The MoO₃ has been the most commonly used material as a hole injection layer for interface engineering in organic electronics. The MoO₃ films are usually prepared via thermal evaporation in high vacuum conditions. However, the actual devices will be exposed to dry N₂ or air environment during the device fabrication or integration, and hence it is necessary to understand the gas exposure effect when using MoO₃ as an interfacial modification layer.

In this work, we reported an ionization potential (IP) dependent air exposure effect on the MoO₃/organic interface energy level alignment by carrying out in situ ultraviolet photoelectron spectroscopy (UPS) and synchrotron light based X-ray photoelectron spectroscopy (XPS) investigations. The electronic structures at MoO₃/organic interfaces comprising various n-conjugated small organic molecules with different IP on MoO₃ substrate have been systematically investigated.

UPS measurements were performed with He I (21.2 eV) as excitation source, a -5 V sample bias was applied to allow the collection of the low kinetic energy part.

In situ synchrotron based high resolution XPS experiments were carried out at the Surface, Interface and Nanostructure Science (SINS) beamline of the Singapore Synchrotron Light Source.

Sublimation purified MoO₃ and organic molecules were thermally evaporated from separated Knudsen cells onto the ITO substrate in an UHV growth chamber with a base pressure better than 3 × 10⁻¹⁰ mbar.

All spectra were recorded at normal emission angle at room temperature.

The air exposure experiments were performed in the fast entry chamber connected to the growth chamber.

The change of HOMO leading edge after 60 min air exposure under 1 atmosphere pressure for various n-conjugated organic thin films with different IP on 10 nm MoO₃ covered ITO substrate. The solid line is added as a guide to eye, the inset shows the HOMO edge values in vacuum before air exposure.

**For low IP molecule**

UPS spectra at (a) the low kinetic energy region (secondary electron cutoff) and (b) the low binding energy region near the Fermi level during the deposition of pentacene molecules on 10 nm MoO₃ covered ITO substrate before and after 60 min 1 atmosphere pressure air exposure.

(c) The plot of WF and HOMO leading edge of pentacene on MoO₃ as a function of film thickness.

(d) Schematic diagram showing the energy level alignment at the MoO₃/pentacene interface.

**For high IP molecule**

UPS spectra at (a) the low kinetic energy region (secondary electron cutoff) and (b) the low binding energy region near the Fermi level during the deposition of ZnPc molecules on 10 nm MoO₃ covered ITO substrate before and after 60 min 1 atmosphere pressure air exposure.

(c) The plot of WF and HOMO leading edge of ZnPc on MoO₃ as a function of film thickness.

(d) Schematic diagram showing the energy level alignment at the MoO₃/ZnPc interface.

**MoO₃ electronic structures**

**Energy level diagrams**

**Conclusions**

- observed an ionization potential dependent air exposure effect on the interface energy level alignment between MoO₃ and organic thin films.
- can provide direct evidence to explain the difference in the device degradation of organic thin films with different IP on MoO₃, after air exposure.
- have great implications when using MoO₃ as an effective HIL via low-cost device manufacturing under low vacuum or non-vacuum conditions.

**Acknowledgements**

Authors acknowledge the support from the Singapore ARF Grants R143-000-440-112, R143-000-505-112, and NUS YIA Grant of R143-000-452-101.