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

Keywords
XPS, UPS, GCIS,
Argon cluster, OLED, TCTA

Application Note MO436(0)
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Overview

Low-energy argon cluster ions were used to depth profile through an organo-electronic (TCTA) thin-film deposited on ITO. XPS and UPS spectra were acquired after each etching cycle. Compositional changes were seen through the film and at the interface with the substrate. Changes in UPS spectra were directly compared to changes in compositional change.

Introduction

Organic light emitting diodes (OLEDs) have attracted tremendous attention due to their promising applications in flat-panel displays and solid state lighting. They are composed of an organic material which emits light in response to an electric current, situated between two electrodes; one of which is usually transparent. The compositional chemistry of this organic thin-film and it's the chemical characteristic at the interface with the electrodes is fundamental to the OLED's performance. Here we will look at the change in composition of an OLED layer deposited on indium-tin oxide. The novel material doped-tris(4-carbazoyl-9-ylphenyl)amine was deposited on ITO to a thickness of ~150nm as characterised by ellipsometry.

Depth profiling was performed using the gas-cluster ion source (GCIS) in cluster mode. Argon clusters are now routinely used instead of monatomic argon to limit surface damage of delicate organic analytes [1]. XP spectra were acquired before and after each etch cycle to see quantitative changes regarding the elemental and chemical state of the surface. Work function and HOMO electronic states of the material were investigated concurrently using UPS.

For modern analytics it is preferable to perform more than one analytical technique on a sample to aid direct comparison of data and to negate the variables of sample handling and treatment. Using the automated methods on the AXIS Supra it is possible to create a multi-technique experiment without intervention during acquisition. Here we demonstrate the capability by depth profiling an OLED device acquiring both XPS and UPS data sequentially without manual intervention or gas handling.

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Results

After introduction into the analysis chamber of the AXIS Supra, the XPS/UPS/GCIS depth profiling method was selected in the software. XPS and UPS spectra were acquired before and between each etch cycle. For this sample the etch conditions were chosen as 5 kV Ar_{1000}^+, typical for delicate polymer materials. Survey spectra were acquired from which a relative depth profile was obtained (figure 1). Here we can see an initial change in surface concentration of N, O and C after the first etch then the concentration of the component elements remaining steady-state throughout the bulk of the material. At the interface a rapid decrease in organic elements is seen and a corresponding increase in indium and tin from the substrate material. The composition evolved to the expected stoichiometric ratio of ITO. With this multimodal method it is possible to directly compare UPS spectral structure with the surface composition and relative depth into the film. In figure 2 we can see the evolution of the HOMO states of the surface as a function of etching – the spectra are offset for clarity with the virgin non-etched surface the lowest vertically. After the first etch cycle there is a slight change with 3 distinct features at 9.25 eV, 6.93 eV and 4.01 eV indicating different densities of states for the OLED material. These features remain constant until the interface is reached where there is a rapid change in distribution. The two higher energy features decrease in intensity with a marked increase in the gradient of slope down to the HOMO edge point. This change maintains constant into the ITO substrate. Figure 3 shows the change in on-set of photoemission with each etch cycle. Initially a KE of 4.35 eV was recorded for the surface, after the first etch cycle this decreased to 4.26 eV, decreasing slightly after each cycle. At the interface the value decreased to 3.9 eV for the bulk ITO.

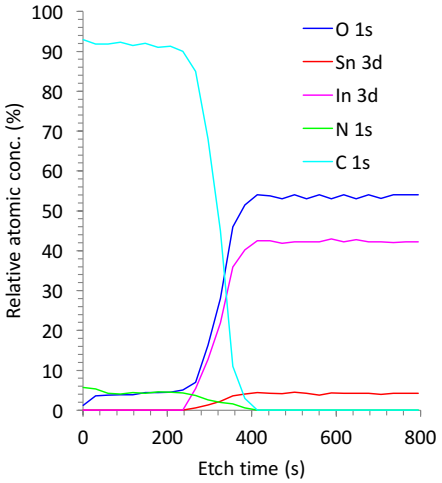

Figure 1: 5kV Ar_{1000}^+ depth profile of thin-film.

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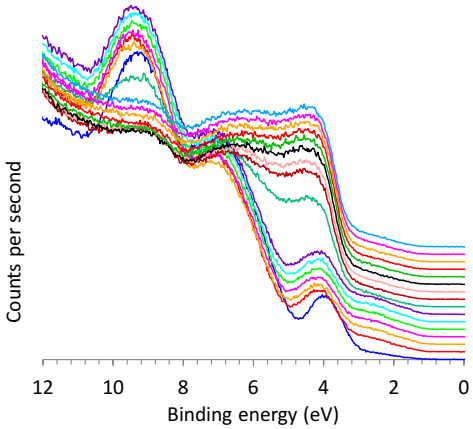

Figure 2: HOMO region of thin film (spectra are offset vertically with etch cycle).

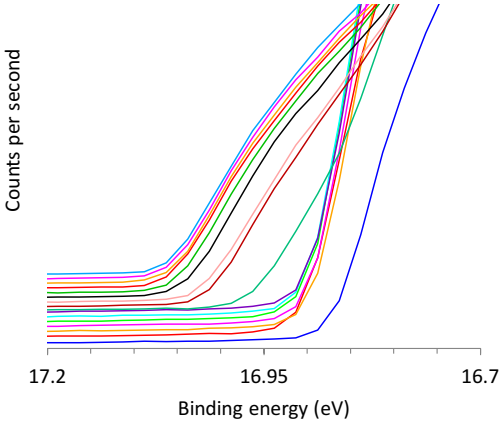

Figure 3: Cut-off region (spectra are offset vertically with etch cycle).

Conclusion

He we show it is possible to run a prescribed method to perform XPS-UPS depth profiles of novel organic electronic devices using Argon cluster ions. The method allows direct comparison between changes in surface composition and the changes in electronic character as seen in the UPS spectra. The automated nature of the prescribed method requires zero manual or computational intervention by the analyst. A truly 'click-and-go' hyphenated technique.

Acknowledgements

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References

1. A. G. Shard, S. Ray, M. P. Seah, L. Yang, Surf. Interface Anal. 2011, **43**, 1240–1250. DOI 10.1002/sia.3705

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