APPLICATION NOTE

Multi-technique surface analysis for structural and chemical characterization of 2D materials

Abstract

The Thermo Scientific™ Nexsa™ Surface Analysis System was used to chemically locate boron nitride (BN) flakes directly grown onto Cu foil using chemical vapor deposition. By using XPS SnapMap, the location of the flakes was quickly found. XPS spectroscopy could then be used to deliver chemical fingerprinting. Using co-incident Raman spectroscopy, the crystal lattice structure is confirmed to be hexagonal.

Introduction

Two-dimensional (2D) materials such as graphene, hexagonal boron nitride, transition metal dichalcogenides, MXenes etc are currently at the forefront of materials research as they offer pathways to new technology, especially electronics.[1] These compounds allow scientists and researchers to create a new library of materials by forming heterostructures of atomic layerthick materials, enabling the creation of tailored properties for specific applications.[1,2] But the development and production of this new class of materials also requires advancement in the technologies to characterise such atomic-layer thick materials precisely. The Nexsa Surface Analysis System uniquely integrates XPS with Raman spectroscopy that can be used to probe the identity, crystallinity, impurity, stress/strainor thickness of a 2D material. With both techniques being co-incident, allowing analysis to be collected from the same position, the result is a more comprehensive analysis of the sample from one versatile instrument.

Nexsa Surface Analysis System.

In this application note, we demonstrate how easily the boron nitride flakes, which are present on the substrate surface at discrete locations, can be found using XPS SnapMap technology using he Nexsa Surface Analysis System. A detailed chemical composition map can be acquired within minutes over the whole substrate that allows quick identification of the 2D flakes. Raman spectra can then be acquired at the regions of interest to study the crystal structure, or stress or strain in the 2D material. XPS and Raman spectroscopy are both quick and non-destructive tools, and a combination of both in one instrument allows the user to obtain the chemical information as well as the molecular structure simultaneously, without having to move the samples between different instruments, with the attendant difficulty in finding the same locations.

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Experiment and results

XPS SnapMap was used to identify the position of BN flakes present on the Cu foil as shown in Figure 1a. Since the peak sensitivity for N1s is much higher than B1s, the whole surface of the sample was mapped for the N1s. The total intensity of the N1s peak across the sample is shown in Figure 1b revealing the presence of nitrogen allover the Cu substrate. A detailed chemical state analysisof the N1s map using the Thermo Scientific™ Avantage™ Software (included with all XPS instruments) revealed that nitrogen was present in two chemical states, organic nitrogen and nitride. The chemical statemap and the average XPS spectra from the two chemical states of N1s is shown in Figure 1c and 1d.

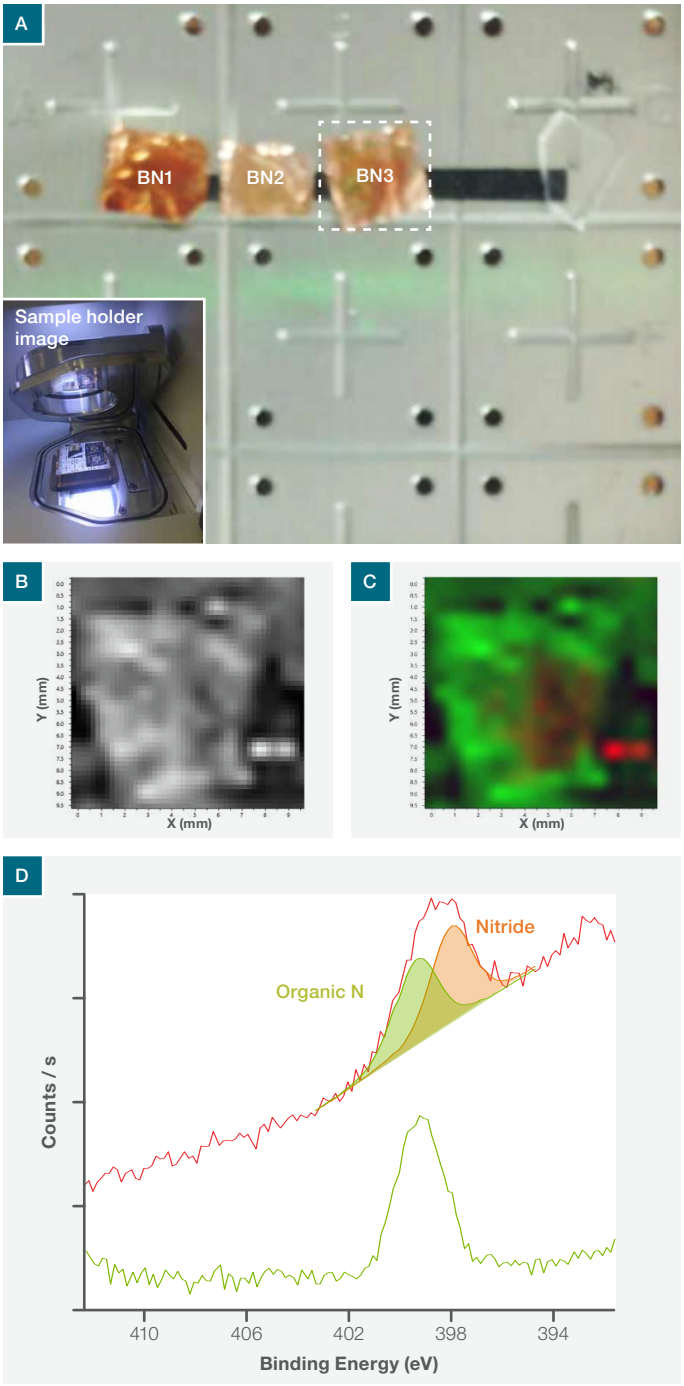

Figure 1: (a) Nexsa Surface Analysis System optical image of the whole sample platter (inset shows the sample holder in loading position), (b) N1s intensity map across whole of the sample (c) chemical state N1s intensity map and (d) N1s average spectra from the green and red regions on map.

A 30 µm X-ray spot size was then used to generate a N1s SnapMap image, of the magnified area as shown in the optical image from the system camera in Figure 2a. This corresponds to the area where nitride was seen in the low resolution N1s image. Each pixel in the SnapMap image has a corresponding spectrum which allows the user to process the data in the same way as that of a conventional XPS spectra, yielding the same chemical state information, and so displaying its distribution across the surface. Figure 2b shows the SnapMap of N1s revealing the presence of organic nitrogen (green region) and nitride (red region). A survey spectrum at the selected points (P1 and P2) in Figure 2b reveals the presence of boron contribution (B1s) only from thered region and not from the green region as shown in Figure 2c. The XPS imaging has therefore confirmed the presence and location of BN flakes.

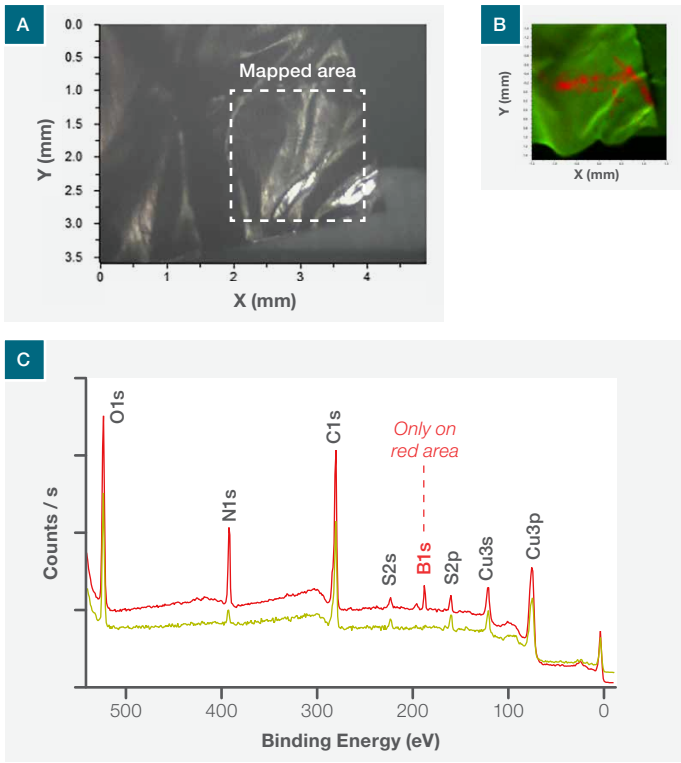

Figure 2: (a) Optical image of the sample from one of the three Nexsa Surface Analysis System cameras, (b) N1s nitride XPS SnapMap image of the mapped area and (c) XPS survey spectra at the points P1 and P2 shown in (b).

High-resolution spectra of B1s and N1s were then acquired to allow the determination of chemical states of the BN flake. The B1s spectrum (Figure 3a) shows the presence of inorganic chloride contamination in addition to peaks due to boron oxynitride and boron nitride. The N1s spectrum (Figure 3b) also shows the contribution from the oxynitride in addition to nitride, confirming the flakes were oxidised.

BN exists in two different polytypes, the sp^2 bonded hexagonal and rhombohedral phase and sp^3 bonded cubic and wurtzite phase. Cubic BN belongs to a zinc blende type structure and the Raman active TO phonon is at 1055 cm^{-1} and and the LO phonon at 1304 cm^{-1}.[1,3].

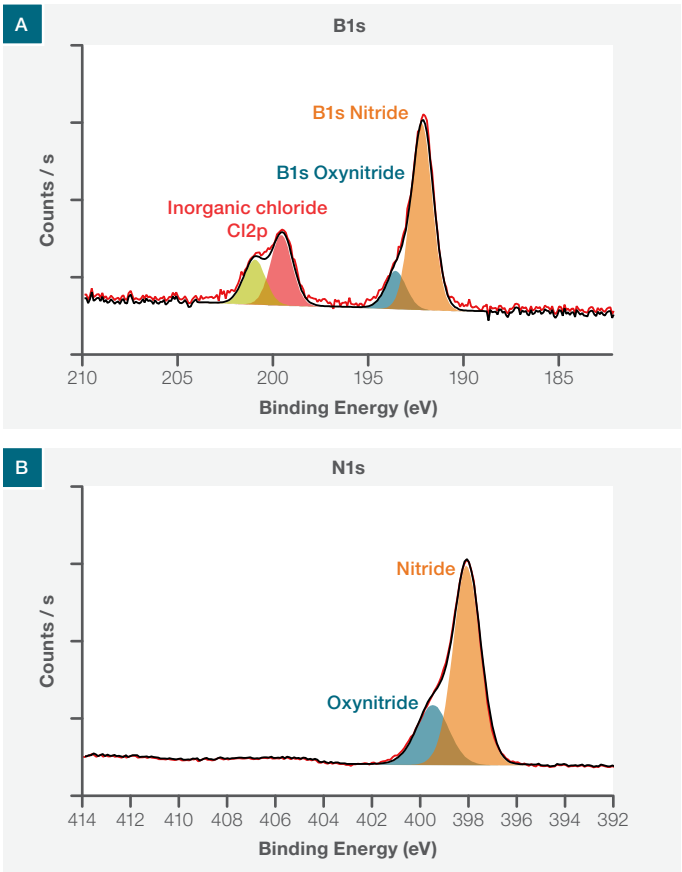

Figure 3: High-resolution deconvoluted XPS spectra of B1s (a) and N1s (b) taken at point P1 showing different chemical states.

In contrast, for hexagonal BN the Raman active high energy phonon E_{2g} is at 1366 cm^{-1}.[1,3] Therefore, Raman spectroscopy can be used to assess the structure of the material in contrast to XPS, which gives the chemical fingerprint. Figure 4 shows the Raman spectrum at the same point P1 (in Figure 2b) showing the presence of the E_{2g} phonon mode at 1366 cm^{-1}, confirming that the BN flakes on the sample are a hexagonal phase.

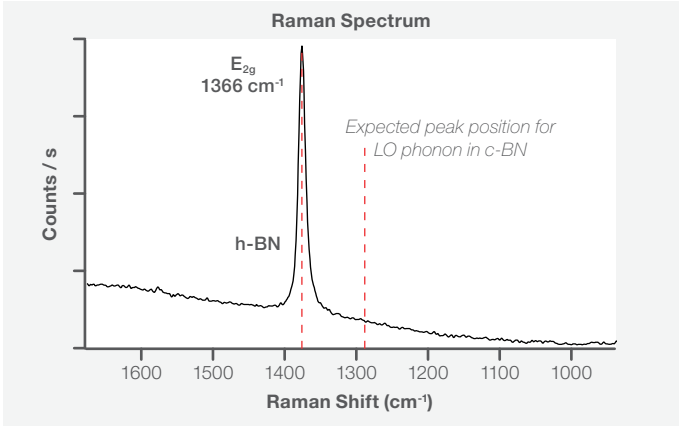

Figure 4: Raman spectra at point P1 using 532 nm laser line.

Conclusion

We have presented an in-depth chemical and structural study on the BN flakes that were located randomly on a copper foil substrate. Our measurements show how a user can chemically locate the discrete nanofeatures using the XPS SnapMap method, determine the chemistry from high-resolution XPS data, and determine the structure and Raman spectral features simultaneously using the Nexsa Surface Analysis System.

References

1. Novoselov, K. S., Jiang, D., Schedin, F., Booth, T. J., Khotkevich, V. V., Morozov, S. V., & Geim, A. K. (2005).Two-dimensional atomic crystals. Proceedings of the National Academy of Sciences, 102(30), 10451-10453.
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3. Reich, S., Ferrari, A. C., Arenal, R., Loiseau, A., Bello, I., & Robertson, J. (2005). Resonant Raman scattering incubic and hexagonal boron nitride. Physical Review B, 71(20), 205201.

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Notes

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