Valence-level photoelectron spectroscopy of MoS$_2$

Overview

Valence level photoelectron spectra (VLPS) were acquired for the material MoS$_2$ using soft X-ray and deep UV photon energies. VLPS were acquired for both as-received and Argon cluster cleaned surfaces.

Introduction

There has been significant interest in 2D materials, and in particular MoS$_2$, due to the unique properties caused by the reduction in the dimensionality. They are often well-suited to applications where the bulk material would be unsuitable. Such promising applications include transistors, sensors, electrodes, topological insulators and valleytronics.

Here we perform surface analysis studies of exfoliated MoS$_2$ thin films to gain further insight into the nature of the surface and the bonding environment.

Despite efforts to limit the time between exfoliation and introduction into the AXIS Supra sample introduction chamber, the XPS survey spectra clearly showed the presence of residual carbon (17.2%) on the surface due to the adsorption of short chain hydrocarbons from the atmosphere. These adsorbates are obviously accumulated directly on top of the MoS$_2$ surface. Assuming even coverage this equates to ~1.5nm of adsorbed material[1].
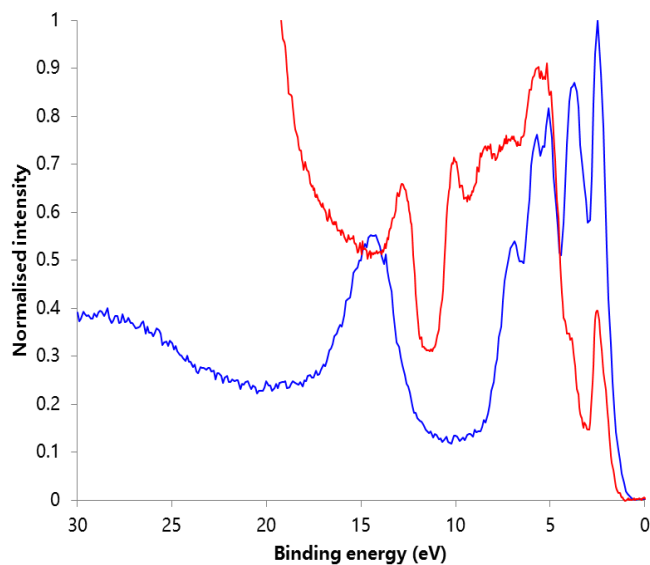
Figure 1 shows the valence level spectra for the fresh surface,

Figure 1: VLPS fo MoS2 — XPS (blue) HeII UPS (red).

analysed using both Al Kα (1486.6eV) and HeII (40.2eV) photon energies. These spectra Indicate the density of states of the valence band throughout the Brillouin zone.

There are significant differences between the spectra acquired with different energies. Several reasons may account for the difference.

Firstly, there will be a variation in photoemission cross-section. Cross-section variations with photon (excitation) energy differ according to which orbitals of MoS_2 are contributing to the initial state that corresponds to the observed peak. For example, peaks derived primarily from Mo 4d orbitals exhibit a phenomenon known as a Cooper minimum (CM). The CM is manifested as a minimum in the relative intensities of such peaks as the excitation energy passes through a particular range.

Secondly, there is a significant difference in sampling depth due to the difference in kinetic energies of the excited electrons. Using Al Kα X-rays the sampling depth across the valence region is practically the same as there is only a 4.6eV (~1%) difference in kinetic energy. For HeII the difference in sampling depth will be more pronounced. The kinetic energies of the UV excited electrons is also significantly lower than those from XPS and therefore much more surface sensitive. This results in the spectroscopic technique being much more surface sensitive and therefore more sensitive to subtle changes including contamination.
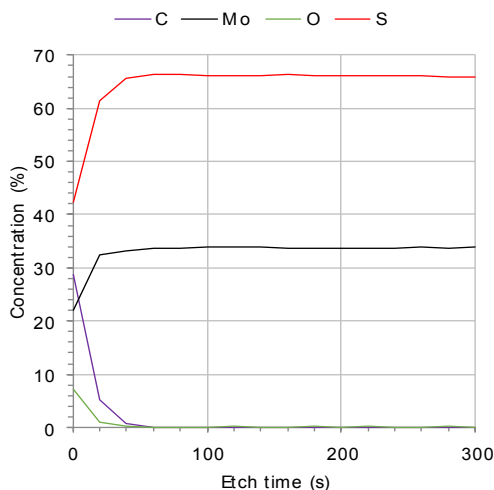
Figure 3: HeII UPS (LEFT) and XPS spectra (RIGHT) acquired after 5kV Ar$_{2000}^{+}$ etching for 0s (blue), 20s (red) 100s (green) and 300s (yellow).

gesting that no preferential sputtering and formation of Sulfur vacancies has occurred during sputtering.

Both XPS and UPS spectra were acquired as part of an automated depth profile with sampled spectra shown in figure 3. Here we can see after the first 20 second etch a dramatic change in the HeII UPS spectra, acquiring the form and peak positions similar to those of the XPS valence band spectra. After the removal of the Carbon no further changes in spectral form were seen.

Conclusions

Here we have analysed exfoliated MoS_2 surfaces with different photon energies to examine the effects of energy source and surface contamination. We see that HeII UPS is much more sensitive to surface contamination (and damage) than traditional valence band XPS.

Acknowledgments

Many thanks to Dr Teddy Salim and Dr Yongmin He of NTU Singapore for help and invaluable discussion on this topic.

References

1. P. J. Cumpson, https://doi.org/10.1002/1096-9918(200006) 29:6<403::AID-SIA884>3.0.CO;2-8

Figure 2: 5kV Ar$_{2000}^{+}$ depth profile.

To explore this effect further the surface was ion etched (figure 2) with 5kV Ar$_{2000}^{+}$ cluster ions to remove the surface contamination. Post etching, high resolution spectra indicated <1% carbon present. No changes in Mo3d peak shape were observed sug-

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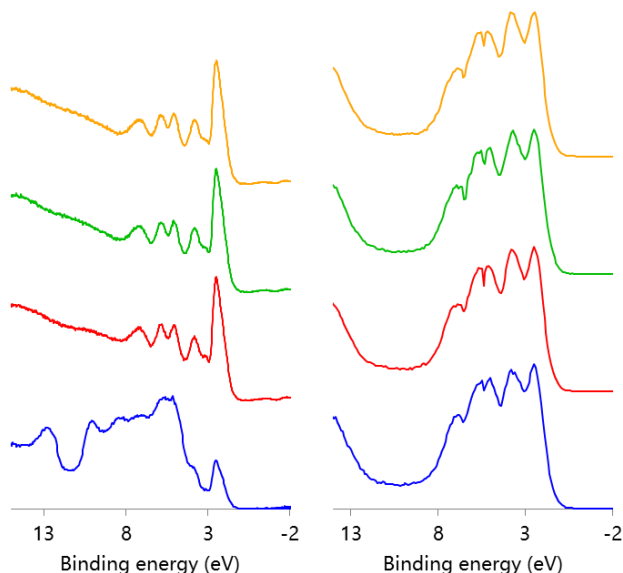MO436 Combined Argon cluster UPS-XPS depth profile of OLED thin-film