

Correlating Optical Microspectroscopy with 4x4 Transfer Matrix Modeling for Characterizing Birefringent van der Waals Materials

*Julian Schwarz**, *Michael Niebauer**, *Maria Kolečnik-Gray*, *Maximilian Szabo*, *Leander Baier*, *Phanish Chava*, *Artur Erbe*, *Vojislav Krstić*, *Mathias Rommel*, *Andreas Hutzler*

Julian Schwarz, Michael Niebauer

Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Electron Devices, Cauerstraße 6, Erlangen, 91058, Germany

julian.schwarz@fau.de, michael.niebauer@fau.de

These authors contributed equally to this work.

Dr. Maria Kolečnik-Gray

Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Applied Physics, Staudtstraße 7, Erlangen, 91058, Germany

Maximilian Szabo

Fraunhofer Institute for Integrated Systems and Device Technology IISB, Schottkystraße 10, Erlangen, 91058, Germany

Leander Baier

Fraunhofer Institute for Integrated Systems and Device Technology IISB, Schottkystraße 10, Erlangen, 91058, Germany

Phanish Chava

Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Institute of Ion Beam Physics and Materials Research, Bautzner Landstrasse 400, Dresden, 01328, Germany

Prof. Artur Erbe

Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Institute of Ion Beam Physics and Materials Research, Bautzner Landstrasse 400, Dresden, 01328, Germany

Prof. Vojislav Krstić

Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Applied Physics, Staudtstraße 7, Erlangen, 91058, Germany

Dr. Mathias Rommel

Fraunhofer Institute for Integrated Systems and Device Technology IISB, Schottkystraße 10, Erlangen, 91058, Germany

Dr. Andreas Hutzler

Forschungszentrum Jülich GmbH, Helmholtz Institute Erlangen-Nürnberg for Renewable Energy (IEK-11), Cauerstraße 1, Erlangen, 91058, Germany

Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Electron Devices, Cauerstraße 6, Erlangen, 91058, Germany

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Van der Waals materials exhibit intriguing properties for future electronic and optoelectronic devices. As those unique features strongly depend on the materials' thickness, it has to be accessed precisely for tailoring the performance of a specific device. In this work, a nondestructive and technologically easily implementable approach for accurate thickness determination of birefringent layered materials is introduced by combining optical reflectance measurements with a modular model comprising a 4x4 transfer matrix method and the optical components relevant to light microspectroscopy. This approach is demonstrated being reliable and precise for thickness determination of anisotropic materials like highly oriented pyrolytic graphite and black phosphorus in a range from atomic layers up to more than 100 nm. As a key feature, the method is well-suited even for encapsulated layers outperforming state-of-the-art techniques like atomic force microscopy.

1 Introduction

Layered materials and systems composed of these are considered an emerging class of materials because of their manifold and tunable properties. These stem from both, the individual layers' properties as well as the interlayer interactions. Specifically the latter is of importance as it can range from purely van der Waals like (e.g. graphene) to, for instance, a covalent-ionic like mix as in the case of black phosphorus (BP). Consequently, a two-fold anisotropy in the optical/optoelectronic properties can be in principle always found in such systems: one within the plane of a monolayer of a stack (e.g. if puckered structure) and perpendicular to the stacking. Thickness dependent charge carrier mobilities and bandgaps ranging from ultraviolet up to mid-infrared wavelengths are especially promising for optoelectronic devices.^{1,2} In addition, the bandgaps are often tunable via electric fields or strain, which enables a large spectrum of applications for photonic devices.^{3,4}

Regarding the crystallographic structure within one single layer, in-plane (i.e. in xy-direction) isotropic and anisotropic materials can be distinguished. In-plane anisotropy as an intriguing degree of freedom has been explored in various devices like optical detectors,^{1,5,6} field effect transistors^{1,7,8} and optical modulators.^{1,5,9} In particular, BP exhibits in-plane anisotropy due to the properties of its orthogonal arm-chair (AC) and zig-zag (ZZ) crystal axes. In addition, an out-of-plane (i.e. in z-direction) anisotropy is inherent for van der Waals materials.^{7,9} In general, anisotropy has to be considered for the optical response of birefringent materials, i.e. for uniaxial as well as for biaxial crystals (for uniaxial two and for biaxial three different refractive indices are required). Highly oriented pyrolytic graphite (HOPG) with its in-plane isotropic and out-of-plane anisotropic behavior is uniaxial, while BP is an example for a biaxial crystal since it shows in- and out-of-plane anisotropy.

To utilize the properties of layered materials for certain applications, in general, it is of utmost importance to have knowledge about the exact material thickness. However, for some materials such as BP, molybdenum ditelluride (MoTe_2) and tungsten ditelluride (WTe_2),¹⁰ the commonly established thickness determination methods can only be applied with great restrictions because of the need of a passivation layer to prevent degradation at ambient atmosphere.^{11,12} These passivation layers, e.g. poly(methyl methacrylate) (PMMA) or hexagonal boron nitride (hBN), inhibit the otherwise immediately starting degradation^{11–15} but further hinder or distort atomic force microscopy (AFM) based measurements.¹⁶ Consequently, the topography is only accessible in vacuum or under inert atmosphere (for instance in a glovebox) or instead has to be accessed after removing the passivation layer and effectively destroying the device. In general, interferometry- and profilometry-based techniques can resolve layer thicknesses down to nanometer and are in addition non-destructive.^{17,18} Raman spectroscopy, as an established technique for layered materials, is on the other hand insensitive for thicknesses above ten layers.^{19–22}

As an alternative, for flake thicknesses above 10 nm, reflectance measurements via microspectroscopy (i.e. combining a microscope with a spectrometer) are a valid option. Especially the small measurement spot sizes used (diameter $< 4 \mu\text{m}$ ²³) allow to characterize mechanically exfoliated flakes exhibiting narrow lateral dimensions. In addition, optical measurements enable determining the thickness of encapsulated layers.

In this work, several elements – well-known transfer matrix modeling as well as novel weighting functions describing the optical system – are combined to introduce a cost-effective and non-invasive approach for thickness characterization of arbitrarily composed stacks containing van der Waals materials. For this purpose, microspectroscopy measurements are correlated with a transfer matrix model of the individual reflectance spectra. A 4x4 transfer matrix method (TMM) introduced in literature²⁴ is adapted to describe the reflectance spectra of both, thin films and flakes of layered materials, within a broad thickness range (from few layers to more than hundred nanometers) accommodating for the optical response of birefringent materials. Therefore, we determine the thickness of individual flakes or films comprising a stack with high precision by modeling the entire reflectance spectrum in a wide spectral range. By evaluating a broad spectral range, the thickness assessment of films with thicknesses greater than a few layers is more suitable. This advantage arises from the fact that using the evaluation of the shift in wavelength and reflectance for a single minimum (as done in our previous studies, where a 2x2 TMM was used)^{23,25} becomes more and more insensitive for a number of layers considerably larger than ten. Besides, the

reflectance spectra of some materials lack distinct features like minima or maxima within a specific wavelength range without an explicitly designed optical layer stack (e.g. 300 nm of SiO₂ are used to enhance the contrast of graphene when employing contrast based methods²⁶). In contrast to other microspectroscopic approaches which involve analyzing contrast spectra^{26,27} or methods based on RGB data,^{28,29} we utilize absolute reflectance values instead of optical contrast^{21,30,31} or relative intensities.^{32–34} Thereby, we accurately replicate actual physical mechanisms and enable direct comparability between acquired spectra.

To access the optical response of small flakes, magnifying objective lenses are used. Therefore, we take the influence of the optical components into account by using an angular weighting factor depending on the numerical aperture (NA) and the illumination pathway.

Although optical modeling using a 4x4 formalism has already been demonstrated in theory,^{24,35,36} we would like to note that there are no studies applying a 4x4 TMM to microspectroscopy. We exemplify the application of a 4x4 TMM for describing the experimentally acquired reflectance spectra of HOPG and BP (as well as tungsten diselenide WSe₂, molybdenum disulfide MoS₂ and hBN, see the Supporting Information).

Besides, we discuss the influence of anisotropy on the accuracy of thickness evaluation using microspectroscopy by comparing the employed 4x4 TMM approach with the results of a frequently applied 2x2 TMM^{37,38} for uniaxial and biaxial materials. The 2x2 TMM only considers a single complex refractive index $\bar{n}$ (i.e. real part n : refractive index, imaginary part k : extinction coefficient).

2 Results and discussion

2.1 Microspectroscopic reflectance measurement and thickness evaluation

The setup of the measurement system used for reflectance microspectroscopy is shown in **Figure 1a**. White light is collimated onto the sample by an 100x/NA 0.89 objective lens and the reflected light is separated by a beamsplitter. One beam is focused onto a CCD camera for imaging while the other is coupled into a glass fiber and further analyzed by a spectrometer in crossed Czerny-Turner configuration. A more detailed description of the setup is given elsewhere.²³ The evaluated spectral range is 440 nm to 690 nm. It is important to note that the measurement system uses unpolarized light.

In **Figure 1b** the process flow of the developed numerical procedure of fitting modeled reflectance spectra to the experimental data using the 4x4 TMM-based approach is shown for an exemplary material stack consisting of three different material layers and a substrate. In the schematic, the second layer (Material 2) is shown as the material of interest. To describe the reflectance spectrum, the complex refractive indices of each material in the stack are required. Vast databases, driven by artificial intelligence (AI), collect refractive indices of materials published in literature.³⁹ Alternatively, an approximation of the refractive index is possible using ab initio atomistic structure simulations.⁴⁰

Objective lenses collect rays which are deflected towards larger space angles within a distinct angular range that is defined by the lenses' numerical aperture. Spectra of deflected rays (i.e. rays entering the thin films at non-normal incidence) superimpose with the normal incidence spectrum, which remarkably influences the dynamic range of measured spectra. We account for the use of an objective lens by establishing an angular weighting function W_{TOT} with the NA as the essential parameter. In addition, this weighting function allows us to obtain consistent results between different objective lenses (see **Table S3** and **Figure S4** in the Supporting Information). Thereby, the angular acceptance range of the objective lens is split into several discretized angles α_n . For each evaluated wavelength λ and angle α_n the reflectance $R(\lambda, \alpha_n)$ is calculated via the 4x4 transfer matrix Γ .²⁴ The resulting angular dependent reflectance spectra are weighted by W_{TOT} and summed up to obtain the total reflectance spectrum $R(\lambda)$. Furthermore, for in-plane anisotropic materials an additional rotation around the z-axis of 45° (labeled by the Euler angle φ ⁴¹) is needed to take the influence of both in-plane axes appropriately into account (cf. **Figure S7** in the Supporting Information). We compare the measured reflectance spectrum with the modeled spectrum using the residual sum of squares (RSS) in the evaluated wavelength range (for

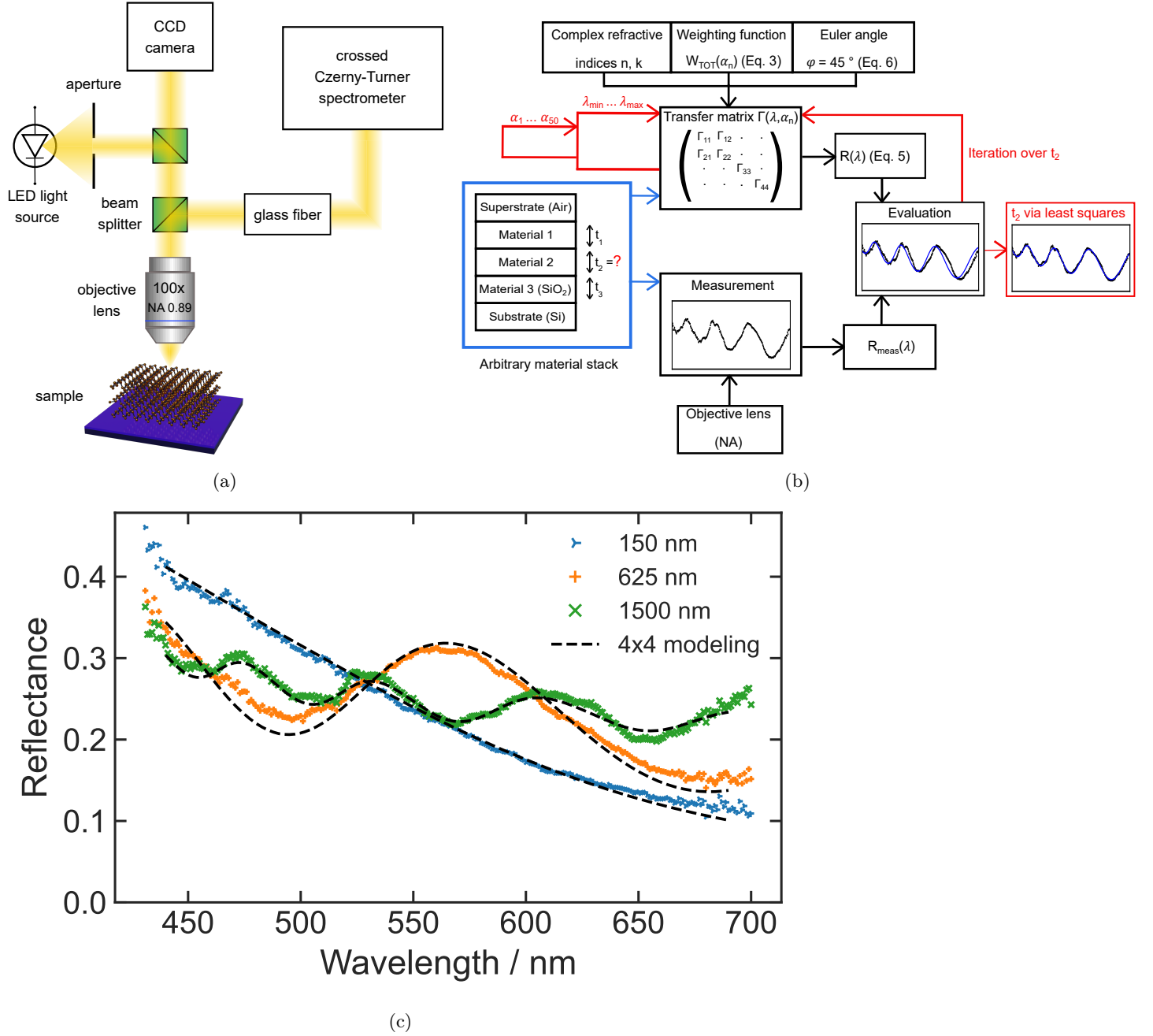


Figure 1: a) Microspectroscopy system used for reflectance measurements. b) Flowchart of the numerical procedure of adjusting the modeled data to the experimental data to determine t_2 , the thickness of Material 2 of the depicted layer stack, with the proposed 4x4 TMM approach (with the matrix elements Γ_{ij}). c) Measured and modeled reflectance spectra for SiO_2 films on Si substrate with different thicknesses as indicated in the legend (objective lens 100x/NA 0.89, measurements are averaged over ten individual spectra).

more details see the Supporting Information). The thickness of the examined material can therefore be determined by iterating over the thickness in the model and minimization of the RSS. A detailed description of the different functional blocks in Figure 1b is given in the 'Methods' section.

To demonstrate the general feasibility of our approach for isotropic materials, **Figure 1c** exemplarily shows the measured and modeled reflectance spectra for three different silicon dioxide (SiO_2) thin films on silicon (Si) substrate using the proposed TMM-based approach. Very good conformance between the modeled and measured reflectance spectra is achieved. The SiO_2 thicknesses measured via spectroscopic ellipsometry (SE) as reference are 146.6 ± 0.7 nm (mean value and standard deviation), 626.5 ± 0.9 nm and 1496.3 ± 2.1 nm. The results obtained via the proposed TMM-based approach match these values well with 147.5 nm (RSS 4.6×10^{-5}), 626.7 nm (RSS 18.1×10^{-5}) and 1493.4 nm (RSS 4.9×10^{-5}).

2.2 Reflectance spectra of in-plane isotropic materials

For isotropic materials (e.g. SiO_2) a single complex refractive index is sufficient. Therefore, the 4x4 and the 2x2 transfer matrix approaches yield identical results (cf. **Figure S5** and Table S3 in the Supporting Information). On the contrary, anisotropic materials exhibit two (for uniaxial crystals) or even three (for biaxial crystals) different complex refractive indices corresponding to the individual axes. BP as a biaxial crystal displays this kind of birefringent behavior.⁴⁰

In this section, we discuss the influence of the out-of-plane (i.e. z-direction) anisotropy on the accuracy of thickness evaluation by comparing the proposed 4x4 TMM-based approach with the results of a 2x2 TMM for in-plane isotropic materials. Reflectance spectra of stacks containing three (flakes of HOPG, WSe_2 , hBN and MoS_2 on SiO_2/Si) or even four materials (PMMA on BP flakes on SiO_2/Si) were examined and the results were compared with 4x4 and 2x2 transfer matrix models. For convenience, the material stacks are also schematically depicted in the figures. Modeling results for the stacks containing hBN, MoS_2 and WSe_2 are shown in the Supporting Information (cf. **Figure S8, S9 and S10**).

In **Figure 2a and 2b** the spectra of two different HOPG samples are depicted. In both cases the curve

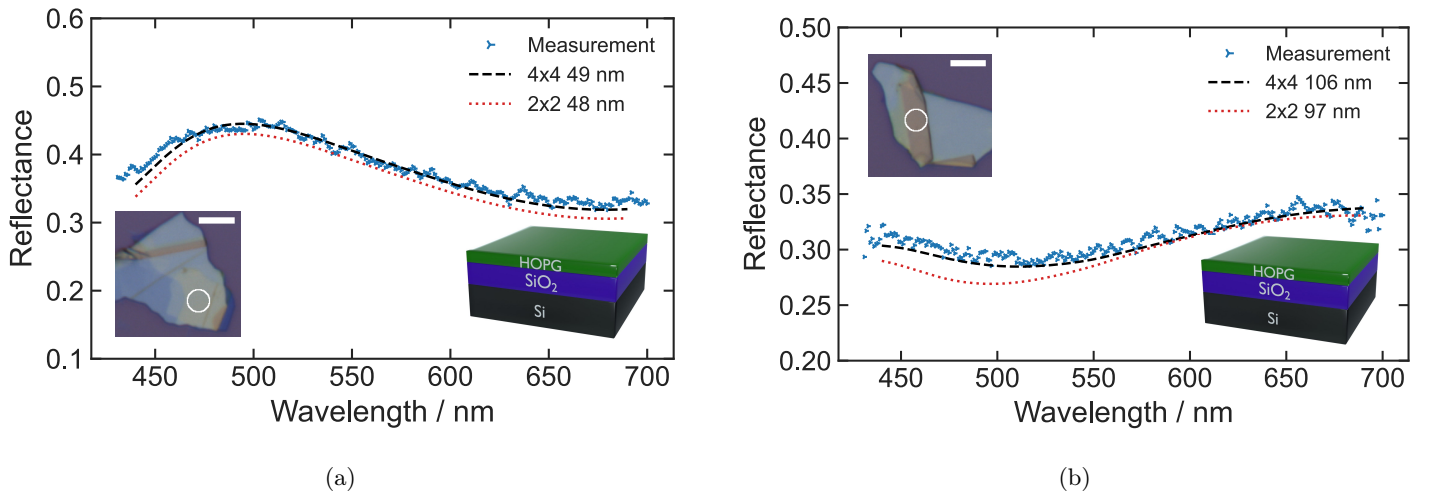


Figure 2: Comparison of modeled spectra (4x4 and 2x2 TMM) with the measured reflectance spectra (objective lens 100x/NA 0.89, averaged over ten individual spectra) for samples consisting of HOPG flakes on SiO_2/Si with a thickness of about a) 49 nm and b) 106 nm (as measured via AFM). The insets show optical micrographs of the regarding flakes with the position of the measurement spot marked. The scale bar is 5 μm .

modeled with the 2x2 TMM deviates from the measured data while the 4x4 transfer matrix model is more accurate. Despite that, for the spectrum shown in Figure 2a both approaches yield thicknesses comparable to the AFM thickness: 48.9 nm (4x4 TMM, $\text{RSS } 6.8 \times 10^{-5}$), 47.8 nm (2x2 TMM, $\text{RSS } 36.4 \times 10^{-5}$) and 48.7 nm (AFM). However, for the spectrum presented in Figure 2b the situation is different: While the thickness fitted using the 4x4 TMM approach (106.3 nm, $\text{RSS } 10.2 \times 10^{-5}$) almost perfectly matches the AFM thickness (106.2 nm), the 2x2 TMM yields a smaller thickness of 96.9 nm ($\text{RSS } 34.7 \times 10^{-5}$), corresponding to an underestimate of approx. 10% (cf. **Figure S11b**). This can be attributed to an increasing influence of the out-of-plane anisotropy with increasing sample thickness, which is not accounted for in the 2x2 TMM. The overall results of this work show that this impact, which can be seen for other HOPG samples as well, is strong especially for graphite (cf. **Figure S11**). This effect is explained in the following with the non-trivial reflection of light for samples consisting of different material layers and thus interfaces.

For unpolarized light, the electromagnetic wave has two linearly polarized components of the electric field of equal weighting, namely parallel (p) and orthogonal (s) polarization which interact differently with matter.^{38,42} In order to draw insight into the impact of interfaces on the reflectance spectra, in **Figure 3** the interaction of p-polarized light at the interface of an isotropic superstrate (e.g. air) and an in-plane isotropic but out-of-plane anisotropic material adjacent to a Si substrate for non-normal incidence is depicted. The direction of oscillation of the electric field is orthogonal to the direction of prop-

agation for p-polarized light as indicated. The incident electromagnetic wave E_i is partly reflected E_0^r and partly transmitted and refracted under the angle α_1 into the material subjacent to the superstrate. The transmitted component E_1^t is again partly reflected and transmitted at the interface to the substrate. The part E_2^{tt} transmitted into the substrate can be neglected since for Si it is completely absorbed in the case of light in the visible range of the electromagnetic spectrum. The reflected fraction E_1^{tr} again experiences transmission and refraction as well as reflection at the interface to the superstrate. Interference between the transmitted component E_0^{trt} and the originally reflected part E_0^r occurs, depending on the phase difference. The reflected fraction E_1^{trr} is undergoing the process of transmission and reflection at the interfaces.^{38,42} Because the intensity of these multiply transmitted or reflected components is relatively small especially for absorbing materials, they are not shown in Figure 3.

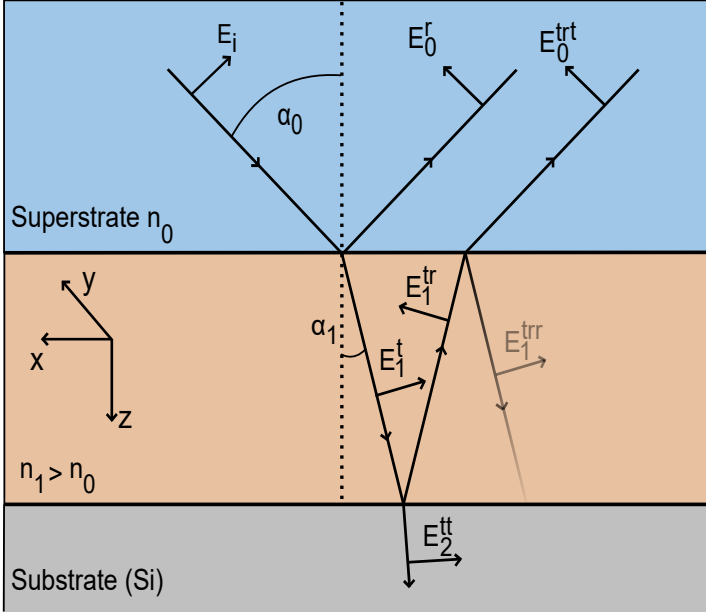


Figure 3: Schematic of light reflection at an interface between isotropic materials (according to literature⁴²).

The s-polarized component oscillates parallel to the y-axis and thus is only influenced by the in-plane complex refractive index. Therefore, s-polarized light is not pictured in Figure 3. In contrast, p-polarized light oscillates partially parallel to the x- and z-axes and hence is impacted by both the in-plane and out-of-plane properties of the material. This differing behavior results in diverging angles of refraction for p- and s-polarized light and describes the phenomenon of birefringence.^{38,42} Several mainly theoretical publications demonstrated this impact of the out-of-plane component on the optical response of layered materials down to monolayers.^{43–45} It was shown that only p-polarized light is affected because of the aforementioned refracted angle through the birefringence effect and the direction of oscillation.^{43–45} For unpolarized light, this effectively halves the impact of the out-of-plane component. In order to gain further insight into the impact of the out-of-plane refractive index anisotropy, we carried out a microspectroscopic study of other uniaxial layered materials: HOPG, WSe₂, hBN and MoS₂. An overview of the measured (via AFM) and modeled thickness of all in-plane isotropic material samples investigated in this work is given in Figure S11. The modeling results of the 4x4 and 2x2 TMM are rather similar for MoS₂ and WSe₂. This confirms the subsidiary role of the out-of-plane component of the refractive index for WSe₂ and MoS₂ in the investigated thickness range from few up to over hundred nanometers since the large real part of the in-plane refractive indices n_{xy} of the investigated materials ($n_{xy, \text{WSe}_2} = 4.66$ and $n_{xy, \text{MoS}_2} = 5.15$ at 550 nm^{46,47}) prohibits a large electric field component oscillating along the out-of-plane direction.⁴⁶ Moreover, the in-plane absorbance of these two transition metal dichalcogenides (TMDs) ($k_{xy, \text{WSe}_2} = 1.43$ and $k_{xy, \text{MoS}_2} = 1.09$ at 550 nm^{46,47}) largely prevents interference effects between light waves reflected at the upper boundary (Air/TMD) and the lower boundary (TMD/SiO₂) with increasing thickness because of the decreasing intensity of the waves reflected at the lower boundary. However, especially light reflected at the lower boundary is affected by the out-of-plane

component due to birefringence as light is partly refracted towards the in-plane crystal axes (i.e. the p-polarized electric field component is amplified in z-direction).

In the case of hBN, the small difference between the in-plane and out-of-plane components of the refractive index, i.e. the small anisotropy ($n_{xy,hBN} = 2.16$ and $n_{z,hBN} = 1.87$ at 550 nm ⁴⁸), explains the almost identical 4x4 and 2x2 modeling results. In contrast, HOPG exhibits a significantly lower real part of the in-plane component of the complex refractive index ($n_{xy,HOPG} = 2.60$ at 550 nm ⁴⁹) compared with the investigated TMDs while the in-plane absorbance is comparable ($k_{xy,HOPG} = 1.34$ at 550 nm ⁴⁹). In addition, a pronounced anisotropy compared to hBN exists ($n_{xy,HOPG} = 2.60$ and $n_{z,HOPG} = 1.34$ at 550 nm ⁴⁹).

In general, we have found that the extent of the influence of the z-component evidently increases with higher sample thickness. It also shows a strong dependence on the material properties (i.e. complex refractive index) since the influence is different for HOPG and hBN. These findings emphasize the necessity of the 4x4 transfer matrix for an accurate thickness determination and modeling of the optical response.

2.3 Reflectance spectra of in-plane anisotropic materials

In **Figure 4a and 4b**, spectra of two BP flakes on SiO_2/Si substrate and coated with PMMA are exemplarily modeled with a 4x4 and a 2x2 TMM and compared with the experimentally acquired reflectance spectrum (note that for wavelengths below 540 nm no values for the complex refractive index were available for modeling).

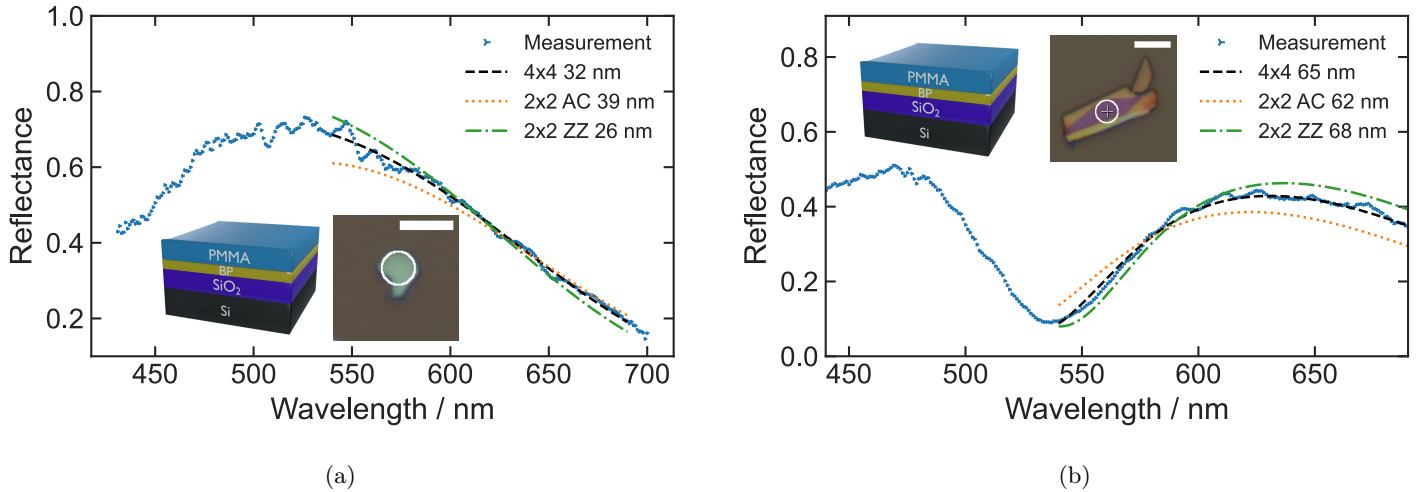


Figure 4: Comparison of modeled spectra (4x4 and 2x2 TMM) with the measured reflectance spectra (objective lens 100x/NA 0.89, averaged over ten individual spectra) for samples consisting of BP flakes on SiO_2/Si and encapsulated with PMMA with a flake thickness of about a) 32 nm and b) 66 nm (as measured via AFM). Note that for wavelengths below 540 nm no values for the complex refractive index were available for modeling. The insets show micrographs of the regarding flakes with the position of the measurement spot marked. The scale bar is $5\text{ }\mu\text{m}$.

Since, as aforementioned, the 2x2 TMM is only capable of applying one complex refractive index, the reflectance spectra were modeled for the AC or ZZ direction separately. The thickness of the SiO_2 was about 300 nm , the PMMA on top slightly varied between all samples in the range of 130 nm to 140 nm . The PMMA thickness was determined for each flake individually (cf. Sec. 'Methods').

As can be seen in **Figure 4**, our TMM-based approach accurately reproduces the measured reflectance values, which therefore allows for a precise thickness determination. The thicknesses fitted using the 4x4 TMM-based approach are 31.8 nm for the flake in Figure 4a and 64.9 nm for the flake in Figure 4b. In contrast, the 2x2 TMM delivers significant deviations from the measured data for the different refractive indices (AC and ZZ). For the AC refractive index the 2x2 modeled thicknesses are 39.3 nm and 62.0 nm and for the ZZ refractive index the modeled thicknesses are 25.8 nm and 67.6 nm . An approximation

with effective yet physically meaningless in-plane refractive indices was also tested with the 2x2 TMM (see Supporting Information for further discussion).

In **Table 1** the estimated thicknesses for all investigated BP samples are compared with the results of AFM measurements. The PMMA capping layer was removed immediately before AFM measurements by immersion in acetone. For the thicknesses calculated with the 4x4 and 2x2 transfer matrix, the residual sum of squares is additionally denoted in Table 1. In most cases, the 4x4 TMM results agree best with the AFM results whereas the 2x2 AC and ZZ approaches yield values with less agreement. The observed discrepancy between AC and ZZ direction in the case of the 2x2 TMM is the consequence of the birefringence of BP since the applied complex refractive indices for the AC and ZZ axes display a large difference in the extinction coefficient whereas the real part features similar values.⁹

Table 1: Comparison of the thicknesses obtained by AFM of different BP flakes with the results obtained by evaluating microspectroscopy measurements with the 4x4 TMM as well as the 2x2 approach (with either AC or ZZ complex refractive indices). For the AFM measurements the standard deviation is denoted according to the procedure described in the Supporting Information. For the modeled thicknesses the residual sum of squares (RSS) is denoted in brackets.

Sample No.	AFM	Thickness / nm (RSS / 10 ⁻⁴)					
		4x4		2x2 AC		2x2 ZZ	
1 ^{a)}	9.9 ± 0.6	7.9	(11.86)	8.3	(1.36)	7.0	(49.40)
2 ^{a)}	19.2 ± 0.9	18.9	(10.23)	21.9	(16.00)	16.5	(11.30)
3	32.0 ± 1.7	31.8	(1.69)	39.3	(11.68)	25.8	(7.55)
4	45.6 ± 0.8	45.6	(12.44)	46.2	(115.80)	39.7	(17.68)
5	53.8 ± 1.1	56.7	(38.10)	51.8	(1.33)	60.4	(119.32)
6	65.5 ± 0.6	64.9	(1.17)	62.0	(22.98)	67.6	(8.33)

^{a)} Please note that the used values for the complex refractive index of BP are only verified for flakes thicker than 30 nm.⁹

Our results demonstrate the advantage of the 4x4 TMM-based approach, as it inherently takes the complex refractive indices of both crystal axes into account and enables a more complete description of the optical response.

We also expect an impact of the z-component on the reflectance for BP. Since the in-plane absorbance of BP ($k_{AC,BP} = 0.52$, $k_{ZZ,BP} = 0.13$ at 550 nm⁹) is distinctly lower than for WSe₂ and MoS₂ ($k_{xy,WSe_2} = 1.43$ and $k_{xy,MoS_2} = 1.09$ at 550 nm^{46,47}), the influence of the out-of-plane anisotropy should be enhanced in contrast to the investigated TMDs. This is further supported by the smaller real part of the in-plane refractive index ($n_{AC,BP} = 4.09$, $n_{ZZ,BP} = 4.23$ and at 550 nm⁹) compared to WSe₂ and MoS₂ ($n_{xy,WSe_2} = 4.66$ and $n_{xy,MoS_2} = 5.15$ at 550 nm^{46,47}) albeit with a reduced impact due to the minor difference in absolute values (see previous section). The 4x4 TMM-based approach is capable of describing both phenomena, in-plane as well as out-of-plane anisotropy. In the case of BP, the influence of the z-component becomes significant with increasing flake thickness (cf. **Figure S13** in the Supporting Information).

2.4 Overview of the results

Figure 5 gives a comparison of the thickness estimated using the 4x4 TMM-based approach to the thicknesses obtained via AFM for all samples investigated in this work. In contrast to AFM, the proposed 4x4 TMM-based approach provides no metric quantifying the uncertainty (e.g. standard deviation) because of the purely numerical procedure of minimizing the RSS. Nevertheless, the spectral resolution of the employed spectrometer (1 nm) is determined by the bandwidth of an individual channel of the detector. The resulting error in modeled thickness was determined via shifting the recorded spectra by ±3 nm (three times the spectral resolution as confidence interval) and determining the thickness from the shifted spectra (see Supporting Information for further details). The good agreement (slope close to unity) over a broad range of flake thicknesses (from around 5 nm up to more than 120 nm) demonstrates the high capability of the proposed approach. In the case of thick HOPG flakes, the error in thickness determination in relation to the AFM measurement can be reduced down to 1 % with the proposed 4x4 TMM-based approach in contrast to 10 % for isotropic modeling (cf. also Figure S11 in the Supporting

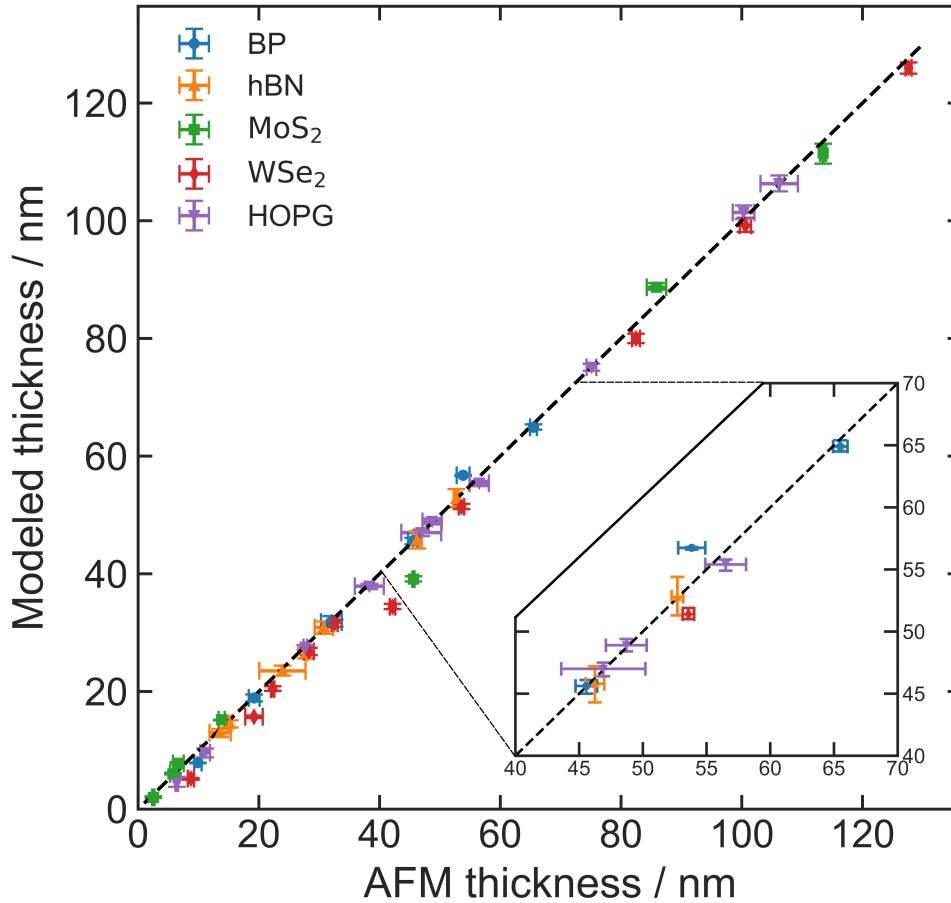


Figure 5: Comparison between the thicknesses of all studied material samples from 4x4 TMM modeling of microspectroscopic measurements (objective lens 100x/NA 0.89) and the thicknesses obtained via AFM. The error bars depict the standard deviation of the corresponding measurements for AFM. The error bars for the modelled thickness are the obtained values if the wavelength uncertainty is assumed 3 nm (three times of the spectral resolution of the spectrometer). Inset: Enlarged section from 40 nm to 70 nm.

Information). Only in the case of WSe₂ a small underestimate error was found, most probably due to inaccurate database values for the refractive indices from literature. In general, only the 4x4 TMM-based algorithm permits a physically holistic description of the investigated materials' optical response and, thus, correctly describe the reflectance of anisotropic materials.

3 Conclusion

Summarizing, by combining known with newly introduced elements, we demonstrate a facile, reliable and nondestructive method for thickness determination applicable to arbitrary stacks of layered materials and thin films in a wide thickness range (from few atomic layers up to several hundred nanometers) which utilizes numerical fitting of microspectroscopic reflectance measurements. The approach is cost-effective and suitable for structures of narrow lateral dimensions due to the small measurement spot sizes. A high precision of thickness assessment (down to 1 % in relation to AFM measurements for HOPG) has been achieved by combining a suitable 4x4 transfer matrix method for optical reflectance modeling with an objective lens dependent weighting. In contrast to other methods like AFM, our approach allows to study devices covered with passivation layers (as PMMA in the case of BP). In addition, the approach is capable of describing the reflectance of stacks of isotropic (SiO₂), uniaxial (HOPG, MoS₂, WSe₂, hBN) and even biaxial (BP) anisotropic materials. In general, the 4x4 TMM-based approach represents a universal method for arbitrary material stacks regardless of their (an-)isotropy as

long as appropriate refractive indices are available.

We demonstrate the reliability of our approach for material stacks of up to four layers (PMMA, BP, SiO₂, Si). However, this method can also be applied to material stacks with a higher number of layers as well as heterostructures of van der Waals materials. Thus, our technique can be useful in a broad range of scientific fields where material stacks and their precise thickness need to be assessed. This includes, for example, medical research,⁵⁰ optical data storage,⁵¹ and hyperspectral imaging.²⁹ Especially in the latter, where spatial and spectral information are equally important, our method is suitable for enhancing precision. In general, the utilization of deep learning algorithms within the model is a promising approach. Possible fields are in situ micro(spectro)scopy and again hyperspectral imaging, which both generate large datasets well-suited for the application of AI. Here, the exploitation of vast, AI driven, libraries of complex refractive indices for training neural networks and the synergistic combination with complementary techniques, retrieving the refractive index on the nanoscale, are intriguing chances.⁵² The proposed approach can also be extended to find the crystal orientation of in-plane anisotropic materials by applying polarized light.⁵³ In addition, the presented modeling could also be used in reverse manner to determine the complex refractive index of material samples with known thickness by measuring the transmission in addition to the reflectance. Finally, the proposed method is easily adaptable to other setups employing microspectroscopy (see **Figure S14** in the Supporting Information).

4 Methods

4.1 Specimen preparation, reflectance measurement and complex refractive indices

The BP flakes were mechanically exfoliated in a glovebox on commercially available 300 nm SiO₂/Si substrates and were subsequently spin-coated with PMMA still under inert atmosphere. HOPG, WSe₂, MoS₂ and hBN flakes were exfoliated onto 300 nm SiO₂/Si substrates in atmosphere. In-house grown SiO₂ films on Si were fabricated as an alternative substrate by wet thermal oxidation and the SiO₂ thickness was determined by laser ellipsometry after processing.

All investigated flakes were analyzed using a Zeta300 measurement system by Zeta Instruments (now KLA instruments) with a 100x/NA 0.89 objective lens (because of its small spot size of approx. 3 μ m). The system uses a high brightness white LED light source and is equipped with a Quest X spectrometer (model BRC112E-V) by BWTEK. In close proximity to each flake, additional spectra were recorded to precisely determine the SiO₂ as well as the PMMA thickness (where applicable). The employed spectra are averages over ten individual spectra taken subsequently. A Bruker Dimension ICON AFM system in intermittent-contact mode was employed for measuring reference thicknesses (cf. **Figure S1** in the Supporting Information). In the case of BP, the PMMA capping layer was removed immediately before AFM by immersion in acetone. Because of the non-optical, physically complementary principle and its associated independence from the refractive index, AFM was chosen as the reference method for thickness extraction. Besides, scanning by AFM provides information on the planarity or respectively the homogeneity in terms of thickness of the examined specimens (assuming the underlying substrate to be planar) required for unambiguous results via microspectroscopy.

Due to the integral nature of optical methods, the measurement spot should be filled with a material stack with uniform thickness. Otherwise, the approach will yield an average thickness. In addition, the model assumes a single material stack within the measured area. For microscopic applications this requirement is easily fulfilled in most cases because of the small spot size of approx. 3 μ m. While the homogeneous thickness is verifiable by coloration in optical inspection, the simultaneous analysis of multiple material stacks could be overcome by applying a "film-island-model". Such an approach is already successfully utilized in spectroscopic ellipsometry, whereby the significantly larger measurement spot dimensions have to be mentioned.⁵⁴ Within the model, the investigated flakes are assumed to be optically smooth. Roughness as a form of thickness inhomogeneity was also tested by AFM. Besides, van der Waals materials generally display negligible roughness stemming from their layered character. Nevertheless, there are existing models describing surface roughness that can be incorporated in the proposed

modular approach⁵⁵ (for more details about requirements and potential enhancements see Supporting Information).

Complex refractive indices of the investigated materials were taken from literature for air,⁵⁶ silicon,⁵⁷ commercially available SiO₂ substrates,⁵⁸ HOPG,⁴⁹ hBN,⁴⁸ WSe₂⁴⁷ and MoS₂.^{46,59} For in-house grown SiO₂ the complex refractive index was determined by spectroscopic ellipsometry (cf. Figure S2a). In case of the highly anisotropic BP, the refractive indices for the in-plane components AC and ZZ are taken from *Lee et al.*⁹ As there are no values available below wavelengths of 540 nm, the modeling for BP was performed in the spectral range of 540 nm to 690 nm. The out-of-plane component is adopted from *Schue et al.*⁴⁰ For BP the determination of the complex refractive indices is more challenging than for in-plane isotropic materials when applying established methods like (microspot) spectroscopic ellipsometry. Especially for the z-component, there are only theoretical values from density functional theory (DFT) calculations available at present,⁴⁰ which further strengthens the difficulty of extracting the three different complex refractive indices of BP with just a single measurement.

We note that the accuracy of the proposed method is dependent on the existence of reliable data containing the complex refractive indices for the investigated materials. In literature, these values vary strongly depending on synthesis of the analyzed flakes and extraction technique. Therefore, only refractive indices that were extracted via optical methods (e.g. using spectroscopic ellipsometry) on samples manufactured under similar conditions were used in this work. Possible synergies arise by exploiting the combinatory use of methods which assess the refractive complex index with lateral precision comparable to AFM (e.g. nanoscale). Such methods can detect inhomogeneities of the refractive index within the measured area.^{52,60} In this way, the requirements of the knowledge of the refractive index and a homogeneously filled measurement spot can be met.

An exemplary study of the dependence of the modeling on the applied complex refractive index for a WSe₂ sample illustrates the large sensitivity regarding the modeled reflectance (cf. **Figure S6**). For this reason, the refractive index for the in-house grown SiO₂ was determined separately.

4.2 Modeling and weighting functions

Since an objective lens collects light in an angular range defined by the numerical aperture, the resulting reflectance spectrum is a superposition of the reflectance spectra of the different angles. Therefore, an approach proposed by *Saigal et al.*⁶¹ is used to scale the angular contributions of an objective lens according to its numerical aperture. These contributions are considered by the angular weighting function W_{NA} .

Another factor to be accounted for is the inhomogeneous illumination of the objective lenses' back focal plane. In the case of differing back focal plane positions, the intensity distribution varies for different objective lenses. Therefore, we introduce an objective lens dependent weighting function W_{obj} to enable portability to other measurement setups. W_{obj} is given by:

$$W_{obj}(\alpha_n) = e^{-0.5 \cdot \left(\zeta \frac{2n-1}{2N}\right)^2}, \quad (1)$$

in which the range of accepted angles of the numerical aperture is discretized in N parts (in this work, $N=50$) and α_n describes each discrete angle of incidence. ζ is an objective lens dependent weighting factor, which is distinct for each objective (see **Table S2**, Figure S4 and according section for a detailed derivation in the Supporting Information). The relation between α , n and N is as follows:^{23,61}

$$\alpha_n = \tan^{-1} \left(\tan \left(\sin^{-1}(\text{NA}) \right) \cdot \frac{2n-1}{2N} \right) \cdot \frac{180^\circ}{\pi}. \quad (2)$$

We measured the NA of objective lenses with a custom-built apertometer based on the work of *Cheshire*⁶² (cf. **Figure S3** and **Table S1**). A precise NA value is necessary especially for objective lenses with large numerical apertures due to larger contributions of high angles of incidence.⁶¹

In conclusion, we account for the contributions of different angles of incidence by multiplying both, W_{NA} and W_{obj} , resulting in a total weighting function W_{TOT} which we apply to the reflectance model-

ing through the whole work. The factors W_{TOT} are normalized that the sum over all n factors amounts to one:

$$W_{TOT}(\alpha_n) = \frac{W_{NA}(\alpha_n) \cdot W_{obj}(\alpha_n)}{\sum_{n=1}^N W_{NA}(\alpha_n) \cdot W_{obj}(\alpha_n)}. \quad (3)$$

The wavelength dependent reflectance is calculated as:

$$R(\lambda) = \sum_{n=1}^N R(\lambda, \alpha_n) \cdot W_{TOT}(\alpha_n). \quad (4)$$

As unpolarized light is used, an equal contribution of p- and s-polarized light is assumed.^{23,25} Thus, the reflectance for unpolarized light is as follows:⁶³

$$R_{unpol}(\lambda) = 0.5 \cdot [R_p(\lambda) + R_{ps}(\lambda) + R_s(\lambda) + R_{sp}(\lambda)], \quad (5)$$

where $R_{p/s}$ is the reflectance of p/s-polarized light and $R_{ps/sp}$ is the cross-polarized reflectance, which is nonzero for birefringent materials.⁶³ Each modeled spectrum is compared with the measured spectrum using least square fitting (see the Supporting Information for a more detailed description).

In the case of (in-plane) isotropic materials, advantage of the rotational symmetry of the circular measurement spot can be taken. Therefore, theoretically only one angle around the z-axis needs to be considered for the model. For in-plane anisotropic materials, this symmetry is broken. Thus, the reflectance of all angles around the z-axis needs to be considered. This is numerically feasible via rotating the permittivity tensor by using the concept of Euler angles and the associated coordinate transformation matrix.^{24,41} The rotation of the laboratory frame around the z-axis is termed φ by convention.⁴¹ In order to incorporate the influence of all angles around the z-axis, these reflectances are summed up by angular steps of 1° and weighted equally due to the symmetric illumination. Hereby, **Equation 4** is extended and the resulting expression reads as follows:

$$R(\lambda) = \frac{\sum_{\varphi=1^\circ}^{\varphi=360^\circ} \left(\sum_{n=1}^N R(\lambda, \alpha_n, \varphi) \cdot W_{TOT}(\alpha_n) \right)}{360}. \quad (6)$$

However, this implementation is computationally time-consuming. Therefore, an optimized approach is developed using a fixed φ of 45° and assuming planar orientation of the sample. Simulations comparing this fixed angle and the calculation according to **Equation 6** show that this computational optimization is sufficient (cf. Figure S7). Furthermore, the assumption of planar sample orientation without any tilt is considered feasible (cf. Figure S7 and according discussion).

The modeling is basically possible from single atomic layers^{23,25} up to thick substrates (cf. Supporting Information). The precision in the region of few atomic layers can be augmented by including the technique presented in our previous studies that are analyzing the wavelength shift of extreme values in the reflectance spectra.²³ Thick layers, on the other hand, lose their thickness dependence regarding reflectance incrementally and the reflection becomes totally independent of the thickness when reaching the coherence length (e.g. they become incoherent). The coherence length is wavelength, material and setup dependent and is the limit where interference disappears in a measured spectrum.³⁸ In the investigation of SiO₂ films on Si, we demonstrate that coherent modeling is applicable at least up to 1500 nm for the used setup, hence providing a broad thickness range (see Supporting Information for a detailed discussion). A related requirement is an at least partial transparency of the investigated materials within the analyzed spectral range. Otherwise, there arises no thickness dependence in reflectance.

4.3 Statistical analysis

Each acquired reflectance spectrum is an average over ten individual, subsequently measured reflectance spectra normalized to a silicon reference spectrum. Additionally, the measured signal of the spectrometer is corrected for its dark signal and the noise at the wavelength boundary is excluded. The AFM data

is presented as mean value and standard deviation, where first an average over the number of lines is built and then the height average over all pixels in this area is calculated; when using the histogram, the counts of both maximum peaks are used for calculation (see chapter "Specimen preparation" above and "Atomic force microscopy" in the Supporting Information). For the modeled thicknesses, since they are not measured but modeled values, an individual metric of uncertainty is defined as described in the chapter "Comparison of modeling precision" in the Supporting Information. All processing of the AFM data (calculation of mean thickness and standard deviation) was either performed in the proprietary measurement software by Bruker itself or by using Python. The pre-processing of the measured reflectance spectra (averaging over ten spectra and dark signal correction) was performed in the software of Zeta Instruments. The modeling (including calculation of the RSS and metric of uncertainty) was performed using custom-built software, which will be made available upon publication.

Supporting Information

Information about atomic force microscopy measurements, numerical aperture measurement, improvement of objective lens dependent weighting function, effective Euler angles for computational optimization, modeled spectra for hBN, MoS₂ as well as WSe₂ and additional BP spectra. Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

J.S., M.N. and M.S. conducted the spectroscopic measurements. Samples were prepared by M.N, P.C., M.K-G. and M.S. AFM measurements were performed by L.B. Formal analysis and data selection were carried out by J.S. and M.N. The used code for the 4x4 transfer matrix modeling was implemented by M.R. and J.S. and discussions on modeling were performed with valuable participation of M.N. and A.H. J.S., M.N., M.R. and A.H. developed the analytical model used for thickness determination. J.S. and M.N. wrote the draft of the manuscript with annotations by A.H., M.R., M.K-G. and V.K. All authors commented on the manuscript.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Notes

Upon publishing, the software for reproducing the presented methodology for reflectance spectra will be available on github. The 4x4 and the 2x2 transfer matrix method is included as well as a function for easy finding of the objective lens dependent parameter ζ of the weighting function W_{obj} (see **Equation 1**) for individual microspectroscopy setups.

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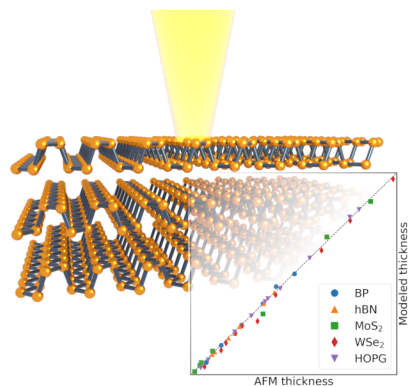
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Microspectroscopy combined with optical modeling is a versatile tool for accessing parameters like the thickness of van der Waals materials. However, models often lack the possibility to describe the optical response of anisotropic materials. In our approach we demonstrate a model based on a 4x4 transfer matrix as a physically holistic approach for precise thickness determination of highly anisotropic materials like black phosphorus.



Correlating Optical Microspectroscopy with 4x4 Transfer Matrix Modeling for Characterizing Birefringent van der Waals Materials