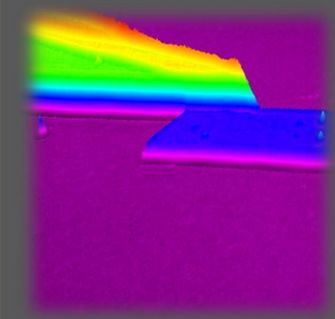
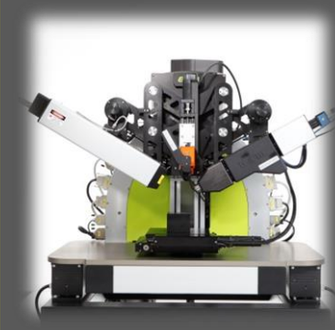
Applications of Imaging Ellipsometry

Graphene and 2D Materials

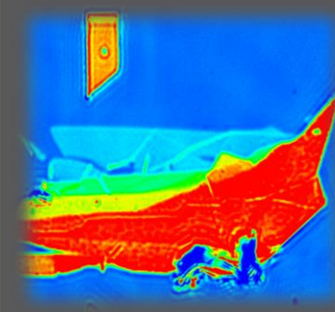
2017



Delta map
Air|Graphene|SiO_2|Si



Imaging Ellipsometer
Nanofilm_ep4



Delta Map
Air| MoS_2| Sapphire

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Imaging Ellipsometry: Localization, Characterization and Quality Control of Graphene and 2D Materials

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Imaging spectroscopic ellipsometry is applied to characterize graphene and other 2D materials. CVD grown, exfoliated and epitaxically grown flakes of 2D materials are investigated with the imaging ellipsometer nanofilm_ep4. This compendium addresses the following topics:

- Imaging of monolayers on different substrates
- Determination of the optical dispersion
- Distinction between mono-, bi- or n-layers
- Automatic flakesearch algorithm for identification of monolayers or well-defined thickness regions
- Exploration of hetero structures
- Quality control by detecting defects and special aspects of 2D nanoplates

Introduction

The research of A. Geim and K. Novoselov leveraged the mechanical exfoliation of graphene as a new preparation method [1]. Frindt and Yoffe [1963] prepared 2D flakes of Molybdenum Disulfide in a similar way [2]. The first step is the exfoliation, the second the identification of the 2D material in between flakes of multilayer- and bulk material areas.

The state of the art is the exfoliation onto a SiO_2 (300 nm) | Si substrate to enable the localization by the use of a light microscope. This procedure has to be performed manually and the result is strongly related to the skills of the operator. Raman spectra are established as the identification method. However, raman mapping of the whole sample is very time consuming.

Complex stacks made from different 2D materials became a new focus in 2D material related research. By stacking e.g. Wse_2 and MoS_2 monolayers the hybrid structures have promising properties for e.g. optoelectronic devices [3]–[6]. Investigations on MoS_2 revealed that the band gap is related to the thickness, hence the layer number [7].

Summing up a method is needed that allows the fast localization and identification of monolayers(or well-defined thicknesses) of 2D materials independent from the substrate. Also a method to obtain the optical properties in relation to the thickness is demanded. Methods of quality control in 2Dmaterial's research are gaining interest and are needed.

Imaging Ellipsometry – what makes the difference?

Imaging Ellipsometry (IE) has the benefit of combining the measurement quantities of ellipsometry with the lateral resolution of microscopy. A user will get ellipsometric enhanced contrast micrographs, thickness and optical constants distribution of its sample, that is measured by the ellipsometric plattform EP4 (Figure 1).

In general, the thickness measurements with an ellipsometer are nondestructive and highly accurate. In the most cases, the optical constants can be deter-mined independently.

To measure micro sized structures conventionally ellipsometry uses a focused light spot. The lateral ellipsometric resolution is thereby limited by the spot size that may go down to approx. 50 µm.

In IE the sample is illuminated with collimated light as shown in figure 2. The lateral ellipsometric resolution is only limited by the objective and the CCD-camera used as detector. With this method a lateral ellipsometric resolution down to 1 µm can be reached.

The CCD-camera offers a live view of the sample. By the rotation of the polarizing components Delta (Δ) and Psi (Ψ) for every pixel can be measured. The user will see the progress and the change in contrast by different polarizations in the live view. The user can also select the area to measure on the contrast image seen in the live view. In contrast to conventional ellipsometry, where the measured region is chosen by the position of the spot, the user in IE can select the measured region in the contrast view at the detector side. This selection enables the use of knife edge illumination – a unique tool to measure thin films on transparent substrates. Figure 3 shows a micrograph of MoS_2 on sapphire. The ghost image on the upper part occurs from the disturbing backside reflections. By the combination of detector side selection and knife edge illumination the user can perform valid ellipsometric measurements inside the green polygon.

Figure 1. EP4 with illumination arm on the left and Analyzer arm at the right. The sample can be placed onto a motorized xy-table.

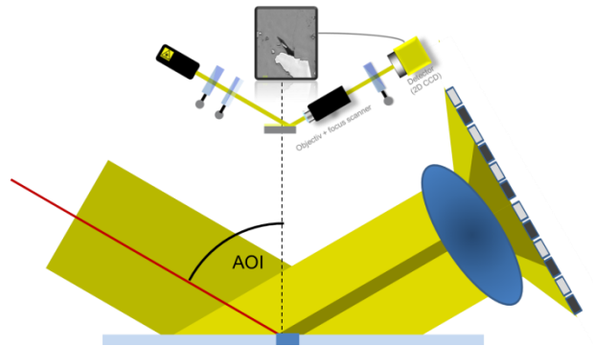


Figure 2. EP4 with illumination arm on the left and Analyzer arm with the optical system at the right. The sample can be placed onto a motorized xy-table.

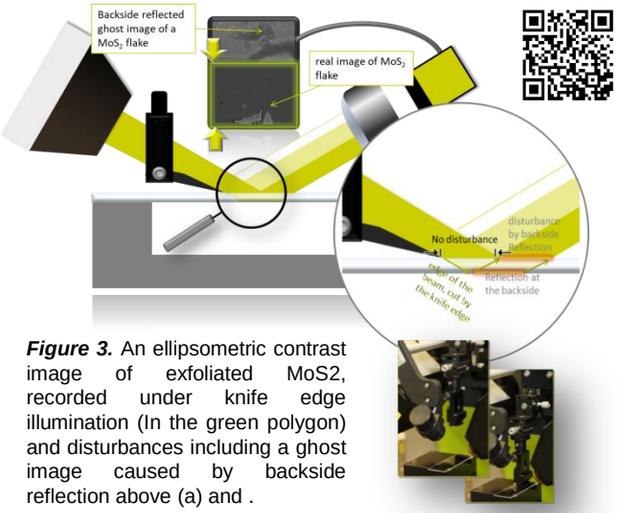


Figure 3. An ellipsometric contrast image of exfoliated MoS2, recorded under knife edge illumination (In the green polygon) and disturbances including a ghost image caused by backside reflection above (a) and .

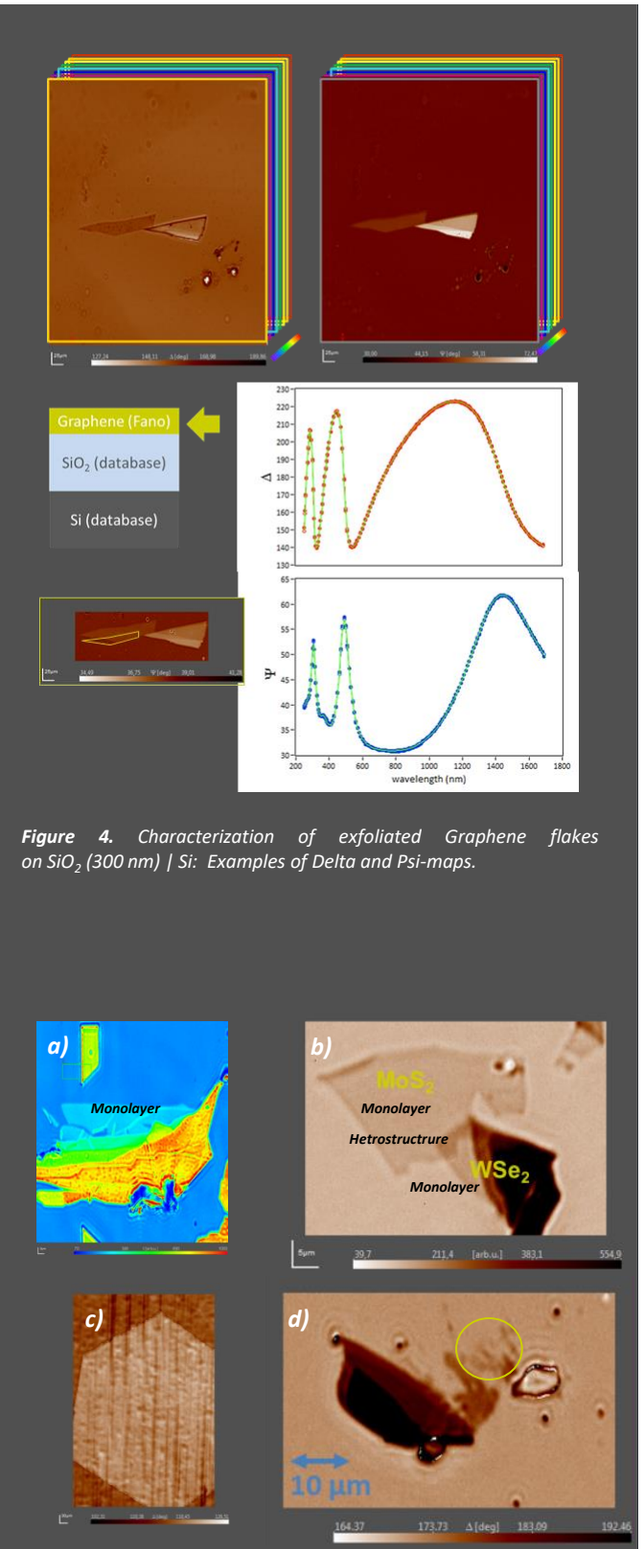


Figure 4. *Characterization of exfoliated Graphene flakes on SiO_2 (300 nm) | Si: Examples of Delta and Psi-maps.*

Figure 5. *Monolayer of MoS_2 on sapphire (a) and glass (b) graphene directly on Copper* (c), and hex BN on SiO_2 (90 nm) | Si.

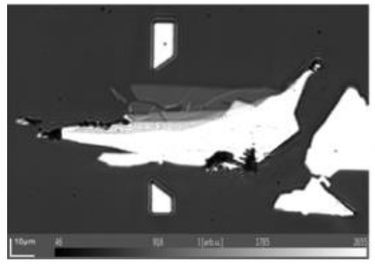
Characterization of Exfoliated Graphene

Matkovic et al. and Wurstbauer et al. showed that imaging ellipsometry is able to characterize the optical properties of small flakes of Graphene [8], [9]. Thermally reduced Graphene was investigated by Jung et al. [10]. Albrektsen et al. reported a thickness map that reveals distinct terraces separated by steps, which have heights corresponding to monolayers or bilayers of graphene [11]. The Delta and Psi spectra in the wavelength range between 250 and 1700 nm displayed in figure 4 d is extracted from averaging all pixels inside the green region of a complete set of spectral maps, figure 4 a-b. This allows to set the analyzed region after the measurement. By applying the optical model as seen in (c) a graphene layer thickness of 0.345 nm is fitted.

Substrate independent method

Graphene flakes are usually transferred to substrate of Si with a 300 nm SiO_2 layer to enable the visualization of monolayer by optical microscopy (OM). Even then the localization is strongly dependent on the skills of the user.

IE in contrast to OM offers visualization by different orientation of the optical components and is hence less depending on the substrate. Closely related to Brewster Angle Microscopy one can rotate the optical components in such way that the signal reflected from the substrate is minimized. Small adjustments of optical components offers high contrast of monolayers and the substrate. Figure 5 shows a monolayer of MoS_2 on Sapphire (a) and on $Si/SiO2_2$ substrate. A monolayer of Graphene on Cu-foil can be seen in figure 5c. hBN bilayer is seen on native Si substrate in figure 5 d.



Imaging Spectroscopic Ellipsometry of MoS2

Funke, S., B. Miller, E. Parzinger, P. Thiesen, A. W. Holleitner, and U. Wurstbauer.

Journal of Physics: Condensed Matter 28 (38): 385301

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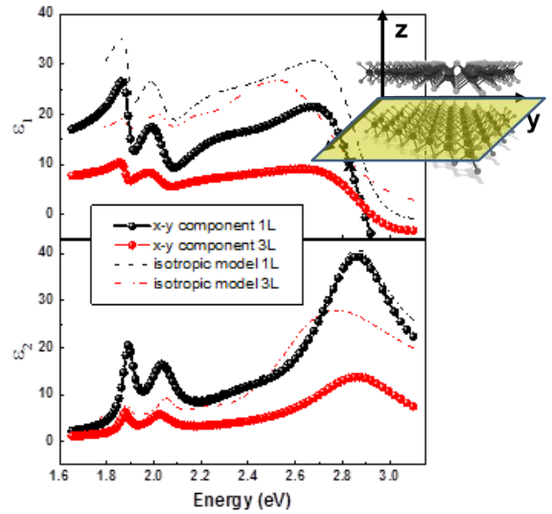
Spectroscopic imaging ellipsometry (SIE) is applied to flakes of micromechanically exfoliated Molybdenum-disulphide (MoS_2) with a size of approx. 10 µm x 50 µm [12]. Optical properties, homogeneities and anisotropic behavior are characterized for flakes of mono- and multilayer of MoS_2. SIE also allows to characterize defects, wrinkles within the flake. MoS_2 is a promising representative of the 2D-materials, including a change of its indirect bandgap for multilayers to a direct bandgap for a monolayer of MoS_2. 2D materials often show superior material properties compared to multilayers. The optical dispersion of MoS_2 is dominated by its excitonic behavior. It is shown that the excitonic behavior can be observed for a sapphire substrate whereas for a common silicon dioxide/silicon substrate optical contrast of mono- to multilayers is given but the excitonic behavior is unseen. To avoid disturbing backside reflection the unique feature knife-edge illumination is used. A lateral distribution of the optical properties towards the edges of the flake is demonstrated. Raman as complementary method is used to exclude that neither strain nor lattice defects are the cause for the variations. They also propose a model with anisotropic behavior (figure 6) of the n and k for the out-of-plane component of MoS_2. The critical point energy of the out-of-plane dispersion is in good agreement with the direct bandgap of a monolayer of MoS_2.



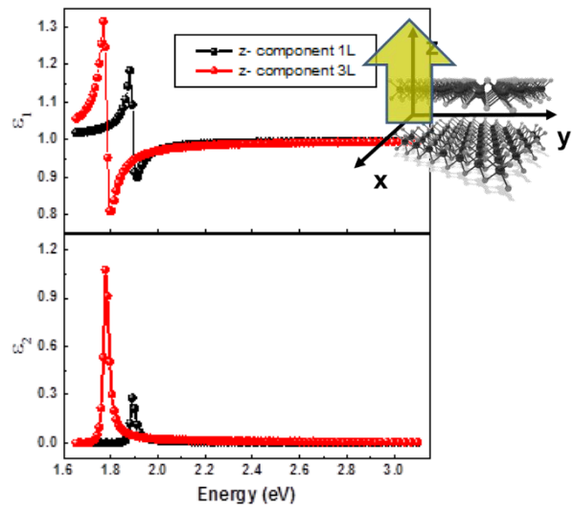


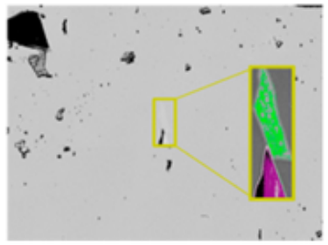
Figure 6. a) pseudo-dielectric funciton of monolayer MoS_2. Isotropic approach is compared to the in plane dispersion of the anisotropic approach b) out-of-plane component of pseudo-delectric function of monolayer of MoS_2

Spectroscopic Imaging Ellipsometry for Automated Search of Flakes of Mono- and N-Layers of 2D-Materials

Funke, S., U. Wurstbauer, B. Miller, A. Matković, A. Green, A. Diebold, C. Röling, and P. H. Thiesen.,

Applied Surface Science, 2016

doi:10.1016/j.apsusc.2016.10.158.



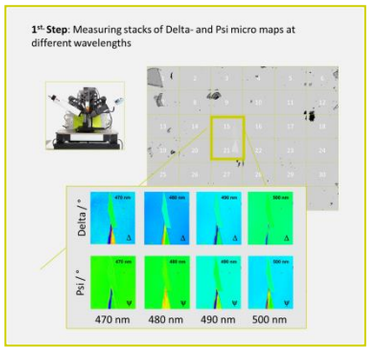


Figure 7. Scheme of flakesearch procedure. 1st step: recording of spectral maps of Δ/Ψ.. 2nd step: Comparison of experimental data to measured data pixel by pixel. 3rd step: found monolayer flake of Graphene on Si/SiO_2 substrate

In the research of 2D materials it is still challenging to find small flakes of 2D-materials with monolayer thickness. Conventional methods, e.g. optical microscopy (OM) work only with the use of contrast enhancing substrates. In this article Funke et al. [13] show the possibilities to use spectroscopic imaging ellipsometry for an automated search of defined layer thicknesses that is less depending on the substrate. Imaging ellipsometry combines the sensitivity of an AFM and the speed of OM for scanning the whole sample. Therefore a pattern of the whole sample of the ellipsometric angles Δ and Ψ is done (Fig. 7). Pixel by pixel is compared to the model with the defined layer thickness, if they agree the pixel will be marked. For instance the pixel for pixel identification allows to localize small flakes of a few µm size of a defined thickness, e.g. a 1 mm x 1 mm area is patterned within 20 min and allows the identification of micron-sized flakes. Monolayer of Graphene can be distinguished from trilayers and a 10 µm x 10 µm of Molybdenum-disulphide is found on an unknown substrate that is characterized simultaneously

An automatic search for flakes in combination with a micro RAMAN integrated in the EP4 (see figure 11) enables the localization with complementary methods..

Hetero structures, 2D based devices and more

To investigate small regions of materials an exact positioning of the measured area is demanded. Free shaped regions of interests can be selected in the live view of the EP4_Software within micron resolution. Figure 8 a shows an ellipso´-metric contrast enhanced micrograph of a hetero structure. A monolayer of MoS_2 and a monolayer of WSe_2 are arranged, so that an overlapped structure of 2 µm x 6 µm is achieved. Spectroscopic maps of Δ (c) and Ψ (b) are recorded. The software alignment and the averaging of all pixels inside selected regions for every recorded wavelength yield to the spectra of Δ and Ψ as shown in figure 8 d. By applying a theoretical model the complex dielectric function may be obtained for all regions within one measurement (figure 8 e).

This procedure also enables the measurement of small devices, e.g. contacted Graphene flake in Fig. 9.

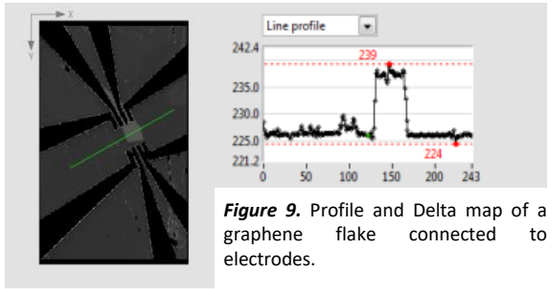


Figure 9. Profile and Delta map of a graphene flake connected to electrodes.

Spectroscopic visualization

In IE the variation of the illuminating wavelength can offer interesting and multiple information. Figure 10. shows, that the variation of wavelength and polarizing optics yield to change in contrast for different layers of the MoS_2 flake upon a Si/SiO_2 substrate. The change in contrast is related to thickness and optical constants.

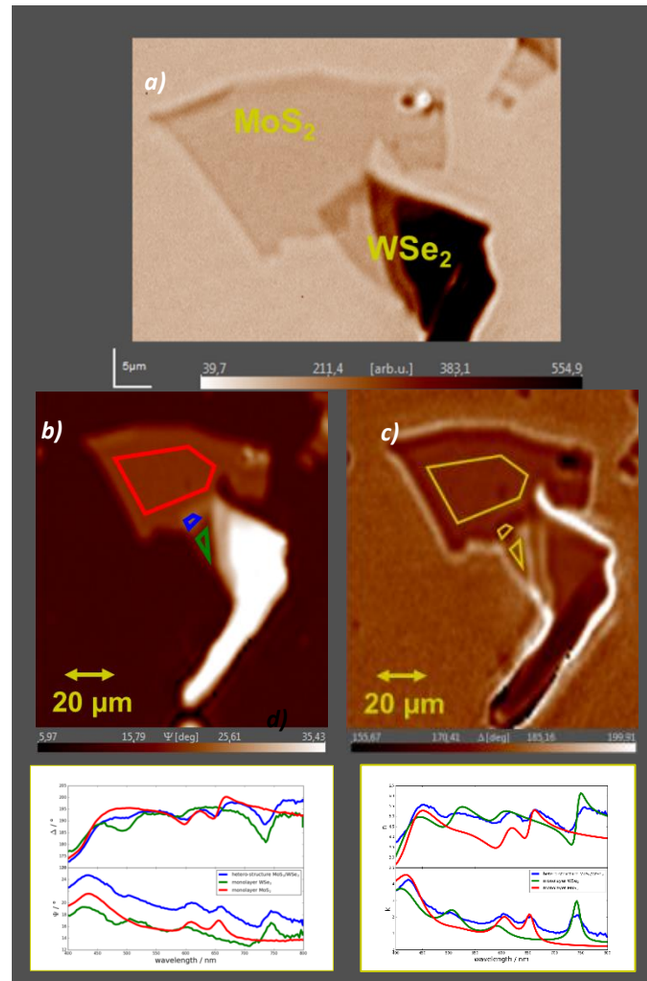


Figure 8. Elipsometric contrast micrograph (a), Δ map (b) Ψ map (c) of A MoS_2 | WSe_2 hetero structure. The wavelength spectra of Δ and Ψ were obtained by the pixel shot approach (d) and yield to the dispersion shown in (e) .

Courtesy to Ursula Wurstbauer, TU München

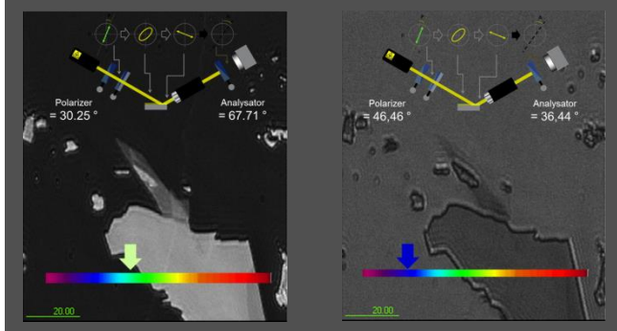


Figure 10. Mechanically exfoliated MoS_2 on a SiO_2 (300 nm) | Si substrate – illuminated with different wave length and imaged at different orientations of the optical properties.

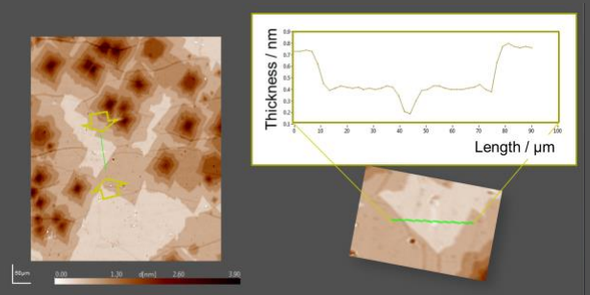


Figure 11. Thickness map of CVD-graphene on a SiO2 | Si substrate)

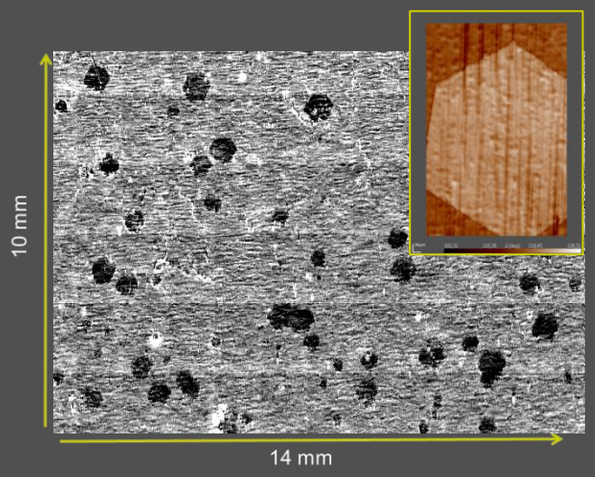


Figure 12. Delta map of CVD graphene on Copper: single microscopic map (a) and microscopic maps stitched together to a macroscopic map (recorded with automatic z-tracking)

Courtesy to Philipp Braeuninger, Stephan Hofmann, University of Cambridge

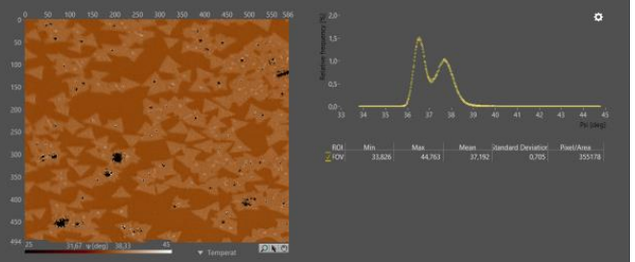


Figure 13. Psi map + histogram of CVD-MoS_2

CVD and Epitaxy

For the production of complete wafers as well as large area graphene, CVD grown graphene upon a Cu-foil substrate and epitaxial growth of graphene on silicon carbide substrate are currently the most promising technologies. One requirement for the characterization of the produced layers is the need to work on transparent substrates or metals. Typical characterization tasks are the number of layers, the localization of defects and testing the homogeneity of the coating.

To cover the increasing demand of high-quality Graphene, CVD grown Graphene upon a Cu-foil substrate or epitaxically grown Graphene on silicon-carbide substrate seem to be very promising ways. However, traditional methods of quality and quantity control, like optical microscopy, SEM, Raman, either do not work or are too slow e.g. on the Cu-foil directly.

The most common investigation of Graphene is done on silicon/silicion-dioxide substrates. Figure 11. shows Graphene islands, ranging from monolayer to multilayer. The lineprofile reveals a defect of Graphene. However, for the characterization on Si/SiO_2 substrate a transfer process is required.

Figure 12 shows Graphene directly grown on Cu-foil. No transfer or oxidation of the Cu-foil is needed to obtain the surface coverage. Especially the highest lateral ellipsometric resolution down to 1 µm of imaging ellipsometry is beneficial for a quantitative analysis. In figure 13 CVD grown MoS_2 on SiO_2/Si substrate can be seen. The histogram on the right shows two peaks, one for the Ψ value of MoS_2 and one for the values of the substrate. The highest lateral ellipsometric resolution combined with included histogram analysis offers information on e.g. surface coverage.

Quality control(QC) – the next critical step

In our daily lab experience we address a number of QC-issues like homogeneity of layers, distribution of layer numbers, winkles, visualization of impurities like local water layers. Additionally we see effects that sometimes are unknown – even to the owner of the samples (figure 14 c). Figure 14 a shows a folding of the MoS_2 flake at its corner. Due to the different temperature coefficients, wrinkles occur for the Graphene grown on Cu-Foil (figure 14 b) during the cooling down process.

Impurities and roughness may cause the experimental data not to fit to the model. These differences between the measured data of the real sample and the expected data for an ideal layer stack may tell a lot – right now an underestimated option in QC, not only for 2D-materials.

Raman spectroscopy is currently the state of the art in 2D-layers identification. Imaging Ellipsometry combines fast imaging with the highest optical sensitivity for ultrathin layers and impurities. All done within microscopic resolution. The combination of the EP4 with the microRAMAN system enables chemical identification. As Raman can be seen as a complementary method to obtain information on the layer numbers for 2D-layered materials, the Raman spectra confirm the layer number. An integration of the mircoRAMAN can be seen in figure 15. This setup allows to identify the spot of the Raman within the image of the EP4.

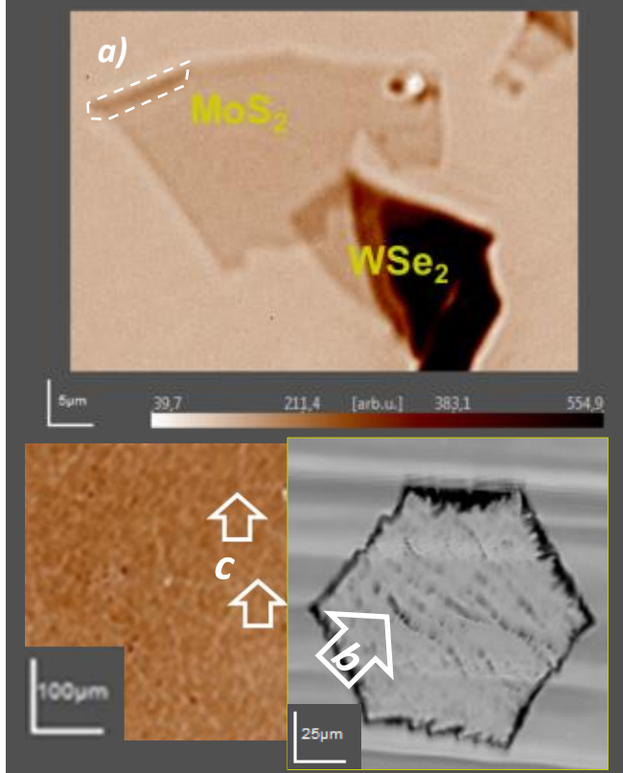


Figure 14. Imaging ellipsometry offers a fast method to detect a varity of defects like folded layers (a), wrinkles (b,c), uncoated areas etc.

Figure 15. Integration of a Micro RAMAN into the setup of the nanofilm_ep4.

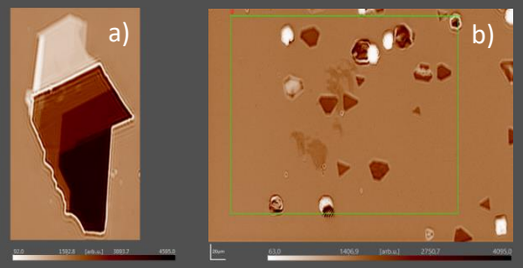


Figure 16. Ellipsometric contrast micrographs of hex-BN Mulltilayer (a) and 2D antimony telluride (Sb_2Te_3) nanoplates (b).

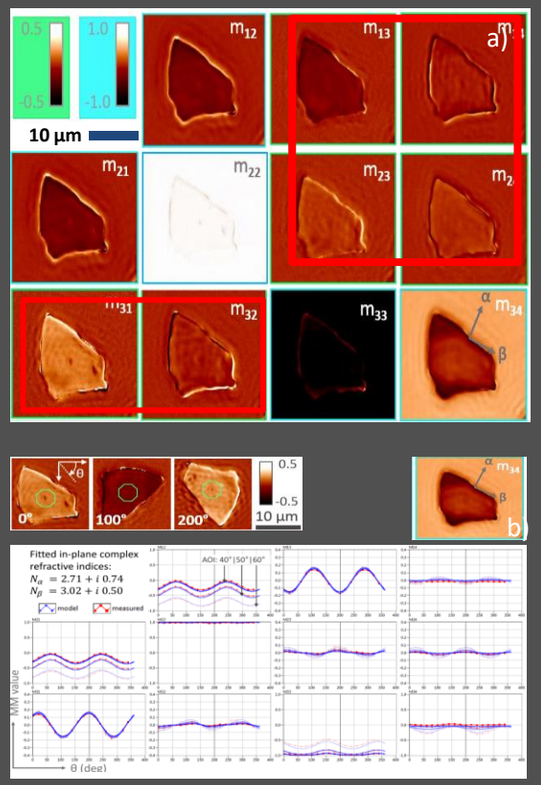


Figure 17. Black phosphorus (43 nm) on silicon substrate: Micrographs normalized (m11 = 1) of 3x4-Mueller-Matrix (a), Orientation of optical axes obtained from Mueller-Matrix θ-scan (b).

Courtesy to Aday J. Molina-Mendoza (University of Madrid, Spain) & Andres Castellanos-Gomez (IMDEA Nanoscience, Madrid, Spain)

Multilayer 2D crystals of black Phosphorus, hex-BN and topological insulators

Interest not only on monolayers but multilayers of 2D-materials is rising. E.g. hexagonal boron-nitride (hBN), Black-phosphorus (BP) and antimony telluride (Sb_2Te_3) gain interest for their multilayer flakes.

In figure 16 the power of the ellipsometric enhanced contrast can be seen. The variation of the polarizing components allows to distinguish in between different layers of hBN (a) or different layered flakes of Sb_2Te_3 (b).

The benefit of imaging ellipsometry is the very precise quantification of the thickness. In combination with a flake search method [13], it enables an automatic search for flakes of a required thickness. This flake search with IE is more independent from the substrates than comparable common methods.

Due to limited long-term stability (oxidation, hydrolyzation) a fast measurement method is required to localize the flakes and to characterize unknown optical properties.

Imaging Microscopic Mueller Matrix Ellipsometry

Imaging Mueller Matrix ellipsometry is an advanced technique necessary for the complete and accurate characterization of anisotropic and/or depolarizing samples. The complete Mueller Matrix is a 4x4 matrix. For a number of applications like refractive index and absorption for uniaxial or biaxial linear anisotropic materials the normalized 3x4-Mueller Matrix is sufficient. One material that requires Mueller Matrix measurements is BP. Figure 17 shows normalized (m11 = 1) micrographs of 3x4-Mueller Matrix (a). The orientation of optical axes are obtained by rotating the sample(θ-scan). The orientation is shown in figure 17 b.

Imaging Mueller Matrix Ellipsometry can be applied to identify isotropic/anisotropic areas of a sample. If the block-off diagonals elements (red boarder Fig. 17 a) are non-zero, anisotropic behaviour is revealed.

Conclusion

Spectroscopic Imaging Ellipsometry(SIE) is a very powerful tool to characterize, analyse and investigate thicknesses, optical properties and defects or impurities of 2D-materials.

The ellipsometric enhanced contrast micrographs offer high contrast for different materials on different substrates. The change in the polarizing components of the system gives a less substrate dependent observation method.

By recording micro maps of the ellipsometric angles Δ/Ψ for different wavelengths optical dispersion for monolayer of e.g. Graphene MoS_2 are obtained. SIE allows to measure the spectra on flake sized down to 1 µm. The pixelshot allows to obtain spectra of Δ/Ψ of a user-defined area after the measurement. The versatile tool is able to stitch microscopic maps to look for flakes of monolayer or of a defined thickness on a complete sample. It turns out, that this method is less dependent on the underlying substrate when compared to conventional methods.

All regions of a hetero structure, build up from two different 2D materials, can be measured simultaneously with highest precision.

For graphene on cupper-foil no oxidation of the foil or a transfer process is needed to identify the surface coverage. If the layer shows anisotropic behaviour the imaging Mueller Matrix feature of the nanofilm_EP4 is able to measure complex materials e.g. BP.

All different applications show the versatility of the nanofilmEP4 device. For any further question or new application idea, please don't hesitate to contact the ACCURION Team .

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