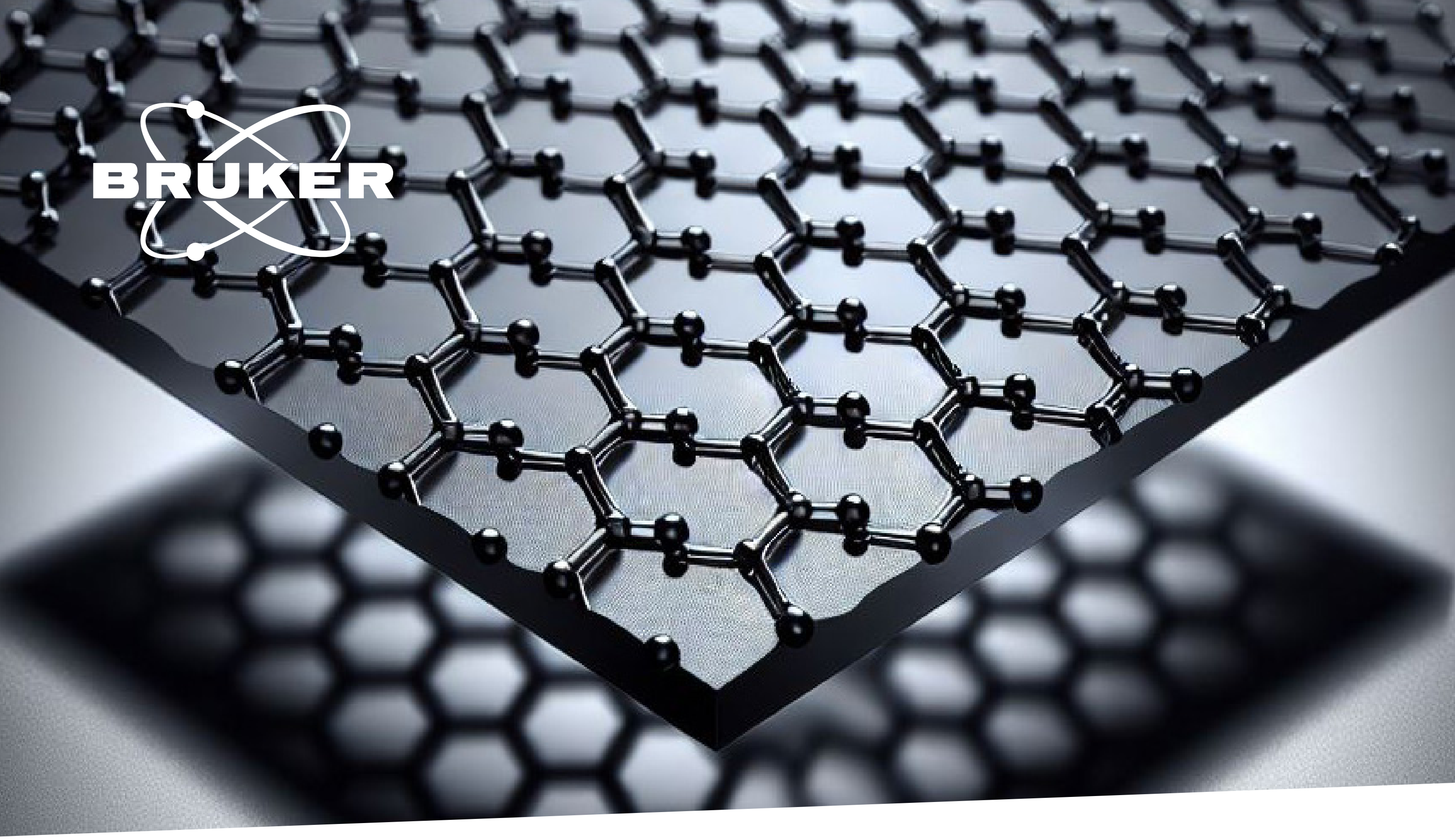

X-RAY DIFFRACTION

Analysis of monolayers and ultra thin WS_2 films using Grazing Incidence X-ray Diffraction

Application Note 631

Introduction

The functionality of thin film devices is highly dependent on their structural properties. X-Ray Diffraction (XRD) and X-Ray Reflecto--metry (XRR) are uniquely non-destructive techniques for the investigation of thin films. They are providing access to structural properties such as layer thicknesses, interfacial roughness, and electron density, as well as crystalline properties with sub-nanometer accuracy.

Investigating these thin films using laboratory X-ray diffractometers is particularly challenging when film thicknesses are in the monolayer range, requiring the application of grazing incidence techniques to obtain a signal from the film.

WS_2 is a promising candidate for being used in next-generation 2-dimensional electronic devices. Its high carrier mobility and thickness-dependent optical bandgap make it suitable for transistors and other semiconductor applications. WS_2 is also ideal for photovoltaic applications, as WS_2-based solar cells can achieve high efficiency due to their optimal bandgap for solar energy conversion. Controlling the thickness and structural properties of ultra-thin WS_2 films is critically important to realize proper functionality.

In this application note, two ultra-thin WS_2 films — consisting of a single monolayer and 10 monolayers, respectively — have been investigated using XRR and XRD in coplanar and non-coplanar grazing incidence geometry.

Experimental Details

Data were collected using a D8 DISCOVER Plus™ diffractometer (Figure 1) equipped with a copper tube operating at 40 kV and 40 mA. The setup included a focusing Goebel Mirror, a centric Eulerian cradle, and a LYNXEYE XE-T detector operating in 0D mode.

For the in-plane grazing incidence diffraction (IP-GID) measurements, axial Soller collimators were used in the primary and secondary beam path. With an angular acceptance of 0.5°, the Soller allow for high transmittance with reasonable resolution, making them perfectly suitable for measuring weak scattering signals. The XRR measurements were performed using 0.2 mm slits on the tube and detector sides to achieve the required angular resolution.

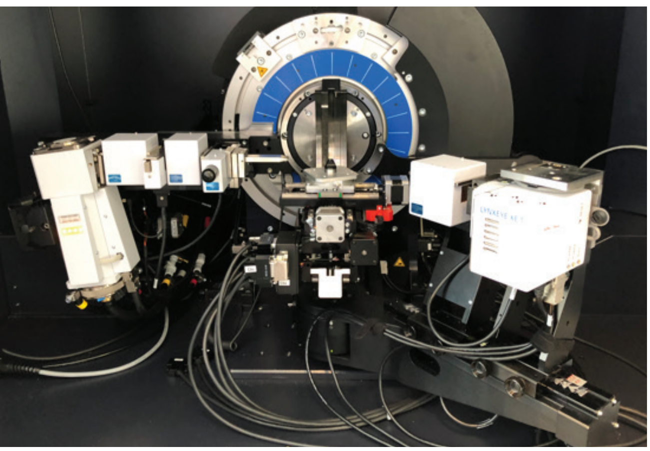

Figure 1

Instrumental setup for non-coplanar diffraction experiment.

Two samples were investigated during this study. They consist of a single monolayer (sample #1) and nominally 10 monolayers of WS_2 (sample #2) on sapphire substrates. XRR, GID, and IP-GID measurements were performed.

For IP-GID measurements, the 2θ range was 25° - 160° for sample #1 and 10° - 130° for sample #2. The measurement time per step was about 100 seconds, resulting in total measurement times of approximately 17 hours. GID measurements were performed from 5° - 130° 2θ with 50 seconds integration per angular step, resulting in a total measurement time of approximately 9 hours. However, a GID signal from the WS_2 film was only observed for sample #2.

To obtain the thickness of the WS_2 films, XRR measurements were executed. For the 10-monolayer film (sample #2), a 2θ range of 0° - 15° with a step size of 0.01° was measured within 12 minutes. For sample #1, the XRR curve was taken up to 30° 2θ. For both samples, the diffusely scattered background was measured in addition to obtain the true specular XRR signal. The respective measurements are depicted in Figures 3 and 4.

Results and Discussion

The IP-GID measurement from the single monolayer was analyzed by performing a full profile fit using DIFFRAC.TOPAS. This result is shown on Figure 2: A single phase of space group P63/mmc with the c-axis set to zero was used to simulate the WS_2 monolayer. No reflections with (00l) components were observed, and the in-plane lattice constant of (a = 3.149 Å) was found.

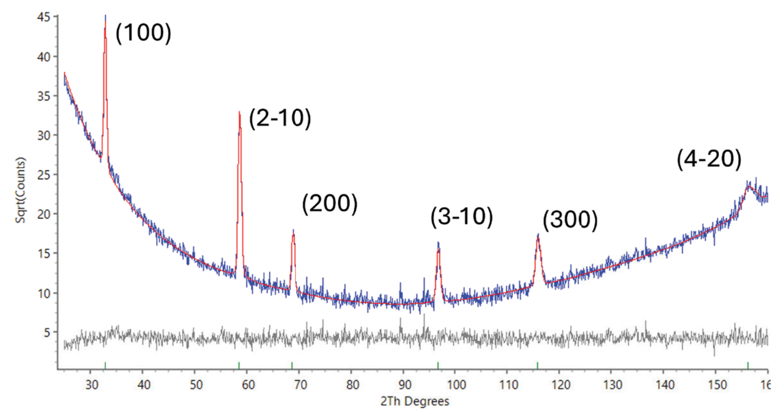

Figure 2

IP-GID measurement of the WS_2 monolayer along with DIFFRAC-TOPAS full profile fit.

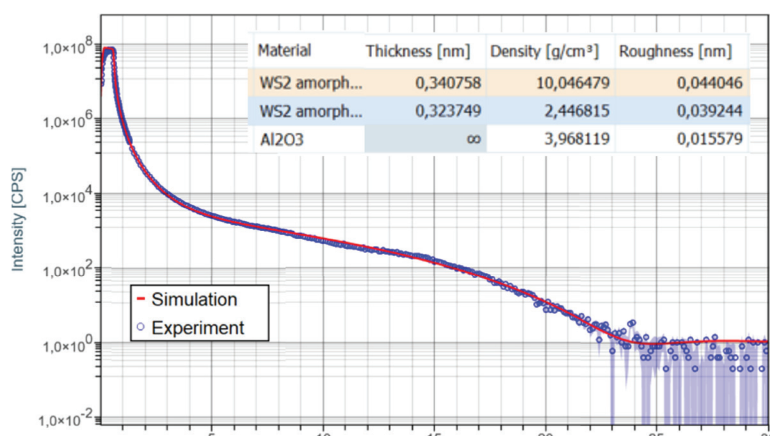

Figure 3

Analysis of XRR data from a single monolayer WS_2 using DIFFRAC.LEPTOS X.

Additionally, the absence of any reflections in the GID geometry (not shown here) confirms the missing c-axis of the layer and hence the sheet-like morphology of the WS_2 monolayer. From the analysis of the XRR measurement (Fig. 3) a film thickness of ~3.4 Å is obtained. To explain the long oscillation, an additional thin layer with lower electron density had to be added to the model.

For sample #2, the analysis of the XRR measurement (Fig. 4) revealed that the WS_2 film had a thickness of approximately 169.7 Å. Like for the WS_2 monolayer, a region of decreased electron density was found at the substrate. Without this additional region, both measured XRR curves cannot be sufficiently well fitted.

The Pawley fit of the GID measurement (Fig. 5) provides lattice constants of a = 3.084 Å and c = 12.830 Å, and the ~170 Å thickness would correspond to approximately 13 monolayers of WS_2. The measurement shows highly intense (002), (004), and (006) reflections, indicating a strong preferred orientation of the WS_2 film with a (001) fiber axis perpendicular to the surface.

The analysis of the IP-GID measurement (see Figure 6) is consistent: the (002) peak has very low intensity, and the other peaks belong to different lattice planes perpendicular to (001), evidencing a polycrystalline WS_2 film with no or very few preferred in-plane orientations. The fact that the lattice constants perpendicular to the surface are larger than those parallel to the surface indicates tensile strain inside the film. However, a more detailed analysis is not possible because only a few broad peaks are fitted against the large number of hkl from the hexagonal cell of WS_2.

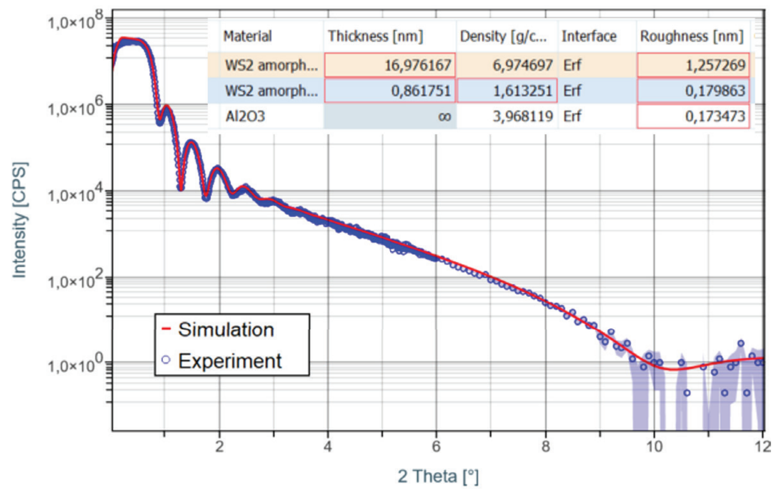

Figure 4
XRR analysis of sample#2 (nominal 10 monolayers of WS_2) using DIFFRAC.LEPTOS X.

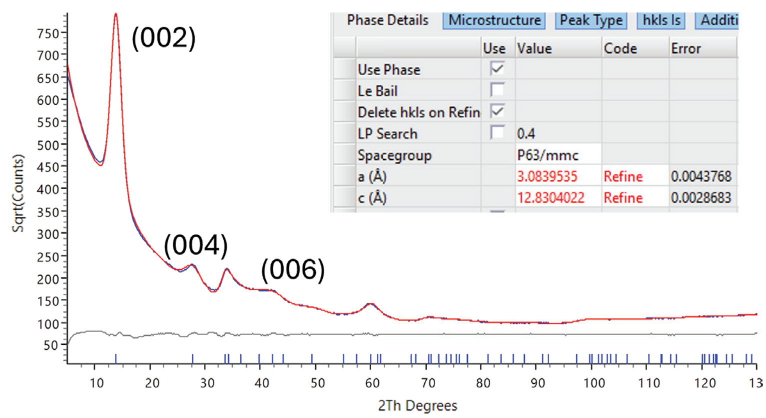

Figure 5
Pawley fit of the GID measurement from sample #2 using DIFFRAC.TOPAS.

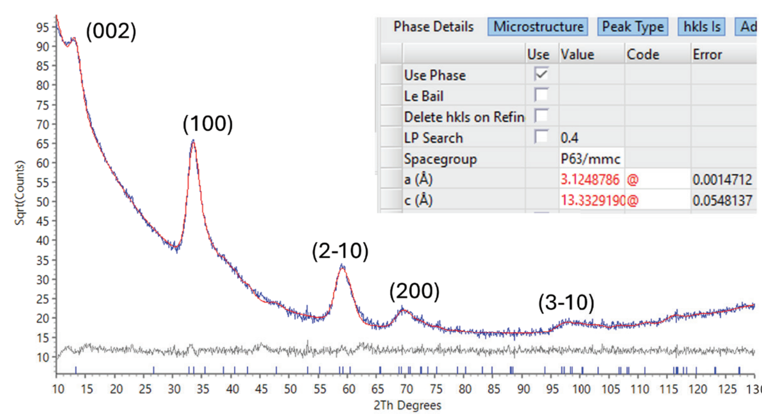

Figure 6
Pawley fit of the IP-GID measurement from sample#2 using DIFFRAC.TOPAS.

Summary and Conclusion

This application note reports the investigation two commercially[1] available samples with ultra-thin WS_2 films on sapphire substrates using a D8 DISCOVER Plus diffractometer. Data were taken in XRR, GID and IP-GID geometry and analyzed using DIFFRAC.LEPTOS X and DIFFRAC.TOPAS:

- For sample #1, GID and IP-GID data confirmed the presence of a single 2-dimensional WS_2 monolayer with a lattice parameter of a = 3.149 Å and a thickness of 3.4 Å obtained from XRR data. The fact that a clear signal from the WS_2 monolayer was obtained demonstrates the outstanding performance of IP-GID in the analysis of thin films.

- For sample #2, the analysis of the XRR data revealed a film thickness of 169.7 Å, corresponding to 13 monolayers with c = 12.830 Å. From the GID and IP-GID data, a pronounced fiber texture with the c-axis perpendicular to the surface was found. The anisotropic lattice parameters parallel and perpendicular to the surface indicate that the film is under tensile strain.

Author: Dr. Fernando Rinaldi and Dr. Martin Zimmermann

[1] WS_2 / Al_2O_3 samples are commercially available from https://2dsemiconductors.com
[2] For properties of WS_2 monolayers see https://c2db.fysik.dtu.dk/material/1WS2-1

Bruker AXS
info.baxs@bruker.com

bruker.com

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