

Determination of the thickness of BN layers on the Al_2O_3 substrate by FT-IR spectroscopy

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Hexagonal boron nitride (h-BN) is an attractive material for applications in electronics. The technology of devices based on BN requires non-destructive and fast methods of controlling the parameters of the produced layers. Boron nitride layers of different thickness were grown on sapphire substrates (Al_2O_3) using the MOCVD method. The obtained films were characterized by FT-IR spectroscopy using IRR and ATR techniques and by the XRR and SEM methods. We showed that by analyzing the ATR or reflectance spectrum in the range of 600-2500 cm^{-1} we can measure the thickness of a BN layer on the Al_2O_3 substrate. Our measuring method allows measuring the layers with a thickness from ~2 nm to approx. 20 nm.

Key words: h-BN layers, ATR, IRR, XRR, thickness measurement, Al_2O_3

Wyznaczanie grubości warstw BN na podłożu Al_2O_3 za pomocą spektroskopii FT-IR

Heksagonalny azotek boru (h-BN) jest atrakcyjnym materiałem do zastosowań w elektronice. Technologia wytwarzania urządzeń z zastosowaniem warstw h-BN wymaga nieniszczących i szybkich metod kontroli parametrów produkowanych warstw. Warstwy azotku boru o różnej grubości wyhodowano na podłożach szafirowych metodą MOCVD. Otrzymane warstwy scharakteryzowano za pomocą spektroskopii FT-IR z użyciem technik IRR i ATR oraz metodami XRR i SEM. Pokazaliśmy, że analizując widmo ATR lub odbicia w zakresie 600-2500 cm^{-1} można zmierzyć grubość warstwy BN na podłożu Al_2O_3 . Nasza metoda pomiarowa pozwala na pomiar warstw o grubości od ~2 nm do ok. 20 nm.

Słowa kluczowe: warstwy h-BN, ATR, IRR, XRR, pomiar grubości, Al_2O_3

DOI: <https://doi.org/10.34769/azkm-y326>

1. Introduction

Hexagonal boron nitride (h-BN) has a layer structure similar to that of graphite, and in the case of thin layers to graphene, with strong sp^2 covalent B-N bonds in the plane and weak van der Waals bond between the planes [1]. Due to the parameters such as: wide energy gap of about 6.0 eV, good dielectric properties and high thermal conductivity, material can be used as a gate or substrate material in 2D electronics [2,3]. It was found that two-dimensional (2D) h-BN is atomically smooth and free from the dangling bonds and the surface charge traps which makes it a good dielectric material for graphene devices [4,5]. To achieve this, it is necessary to deposit the layers with good structure and different thicknesses in a reproducible manner and to develop non-destructive and fast measuring methods for controlling the thickness

of the produced layers. When analyzing the literature data, it can be seen that several measurement methods are used to determine the thickness of the produced BN layers, and the choice of the method depends largely on the type of substrate on which the BN layer is located and on the thickness of the layer itself. The authors of the works by Q. Paduano et al. [6] and X. Yang et al. [7] measured BN thin layers on Al_2O_3 using X-ray reflectometry (XRR). Atomic force spectroscopy (AFM) was used to characterize BN layers on sapphire with a thickness of the order of single nm [8]. The BN layers on Si/SiO_2 were measured by Raman spectroscopy [9,10].

FT-IR spectroscopy is a technique widely used to characterize the crystallographic structures of boron nitride layers. [7,8,11-13]. The article presents the method for determining the thickness of sp^2 -BN layers on the Al_2O_3 substrate based on the analysis of absorption spectra in the range of 600-2500 cm^{-1} .

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2. Experiment

Boron nitride (BN) layers were deposited on the Al₂O₃(0001) substrate using the MOCVD method. Triethylborane (TEB) and ammonia (NH₃) were used as precursors of boron and nitrogen, respectively. Argon (Ar) or hydrogen (H₂) was used as the carrier gas.

Samples with BN layers of various thickness were characterized by Fourier spectroscopy (FT-IR) using Specular Reflectance (IRR) and Attenuated Total Reflection (ATR). Single reflection ATR accessory with Ge crystal (diameter 1,8 mm) and a clamp with digitally controlled pressure were used in the studies. Reflection measurements for the tested BN layers were done using an IR microscope, the aperture value was set to 100 μm. FT-IR measurements were taken in the spectral range from 600 to 5000 cm⁻¹ with a resolution of 2 cm⁻¹ (ATR) and 4 cm⁻¹ (IRR) at room temperature on a Bruker Vertex 80v FT-IR spectrometer. The BN layers thickness was also determined by other experimental techniques such as X-Ray Reflectivity (XRR) using a Smartlab Rigaku X-ray diffractometer and Scanning Electron Microscopy (SEM) on a Field Emission SU8230 Hitachi.

3. Result and discussion

The ATR spectra in the range of 600-1800 cm⁻¹ for several samples with different layer thickness are shown in Fig. 1. The measured reflection spectra of these samples in the same spectral range are shown in Fig. 2. The course of the absorption spectra indicate that the investigated boron nitride had a structure with a sp² bonds (sp²-BN). Absorption lines observed in the spectra at 1370 cm⁻¹ and at 825 cm⁻¹ correspond to transverse E_{1u}(TO) and longitudinal A_{2u}(LO) optical phonon of the sp² bonded BN (h-BN/r-BN) respectively. In the figure 1 and 2 it will be seen that the intensity of the absorption lines originating from vibrations of B-N bonds in-plane (E_{1u}, (TO)) increases with the increasing layer thickness.

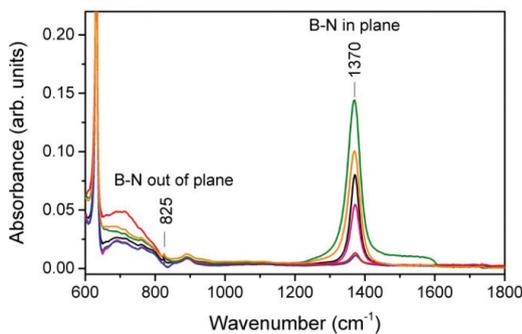


Fig. 1. ATR spectra of sp²-BN layers with different thickness deposited on an Al₂O₃ substrate.

Rys. 1. Widma ATR warstw sp²-BN o różnej grubości osadzonych na podłożu Al₂O₃.

This fact was used to develop a method for determining the thickness of BN layers on an Al₂O₃ substrate from absorption measurements. Using the SCOUT [14] program, a numerical model of the studied structures was created, in which BN layer thickness was one of the parameters. Theoretical ATR or reflection spectra were then calculated from this model. The thickness of the layers was determined by the best fit of the theoretical spectrum to the experimental data.

The calculated spectra of the Al₂O₃/BN structure were obtained by a standard multilayer technique [15]. The dielectric function $\epsilon(\omega)$ of the Al₂O₃ substrate and the BN layers were described by the damped harmonic oscillator model for each IR-active phonon. We used a modified classical dielectric function model for calculations, where the contribution from the TO phonon damping constant and the LO phonon damping constant are independent of each other [7]

where ϵ_∞ is the high-frequency dielectric constant, ω_{TO} ,

$$\epsilon(\omega) = \epsilon_\infty \prod_j \frac{\omega_{jLO}^2 - \omega^2 - i\gamma_{jLO} \omega}{\omega_{jTO}^2 - \omega^2 - i\gamma_{jTO} \omega} \quad 1$$

ω_{LOj} are the resonance frequencies of the jth TO and LO phonons and γ_{jTO} , γ_{jLO} are damping constants for each of the phonons. In the case of the Al₂O₃ substrate, the interaction of the electromagnetic wave with free carriers was also taken into account using the Drude-Lorentz model [16] and the dielectric function took the form

$$\epsilon(\omega) = \epsilon_\infty \prod_j \frac{\omega_{jLO}^2 - \omega^2 - i\gamma_{jLO} \omega}{\omega_{jTO}^2 - \omega^2 - i\gamma_{jTO} \omega} - \frac{\epsilon_\infty \omega_p^2}{\omega^2 + i\omega\gamma} \quad 2$$

The term ω_p is the plasma frequency, given as

$$\omega_p^2 = \frac{4\pi N e^2}{m^* \epsilon_\infty} \quad 3$$

where N , m^* , e and γ are the free-carrier concentration, effective mass, electron charge and free-carrier damping constant, respectively.

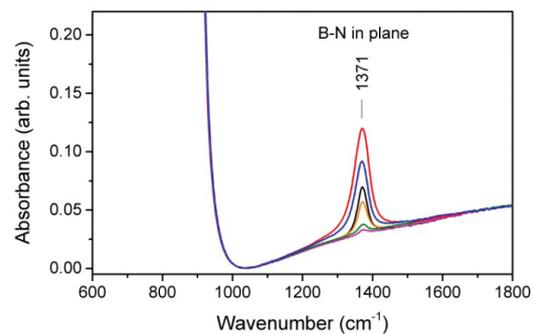


Fig. 2. Reflection spectra of sp²-BN layers with different thickness deposited on an Al₂O₃ substrate.

Rys. 2. Widma odbicia warstw sp²-BN o różnej grubości osadzonych na podłożu Al₂O₃.

The parameters used to calculate the Al_2O_3 spectrum, such as the frequency of the TO and LO phonons of the E_{1u} mode and the A_{2u} mode as well as their damping coefficients and the dielectric constant $\epsilon_\infty = 3.1$ were taken from the papers [16,18,19]. In the case of BN layers, the initial values of the parameters were assumed to be the data from the works [20,21,22]. Phonon frequencies for the A_{2u} mode were $\omega_{TO} = 783 \text{ cm}^{-1}$, $\omega_{LO} = 828 \text{ cm}^{-1}$ and for the E_{1u} mode $\omega_{TO} = 1367 \text{ cm}^{-1}$, $\omega_{LO} = 1610 \text{ cm}^{-1}$ and the dielectric constant $\epsilon_\infty = 4.3$. The actual frequencies ω_{TO} and ω_{LO} and their damping coefficients for a given BN layer were determined experimentally by means of an optimum fit of the theoretical spectrum to the spectrum measured for the tested sample. In reflection measurements, the angle of incidence of the electromagnetic wave on the sample was 11° and 16° for measurements

on the microscope and in the ATR the wave penetrates the sample as in the case of transmission measurements, hence the value of the dielectric constant for the BN layer is $\epsilon_\infty = 4.3$, which corresponds to the value of the dielectric constant for E_{1c} .

The infrared reflectance or the ATR spectrum was calculated as a function of the wavenumber and then fitted to the measured spectrum by adjusting the values of the parameters where one of the parameters was thickness of the layer. Figures 3 and 4 show the experimental and calculated ATR and reflectance spectra obtained by curve fitting for the BN layer thickness of about 4 nm, and Figures 5 and 6 for the BN layer thickness of about 13 nm.

To assess the developed method of analysis of absorption spectra and the correctness of BN layer thickness determination on Al_2O_3 using FT-IR spectroscopy, the-

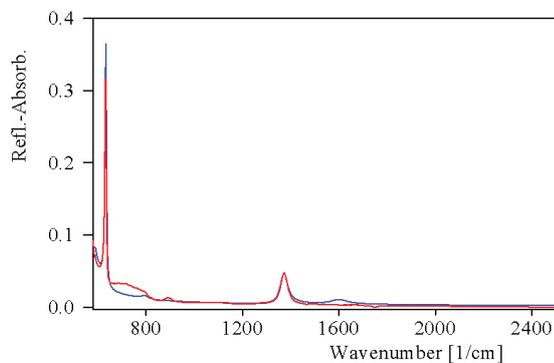


Fig. 3. ATR spectrum (red line) and fitted calculated curve (blue line). The determined layer thickness is 4.3 nm.

Rys. 3. Widmo ATR (linia czerwona) i krzywa dopasowania (linia niebieska). Wyznaczona grubość wynosi 4,3 nm.

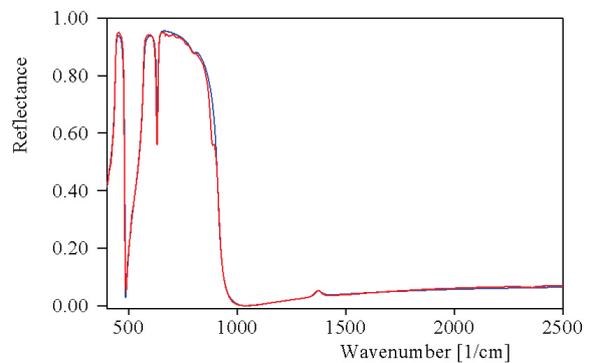


Fig. 4. Measured reflection spectrum (red line) and fitted calculated curve (blue line). The determined layer thickness is 4.6 nm.

Rys. 4. Widmo odbicia (linia czerwona) i krzywa dopasowania (linia niebieska). Wyznaczona grubość wynosi 4,6 nm.

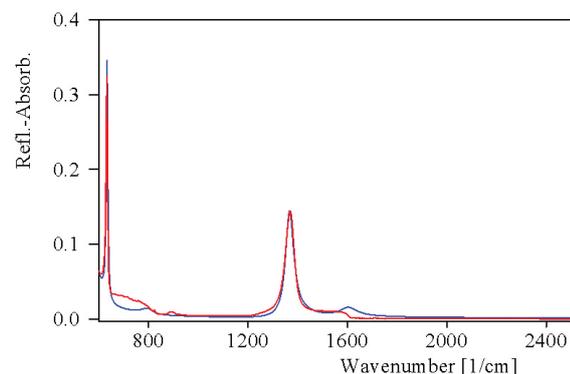


Fig. 5. ATR spectrum (red line) and fitted calculated curve (blue line). The determined layer thickness is 13.6 nm.

Rys. 5. Widmo ATR (linia czerwona) i krzywa dopasowania (linia niebieska). Wyznaczona grubość wynosi 13,6 nm.

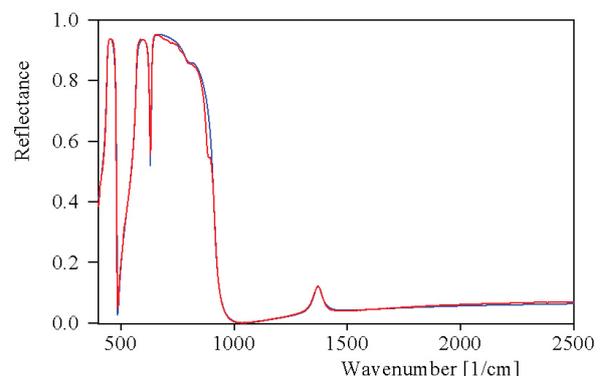


Fig. 6. Measured reflection spectrum (red line) and fitted calculated curve (blue line). The determined layer thickness is 13.5 nm.

Rys. 6. Widmo odbicia (linia czerwona) i krzywa dopasowania (linia niebieska). Wyznaczona grubość wynosi 13,5 nm.

sted samples were also measured by X-Ray Reflectometry (XRR). The layer thickness was obtained by fitting the calculated reflectance to that measured using the Global-Fit2 program provided by the Rigaku Corporation. Figures 7 and 8 show the examples of typical XRR profiles measured for the BN layers on Al₂O₃, for the 2.09 nm and 7.77 nm thick layer, respectively.

Several samples selected from those with a BN layer over 5 nm thick, were characterized also using a scanning electron microscope (SEM). SEM observations were made on the cross-sections of the samples. Representative images for two different layer thickness are shown in Figures 9,10. As it can be seen in the presented images, the surfaces of the thick sp²-BN layers were not smooth.

The surface morphology of the BN layer and graininess of the structure affect the accuracy of thickness determination in each measurement method used in the work. Since BN thick layers have a pronounced roughness, each measurement method determines the average thickness value. Nevertheless, the correlation of the results between the methods is good. The layer thicknesses obtained from the ATR, IRR and XRR measurements are given in Table 1. Figure 11 shows the relationship between the data from the ATR and IRR measurements and the results obtained from the XRR measurements.

In the case of thin sp²-BN layers, up to approx. 2 nm thick, the thicknesses determined using ATR and IRR were in most cases slightly smaller than those determined from

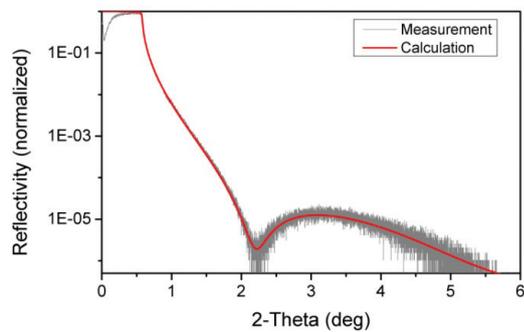


Fig. 7. Measured reflectometric profile and fitted curve. The determined layer thickness is 2.1 nm.

Rys. 7. Zmierzony profil reflektometryczny i krzywa z dopasowania. Wyznaczona grubość warstwy to 2,1 nm.

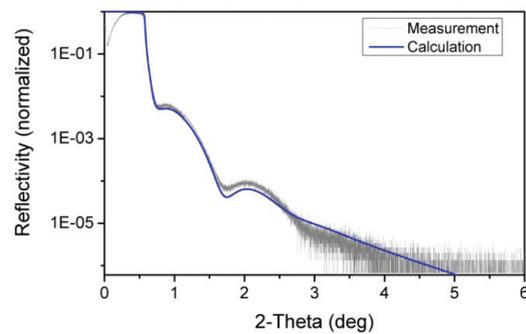


Fig. 8. Measured reflectometric profile and fitted curve. The determined layer thickness is 7.8 nm.

Rys. 8. Zmierzony profil reflektometryczny i krzywa z dopasowania. Wyznaczona grubość warstwy to 7,8 nm.



Fig. 9. SEM image of BN layer with thickness ~10.7 nm.

Rys. 9. Obraz SEM warstwy BN o grubości ~10.7 nm.

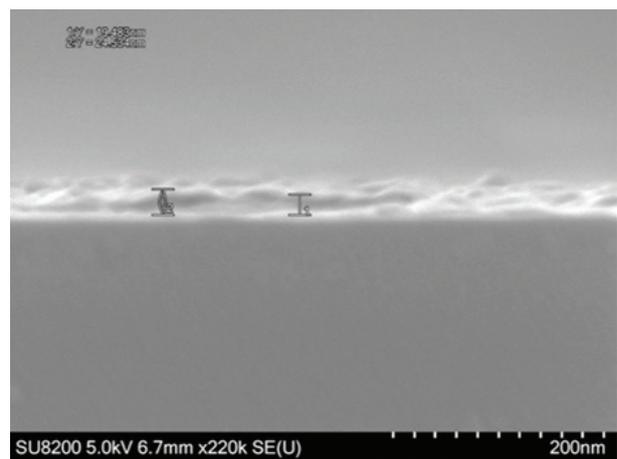


Fig. 10. SEM images of BN layer with thickness ~19.5 nm.

Rys. 10. Obraz SEM warstwy BN o grubości ~19.5 nm.

XRR. It is known that very thin layers may not fully cover the substrate, which may cause the observed differences, as the intensity of the absorption line depends on the number of bonds present in the measured area. The thickness distribution on the sample can also affect the result obtained from each of the measurement methods, because each method collects data from an area of a different size, and the measurements were not carried out at the same place on the sample. A Visible drastic difference between the results from XRR and FT-IR and SEM for one sample may result from the error or limitations occurring in the numerical analysis of XRR spectra itself.

The bias of this technique has not been established. The repeatability of the measurement depends mainly on the quality of the BN layer. The BN layers with a thickness of <3 nm were sufficiently smooth and the repeatability for ATR or reflection measurements was <3%. For thicker BN layers, the uniformity of the thickness over the entire sample was not so good, therefore the repeatability of the measurement was worse, reaching 20%. The deviation of the simulated and measured spectrum was better than 2×10^{-4} .

Tab. 1 Summary of BN layer thicknesses on Al_2O_3 obtained from XRR, ATR and IRR measurements

Tab. 1 Zestawienie grubości warstw BN na Al_2O_3 uzyskanych z pomiarów XRR, ATR i IRR

Sample no.	XRR d [nm]	ATR d [nm]	Refl. d [nm]
1	1.20	1.14	1.05
2	1.76	1.12	-
3	1.88	1.16	1.2
4	1.82	10.4	10.1
5	1.85	1.4	1.2
6	2.09	1.82	1.9
7	2.22	2.4	2.13
8	2.35	3.67	3.6
9	2.11	1.42	1.84
10	2.60	2.7	-
11	3.02	2.8	2.4
12	3.55	5.94	-
13	4.33	4.49	4.0
14	4.59	4.3	4.6
15	5.50	5.41	5.9
16	7.77	8.7	8.55
17	7.11	6.84	-
18	12.90	13.6	13.5
19	18.70	16.8	16.4

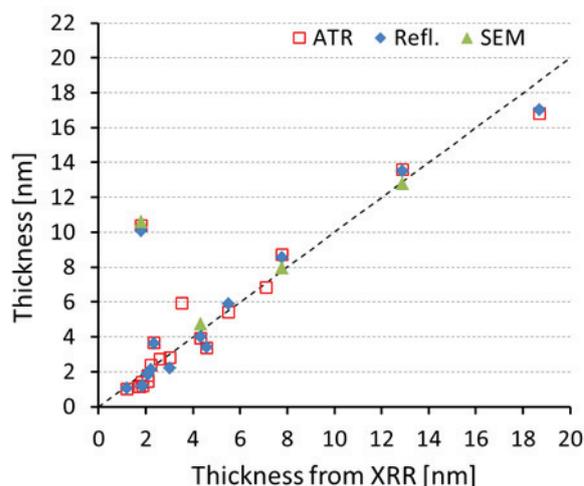


Fig. 11. BN layers thicknesses obtained from ATR and IRR measurements as a function of thickness determined by XRR.

Rys. 11. Grubości warstw BN otrzymane z pomiarów ATR and IRR w funkcji grubości określonej metodą XRR.

4. CONCLUSIONS

In this report, we presented a method for determining the thickness of BN layers grown on an Al_2O_3 substrate using FT-IR spectroscopy. We showed that the thickness of a BN layer can be measured by analyzing the ATR or reflectance spectrum in the range of $600\text{--}2500\text{ cm}^{-1}$. Our measuring method allow measuring the layers with a thickness from $\sim 2\text{ nm}$ to approx. 20 nm . The results of BN layers thickness obtained with the use of the developed method were compared with the results from the XRR method. The correlation between the results from these two methods is good.

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