KRATOS ANALYTICAL
A SHIMADZU GROUP COMPANY

Applications Note

Building the energy level diagram of a 2D material using coincident UPS and IPES

MO464(A)

Keywords MoS_2, IPES, UPS, 2D materials, GCIS.

Overview

MoS_2 studied using UPS and IPES.

Introduction

Novel materials – in particular 2D materials – are becoming increasingly relevant in state of the art device development. The expanding interest in transition-metal dichalcogenides stems from their wide variety of applications, ranging from batteries to electronic devices. Indeed, by adjusting either their chemical composition or the number of layers, one can tune their electronic, vibrational and magnetic properties in a manner irreproducible by other two-dimensional and layered materials. Understanding the nature of the electronic configuration and properties of these materials is important for their development. Conventional methods to analyse 3D materials struggle to determine the properties for ultra-thin films, and these thin layers are what exhibit the revolutionary properties. Using a combination of the surface sensitive techniques Inverse Photoelectron Spectroscopy (IPES) and Ultraviolet Photoelectron Spectroscopy (UPS), however, we demonstrate how the analyst can obtain information on the nature of the electronic properties for single and multi-layer stacks. In this example the properties of a thin layer of MoS_2 are investigated. Bulk MoS_2 is a diamagnetic, indirect bandgap semiconductor similar to silicon, with a bandgap of ~1.2 eV. However, with reduced thickness the bandgap increases [1,2], with a confinement-induced shift of the indirect gap from the bulk value. Thickness/growth control is therefore critical to the performance of this material in next-generation devices.

Experimental

Mineral-based MoS_2 was exfoliated before introduction into the AXIS Supra$^+$ to produce a fresh surface. Unfortunately, even a limited amount of air exposure leads to adsorption of adventitious carbon which can obscure the results, as the sampling depth of both techniques is so shallow. Unlike graphene from graphite, MoS_2 exfoliation has been shown not to produce single layers. It is nonetheless illustrative of what is possible with these experiments. The analysis positions set up for XPS, UPS and IPES techniques are coincident on the sample in the AXIS Supra$^+$ analysis chamber.

Results and Discussion

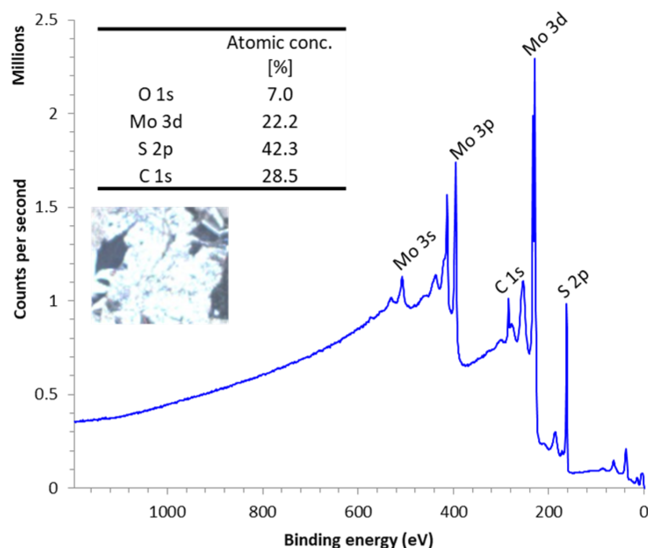

Figure 1: XPS survey spectrum of as-received exfoliated MoS_2. (Insert – atomic concentration and optical image of sample).

Even with the efficient sample preparation and rapid pump-down of the flexi-lock, adventitious carbon was still observed via XPS analysis (~18 at.%), and it is all confined to the top surface (Figure 1). In order to remove these adsorbates, the sample was sputtered lightly with Argon cluster ions – this technique has the advantage of removing lightly held species without etching the surface below. No sputter reduction of Mo to the metallic state was observed for the Mo 3d peak and no reduction in the sulphur content (Figures 2 and 3). This method is also relatively quick – after 20 s of etching the C content had decreased by 82 %. After a further 280 s, no C was visible in the high-sensitivity survey spectrum. For comparison, the Mo:S ratio from conventional sputter cleaning is shown which reveals a change in the expected stoichiometry of 1:2.

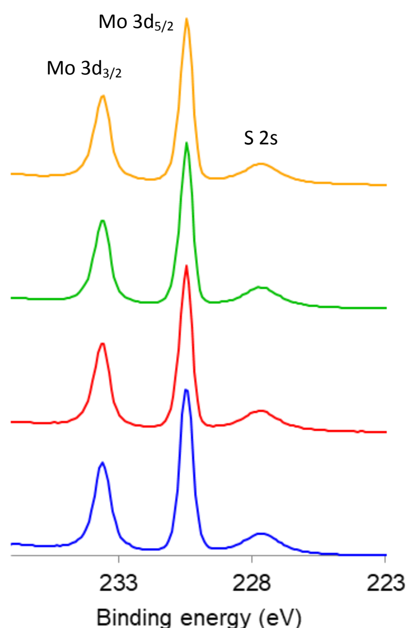

Figure 2: Mo 3d spectra for the sample sputter etched - BLUE (0s), RED (20s), GREEN (100s) and YELLOW (300s).

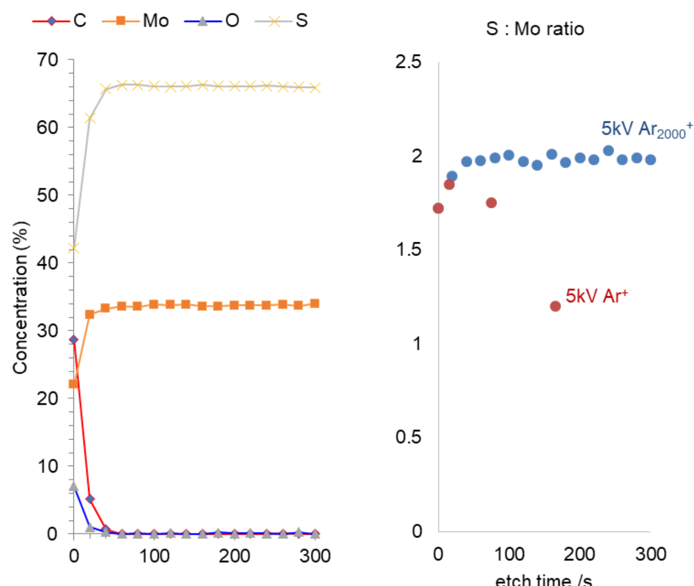

Figure 3: LEFT: atomic concentration of surface species vs etch time. RIGHT: ratio of S:Mo.

Once cluster cleaned, the surface was then ready for the analysis of the uppermost occupied valence states using UPS. The minimal energy state in the conduction band was analysed using IPES. Figure 4 shows a combined Density of States (DOS) spectrum as revealed by the two techniques, showing the difference between the occupied and unoccupied electronic states of the material.

The peaks present in the UPS portion of the spectrum represent the occupied valence levels of A_1', A_2'', E'', E' and A_1' in decreasing energy with respect to the Fermi level [3]. These bonding and anti-bonding states are filled from the Mo 5p, 5s and 4d orbitals and S 3p and 3s orbitals.

The IPES section (the portion above the Fermi level) represents the lowest possible states to be occupied post excitation. The peak at 2.3 eV corresponds to the lowest unoccupied bonding orbital of E'. The edges of the HOMO and LUMO peaks were determined via linear extrapolation after the application of an arbitrary smooth background (not shown for clarity). These positions represent the threshold ionisation energy, I_s (-1.2 eV) and conduction band edge, CB (0.2 eV). The difference between these two values determines the band gap (or transport energy gap) of the surface – in this case 1.4 eV (±0.2 eV), slightly higher than the literature values for bulk MoS_2. By measuring the onset energy (using UPS) it was possible to determine the work function of the surface as 4.5 eV. The electronic work function is acquired spectroscopically by measuring the difference between the Fermi Level and the cut-off of the 'tail' at the low kinetic energy end of the spectrum (a.k.a. spectrum width) and subtracting this value from the incident photon energy. The difference between the electron affinity, E_a and ionisation energy, I_E can also be determined allowing for the creation of a full energy level diagram for the surface material.

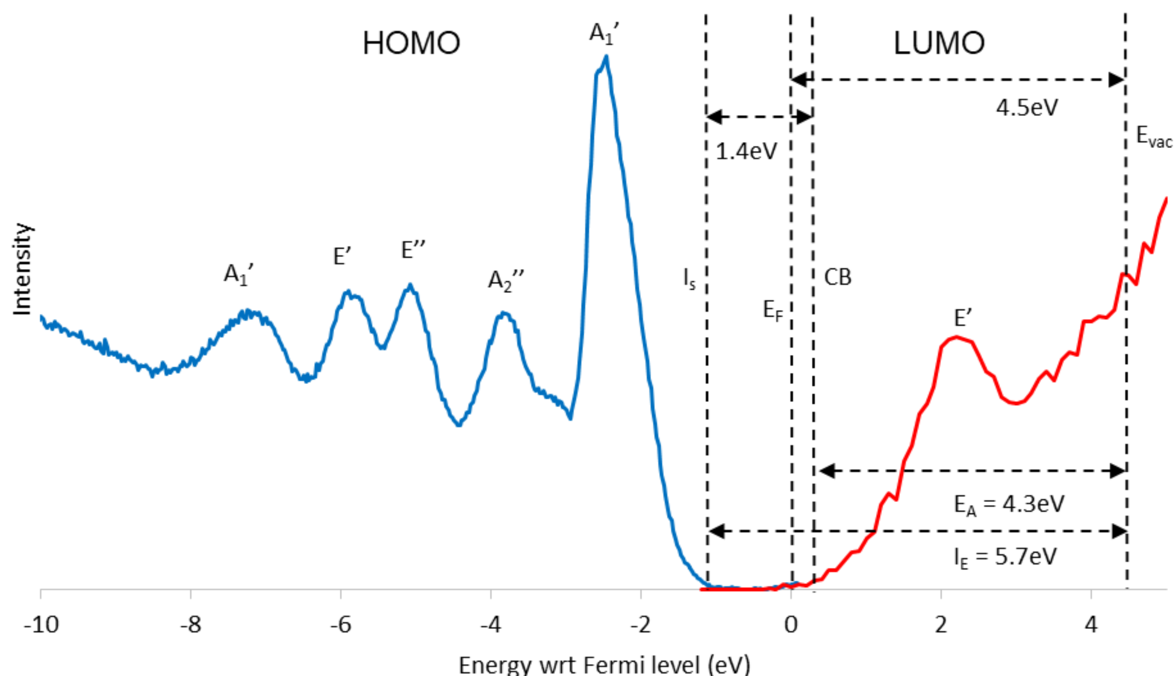

Figure 4: UPS-IPES combined spectra. RED (IPES), BLUE (UPS). The zero energy corresponds to the Fermi level (E_F).

Conclusions

This combination of spectroscopic techniques provides us with a complete picture of the frontier energy levels on either side of the transport energy gap. We can determine the electronic structure, the band gap, work function, electron affinity and ionisation energy at the surface of an analysed material – particularly the uppermost atomic layer(s), which is the bulk of a 2D material.

Acknowledgements

Many thanks to Chris Moffitt, Teddy Salim and Hao Lu for discussion, thoughts and insight.

References

[1] T. F. Heinz *et al.*, DOI:1004.0546.

[2] P. D. Fleischer, ASLE Trans. 1984, 27, 82–88.

[3] Pike, Nicholas & Van Troeye, Benoit & Dewandre, Antoine & Petretto, Guido & Gonze, X. & Rignanese, G.-M & Verstraete, Matthieu, 2017, Physical Review B. **95.** DOI:10.1103/PhysRevB.95.201106.

Related documents online:

MO460 Sample Rotation during Depth Profiling

MO459 Valence-Level Photoelectron Spectroscopy of MoS_2

MO457 A Multi-Technique Characterization of Polymer Materials with XPS, UPS and REELS

KRATOS ANALYTICAL
A SHIMADZU GROUP COMPANY
ISO 9001

Wharfside, Trafford Wharf Road, Manchester M17 1GP

Phone: +44 161 888 4400 Fax. +44 161 888 4402

www.kratos.com

Kratos Analytical Ltd, a wholly owned subsidiary of Shimadzu Corporation, has been manufacturing surface analysis instruments for over five decades. Throughout this period Kratos has continued to lead the development of new technologies relating to X-ray photoelectron spectrometers and associated accessories for surface and materials characterisation. All Kratos Analytical products are designed, assembled and supported from our headquarters in Manchester, UK.

Kratos Analytical Ltd has a policy of continuous product development and improvement and therefore reserves the right to make changes to specifications without notice.

© Copyright April 2020