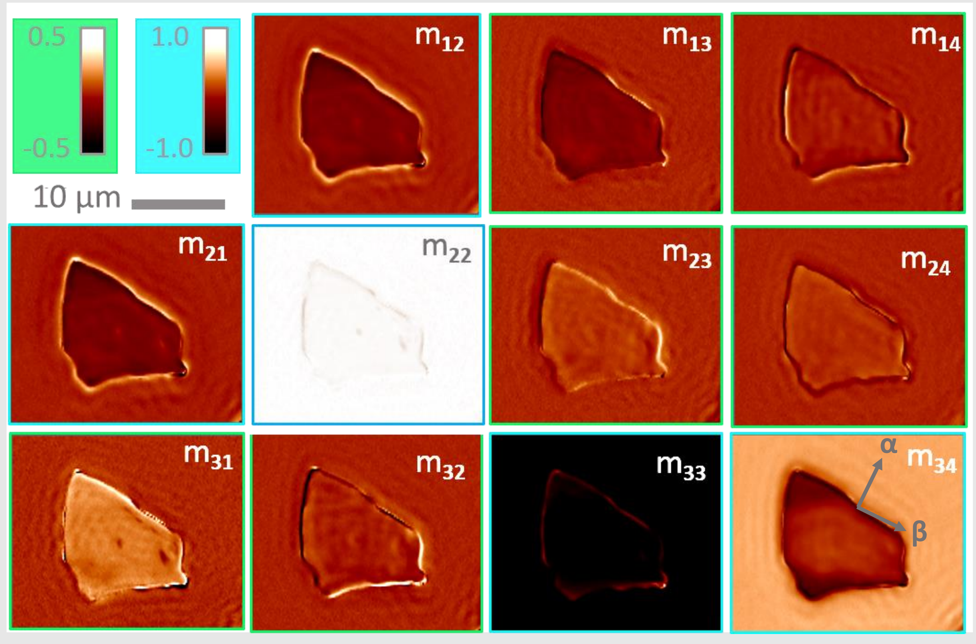
For additional information, please visit our website

Imaging Mueller Matrix Ellipsometry θ-scans

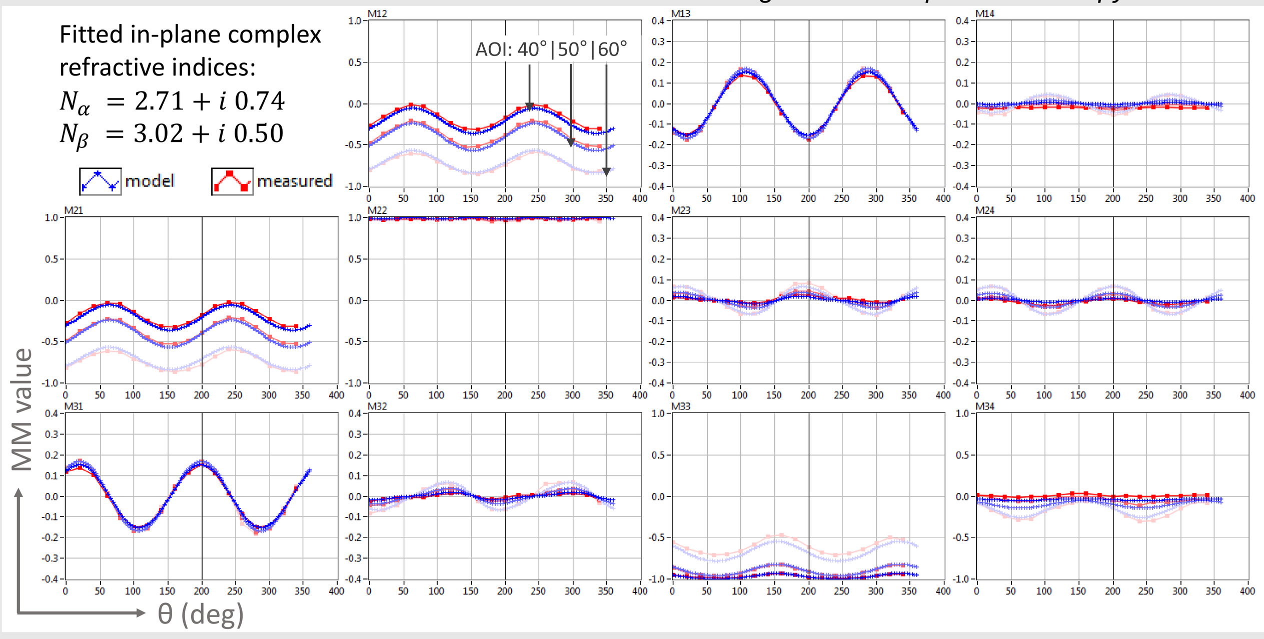
- non-zero off-diagonal blocks of MM-micrographs reveal the b-P-flake's anisotropy (wavelength of illumination λ=550 nm)
- θ-scan: rotate the flake around its center point & record MM-micrographs at each position (rotation from 0° to 340° in 20°-steps)
- evaluating central region of interest (ROI, c. fig. right) on each MM-micrograph for all θ-positions yields Mueller-Matrix θ-spectrum
- observed periodicity of 180° complies with an orthorhombic, biaxial model for b-P (one axis orthogonal to the sample surface)
- using the flake thickness obtained from AFM-measurements (43 nm) for optical modelling yields the in-plane refractive indices and the orientation of the in-plane principal axes of the index ellipsoid



MM-micromaps of black phosphorus (MM-element m_{31}, λ=550 nm) at different rotational angles θ: MM-value changes due to in-plane anisotropy.



Micromaps of normalized MM (m_{11}=1) at θ=0° and λ=550 nm. Mind different scale bars for block diagonal (blue frames) and block off-diagonal (green frames) matrix elements. Arrows in m34-graph indicate the orientation of in-plane optical axes obtained from ellipsometric modelling of θ-scan.

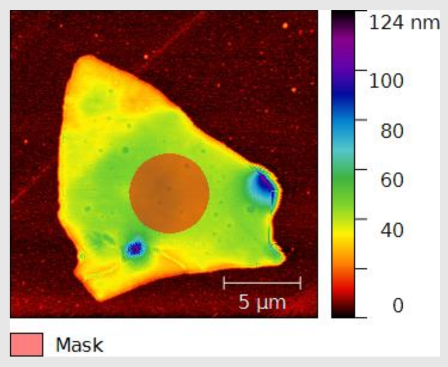


θ-spectrum of the normalized 3x4 MM of black phosphorus at different angles of incidence obtained from ROI-evaluation of MM-micromaps. Indices of fitted complex refractive indices N_α and N_β refer to principal in-plane axes of index ellipsoid (c. figure left, inset in m_{34}-micrograph). Mind different y-scales for block diagonal and block off-diagonal MM-elements.

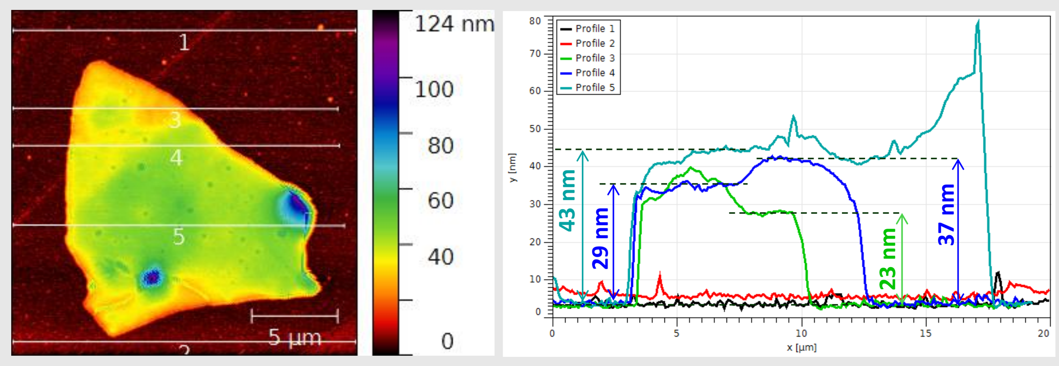
AFM measurements

- atomic force microscopy (AFM) topography measurements yield layer thicknesses *d* of different parts of the flake
- statistical analysis of central region (circular mask, c. image right):
  d = 43 ± 3 nm
- line profiles yield approximate thicknesses of different plateaus

AFM measurements were carried out at University of Goettingen by Anna Sinterhauf and Dr. Martin Wenderoth.



Set mask for derivation of mean thickness and standard deviation of layer thickness in the flake's center.



Topography image obtained from AFM measurements (left) and horizontal line profiles with derived layer thicknesses (right).

Spectroscopic Imaging Mueller Matrix Ellipsometry

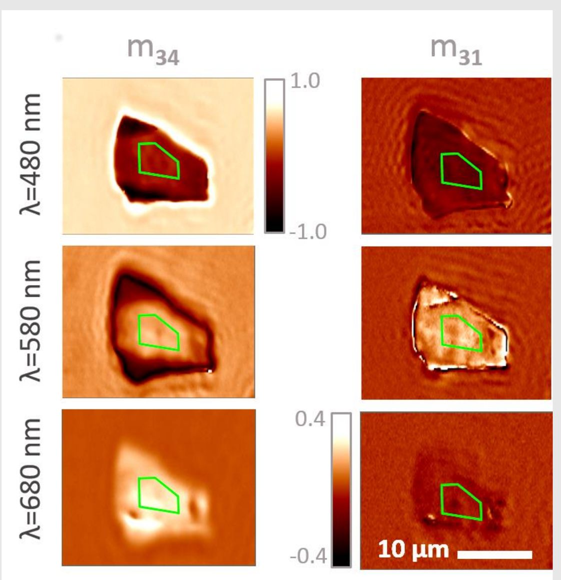
- acquire overall focused Mueller-Matrix micrographs
- vary wavelength of illumination (λ=480-690nm in steps of 10nm)
- micrographs reveal significant decrease of anisotropy for λ→ 680 nm (c. m_{31} graphs below)
- set ROI for stack-evaluation ("pixelshot")

ROI analysis

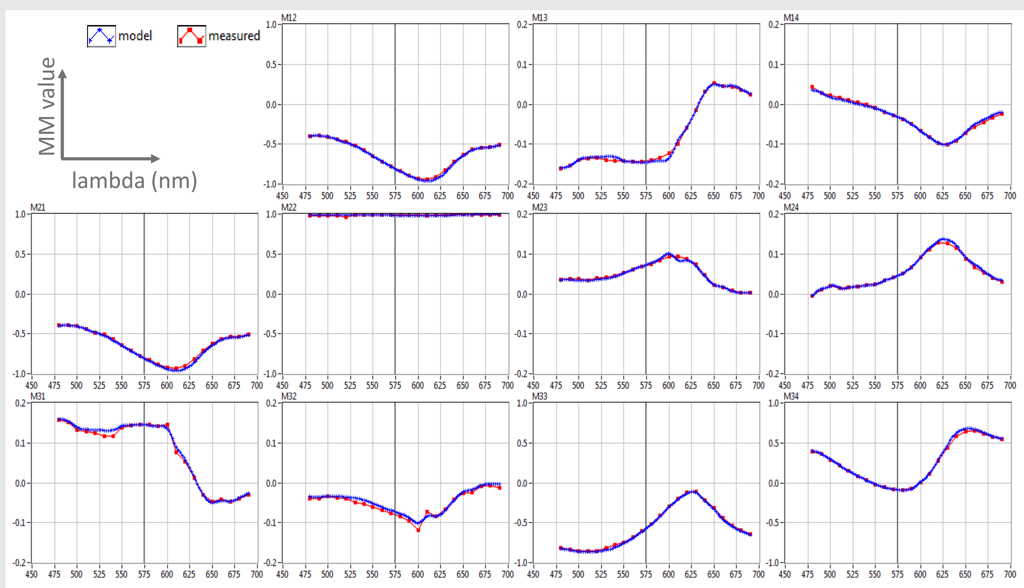
- ROI calculates average over the enclosed micrograph pixels for each wavelength and for each element of the measured normalized 3x4 Mueller Matrix
- result: MM-SE spectrum (c. fig. below) of sample area of ~25 µm²

ellipsometric modelling

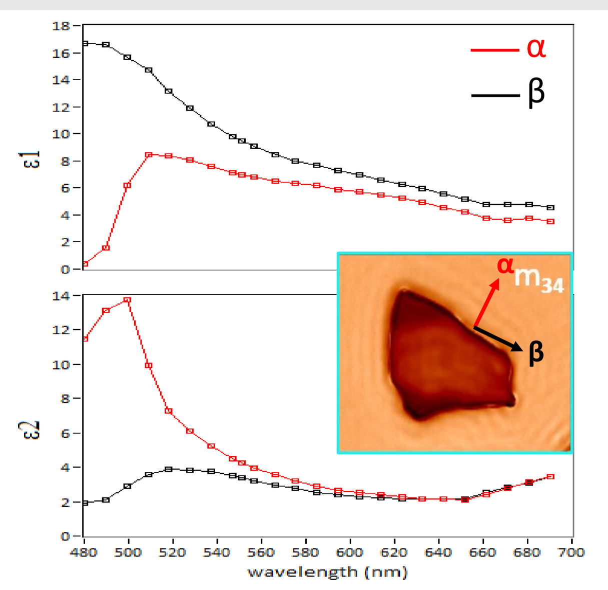
- fitting in-plane complex refractive indices (wavelength by wavelength) yields optical dispersion in examined spectral range (c. fig. below). Note the convergence of ε_2 for λ>600nm.
- constant real value for out of plane refractive index N_z was used for modelling and calculation of in-plane values (N_z not accessable for single AOI).



Selected MM micrographs (elements m_{34} and m_{31}) at different wavelengths of illumination. Green boxes highlight areas used for stack calculation of MM-spectrum.



Experimental (AOI = 55°) and modeled spectroscopic MM data for central ROI of the flake. In-plane complex refractive indices were obtained via wavelength by wavelength fitting of experimental MM-data to the ellipsometric model that was developed from IMME-θ-Scan



Calculated in-plane dispersion functions, assuming constant $N_z = 5.0 + i \cdot 0$ and layer thickness of 43nm according to AFM data.

Summary

A microstructured flake of exfoliated black phosphorus was characterized by means of Imaging Mueller Matrix Ellipsometry (IMME). The flake-size was below the x-y-resolution limits of conventional ellipsometers. Thus, IMME is a technique to extend Mueller-matrix analysis of anisotropic 2D-materials to microstrucured samples.

IMME-θ-scans:
- non-zero off-diagonal MM-blocks of b-P-flake (MM-micromaps) reveal the anisotropy of thin-layer flake
- recorded θ-scans were successfully modeled by assuming a simple orthorhombic crystal structure with biaxial anisotropy for b-P-layer with one axis orthogonal to the sample's surface
- in-plane complex refractive indices and orientations of in-plane optical axes were obtained for a single wavelength (λ=550 nm) from fitting the model to IMME-θ-scans for three different angles of incidence using predetermined layer thickness (AFM) and real refractive index in z-direction
- in-plane fit results are almost independent of refractive index in z-direction

Spectroscopic IMME:
- once having found an ellipsometric model and in-plane orientations of optical axes obtained from IMME-θ-scans, a spectroscopic IMME measurement yielded the optical dispersions of in-plane components of b-P for the wavelength-range of 480-690 nm (assuming constant real refractive index for z-direction)
- MM raw data and fitted dispersions both revealed significant reduction of in-plane anisotropy for spectral range of 600-700nm
- Obtained dispersions might still depend on assumed value for refractive index in z-direction. Additional data at different AOI or sample rotations θ might decouple in-plane and out-of-plane refractive indices upon numerical analysis.

References:
[1] A. Castellanos-Gomez, *J. Phys. Chem. Lett.*, vol.6, no.21 (Nov. 2015)
[2] A. Castellanos-Gomez et al., *2D Materials*, vol.1, no.2 (June 25, 2014)

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