Applications Note

XPS and UPS Characterization of a Hybrid PbBr Perovskite Material with Work Function Measurement

Overview

UPS analysis of (semi)conducting samples allows the measurement of the work function of a material. Combined with XPS, this is a powerful combination of techniques to gain information about the valence structure of the surface. Here, a thin film, hybrid organic-inorganic lead bromide perovskite is analysed using a Kratos AXIS spectrometer. A comparison of the data is made after the removal of adventitious carbon with the Gas Cluster Ion Source (GCIS) to interpret how the work function of the material is affected.

Introduction

Hybrid organic-inorganic lead halide materials have shown great potential for application in photovoltaics and opto-electronics as a result of their layered thin film structural assemblies and semiconductor properties.[1, 2] Recent work has reported their ability to undergo switchable dielectric behaviour making them of significant interest in solar cell preparation. The investigation reported in this application note examines a thin film perovskite material, $CH_3NH_3PbBr_3$, to explore its interesting surface structure. Using a combination of X-ray Photoelectron Spectroscopy (XPS) and Ultraviolet Photoelectron Spectroscopy (UPS), it is possible to probe the valence band of this material and gain an insight into the influence of the surface structure on its semiconducting properties.

As the valence band of a material is filled with electrons up to the Fermi level, the energy difference between the Fermi and vacuum level is known as the work function. This is a measure of the energy required to remove an electron from the material and can be determined by He I UPS, which gives information about the bonding electrons at the surface.

Removing the adventitious carbon overlayer of a material has a large effect on the UPS data as UPS has a shallow sampling depth of up to 3 nm. It is possible to remove this carbon contamination using the Gas Cluster Ion Source (GCIS) without damaging the material itself, so one can then analyse the valence band without interference from adventitious carbon. This will also effect the work function measurement from the UPS data as the work function of a material is strongly influenced by the condition of the surface. The overall effect on these hybrid lead halide materials is seen during the study presented here.

Experimental

A hybrid organic-inorganic lead bromide perovskite material, $CH_3NH_3PbBr_3$, was analysed using the state-of-the-art, multi-technique Kratos AXIS spectrometer, fitted with a UPS lamp and GCIS. Survey spectra were acquired over a large energy range of 0 to 1350 eV, whilst high resolution XPS spectra were acquired over a small energy range for each particular region.

He I UPS data was acquired with a photon energy of 21.22 eV to analyse the low binding energy electrons. This makes UPS a more surface sensitive technique than XPS with an information depth of up to 3 nm (the sampling depth of XPS is typically quoted to be 10 nm), and allows the valence structure of a material to be examined.

The multi-mode GCIS was used to gently remove adventitious carbon. It is designed to operate in both monatomic Ar^+ and cluster Ar_n^+ modes, making it suitable for sputter cleaning and depth profiling different materials. Through a combination of cluster size and acceleration voltage, a broad range of materials may be sputter cleaned or depth profiled without chemical damage to the surface. The cluster mode used for cleaning these samples was 5 keV Ar_{2000}^+, which provides a low etch rate for gentle sputter cleaning and removal of adventitious carbon.

Results and Discussion

A survey spectrum of the organic semiconductor material revealed the sample composition was as expected. A high resolution spectrum of the Pb 4f region was acquired, as seen in Figure 1, where the $4f_{5/2}$ peak has been fitted with components. This reveals two chemical states, predominantly $PbBr_3$, as expected.
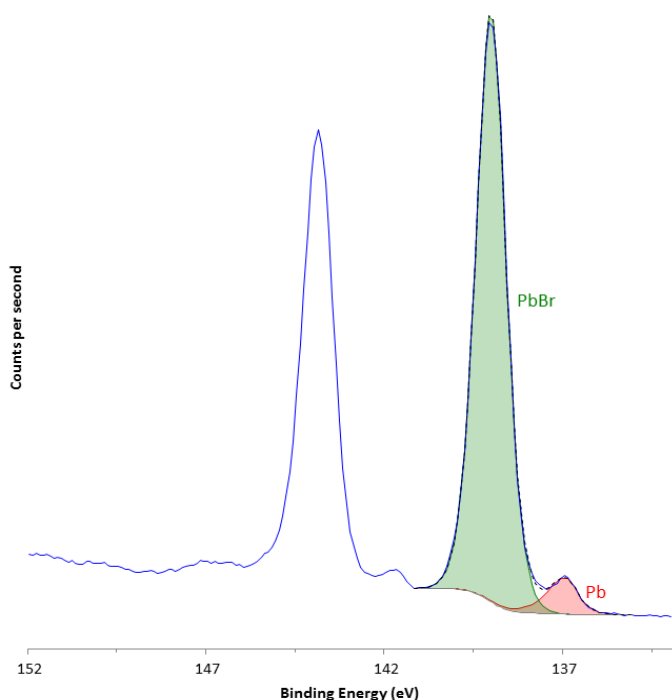

Figure 1. XPS Pb 4f spectrum of the material, as received, showing two chemical states of Pb.

He I UPS data for the hybrid $PbBr_3$ perovskite sample was acquired to determine the work function of this semiconductor material. UPS uses a lower photon energy than the conventional Al $K\alpha$ XPS source and therefore can only excite the low binding energy valence electrons. Due to the lower kinetic energy of the photoelectrons excited with the He I radiation relative to the Al $K\alpha$ X-rays, UPS is a more surface sensitive technique.

The work function of a conducting material can be determining from a UPS spectrum using the following equation,
$\phi = h\nu - E_0 - E_F$ (equation 1)
where ϕ is the work function, **$h\nu$** is the source energy (21.22 eV for He I photons), **E_0** is the secondary electron cut off (measured to be 17.35 eV binding energy) and **E_F** is the Fermi energy (measured to be 0.05 eV binding energy).
Figure 2 shows the He I UPS spectrum for the hybrid $PbBr_3$ semiconductor sample which was used to measure a work function of **ϕ = 3.82 eV**.
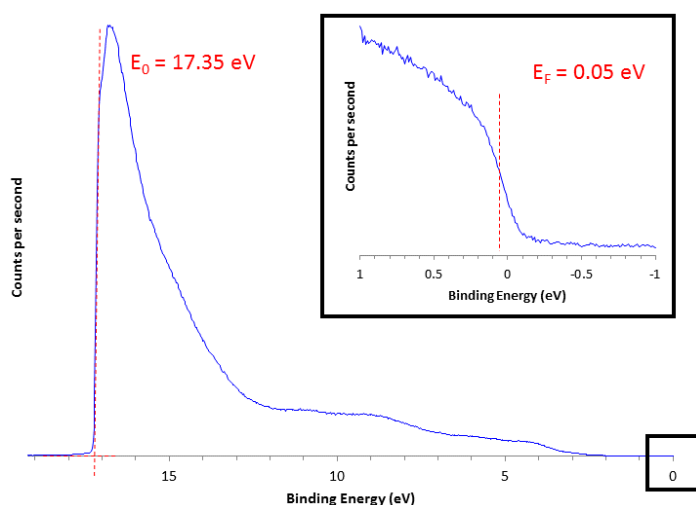

Figure 2. He I UPS spectrum used to calculate the work function of the material, where the insert reveals a zoomed-in region of the Fermi edge. The E_0 and E_F energies are highlighted in red.

The work function of a material is strongly influenced by the condition of the surface. The presence of contamination or a reaction which has occurred at the surface, such as oxidation, can have a large effect on the work function measured. Substantial shifts in the work function are commonly seen for metals and semiconductors as changes to the topmost layer results in the formation of electric dipoles at the surface, in turn changing the energy an electron needs to leave the sample.[3]

To analyse the extent of contamination on this $PbBr_3$ sample, it was gently cleaned to remove the adventitious carbon, using the 5 keV Ar_{2000}^+ GCIS mode, before characterization. This caused no damage to the surface structure, but did result in a change in the He I UPS spectrum and an increase in the work function of the material from **3.82 eV** to **3.99 eV**.

Figure 3 shows the He I UPS spectrum after removal of adventitious carbon. The work function is again determined using equation 1, where for the sputter cleaned sample, E_0 = 17.17 eV binding energy and E_F = 0.06 eV binding energy such that the work function of the sputter cleaned material is **ϕ = 3.99 eV**.
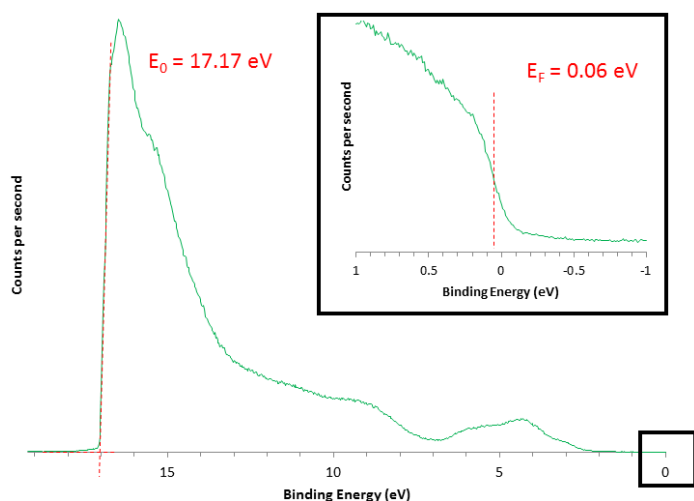
Figure 3. He I UPS spectrum used to calculate the work function of the material after removal of adventitious carbon with the GCIS, where the insert reveals a zoomed-in region of the Fermi edge. The E_0 and E_F energies are highlighted in red

The work function is a measure of the energy required to remove an electron from the Fermi level into vacuum. This increase in work function must therefore be attributed to a higher energy now required to remove an electron, a result of the removal of adventitious carbon. The thin film must have an increased stability and therefore it is harder to remove an electron from the Fermi level.
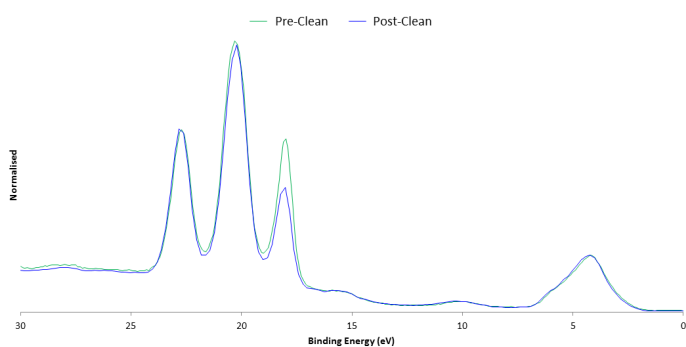

Figure 4. A comparison of the XPS VB spectra before (blue) and after (green) removal of adventitious carbon with the GCIS.

This is also supported by the change in the Valence Band (VB) electronic structure, which is represented by the comparison of the XPS VB spectra in Figure 4. The VB region provides the fingerprint of a material, which contains information about the bonding electrons. As the appearance of this spectra looks different before and after the removal of adventitious carbon, this agrees with there being a change in the uppermost surface bonding electrons of the material, as seen with UPS.

Conclusions

Hybrid organic-inorganic lead halide perovskites have great potential as materials in the preparation of solar cells. Analysis of one of these thin film materials, $CH_3NH_3PbBr_3$, with XPS and UPS allowed the characterization of the surface structure and measurement of its work function, which was found to be **3.82 eV**. The surface was gently cleaned with the GCIS to remove adventitious carbon and the surface was reanalysed for comparison. The removal of this carbon contamination resulted in an increase in the work function of the material to **3.99 eV**.

Acknowledgements

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References

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