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Report:

We present the chemical characterization of deeply buried OSVs organic-inorganic interfaces by Hard X-ray Photoelectron Spectroscopy (HAXPES). We probed core-level spectra for Co(15 nm)/Alq₃(50 nm)/Si and Co(15 nm)/Al₂O₃(2 nm)/Alq₃(50 nm)/Si buried interfaces to elucidate the interaction of the overlying Cobalt with the underlying Alq₃ molecules (chemical formula: Al(C₉H₆NO)₃), and the role of the insulating tunnel barrier. HAXPES measurements were performed ex-situ at the ID16 beamline within the frame of the European VOLPE (VOLume PhotoEmission from solids) project, which makes available high kinetic energy resolution typically of the order of 70-100 meV at the 6-8 keV photon energy range. The incoming beam energy was set at $h\nu = 7.6$ keV to improve adequately the depth sensitivity. The x-ray beam was impinging at 45° while photoelectrons were detected at normal emission. The overall resolution of the analyzer combined with the photon bandwidth was 450 meV. For all samples the HAXPES measurements probed the C1s, N1s, O1s, Al1s signals at room temperature. To reduce beam damage effects and verify the interface homogeneity we measured the spectra on different sample positions.

Figure 1 shows all the 1s core level peaks detected for the Alq₃ atomic constituents, from samples with the Al₂O₃ tunnel barrier between the Cobalt and the molecules, without it, and for a bare Alq₃ thick film (50 nm) without any overlayer. The spectra are normalized to compare the lineshapes. The binding energies of the main peaks fully agree with results in literature, hence terms due to molecule fragmentation or x-ray induced damage do not seem to dominate the spectra. It is worth to mention that the photoionization cross section of the N1s and O1s lines is about 10⁻³ times weaker at 7.6 keV than for excitation energies below 1.5 keV, and the atomic concentration of N and O is quite small. Detection of these spectra from regions 15 nm deep inside the samples demonstrates the feasibility of HAXPES to probe organic materials. Even without analytical data processing, it is possible to distinguish intense features not present in the bare Al₃ sample. The N1s spectrum for the Co/Alq₃ interface has a strong component at lower binding energy, which is largely attenuated when the oxide barrier is present. A similar feature appears also for O1s, although much less intense with respect to the main peak, and of comparable intensity for both interfaces. All the

spectra have an asymmetric tail to higher binding energies which is more evident for O1s than for N1s. C1s and Al1s signals are more intense than N1s and O1s because of the large number of C atoms and of the strong Al1s cross section (one order of magnitude larger than for the other elements). The Al1s peak was the only one detectable for Aluminum because of the extremely small photoionization cross section for the 2p core levels and the diluted atomic concentration. Even these peaks are sensitive to the overlayer deposition, although changes are less evident than for Nitrogen and Oxygen. The Cobalt deposition promotes a very small enlargement of the Al1s spectrum. The contribution of the Al₂O₃ further enlarges the peak. A full interpretation of these spectra requires a careful fit analysis that is currently in progress. The C1s behaviour is qualitatively different from Al1s. We observe a loss structure associated to shake-up π - π^* excitations occurring at about 291 eV. A small enlargement of the main peak (+0.2 eV) occurs only for the Co/Alq₃ interface, while the lineshapes for the other samples are basically identical. This behaviour is less ambiguous than for Al1s because there is not overlap of contributions from different materials. In absence of the Al₂O₃ the spectral weight of the C1s spectrum increases significantly around 284.7 eV, as shown in the difference spectrum, in close agreement of what has been observed in other studies, in particular for calcium deposition above Alq₃.

These results indicate that in absence of the tunnel barrier there is an effective charge transfer from Cobalt to the Alq₃ in the interdiffused region, thus cobalt atoms or clusters donate electrons to the Alq₃. The different perturbation of N and O electronic structure suggests that Cobalt should be located closer to the nitrogen atom. The strong interaction with the cobalt leads to the formation of charge states at the interface that reduce the spin conservation through spin localization and makes the organic spin valve devices unstable because of multistep conduction through these gap states. The case of ternary interface is more difficult to manage, however the spectra demonstrate that the presence of the tunnel barrier reduces the Co-Alq₃ interaction very efficiently, thus it is definitively required to protect the molecular film from the overlayer deposit, avoiding both interdiffusion and strong changes in the interface electronic structure.

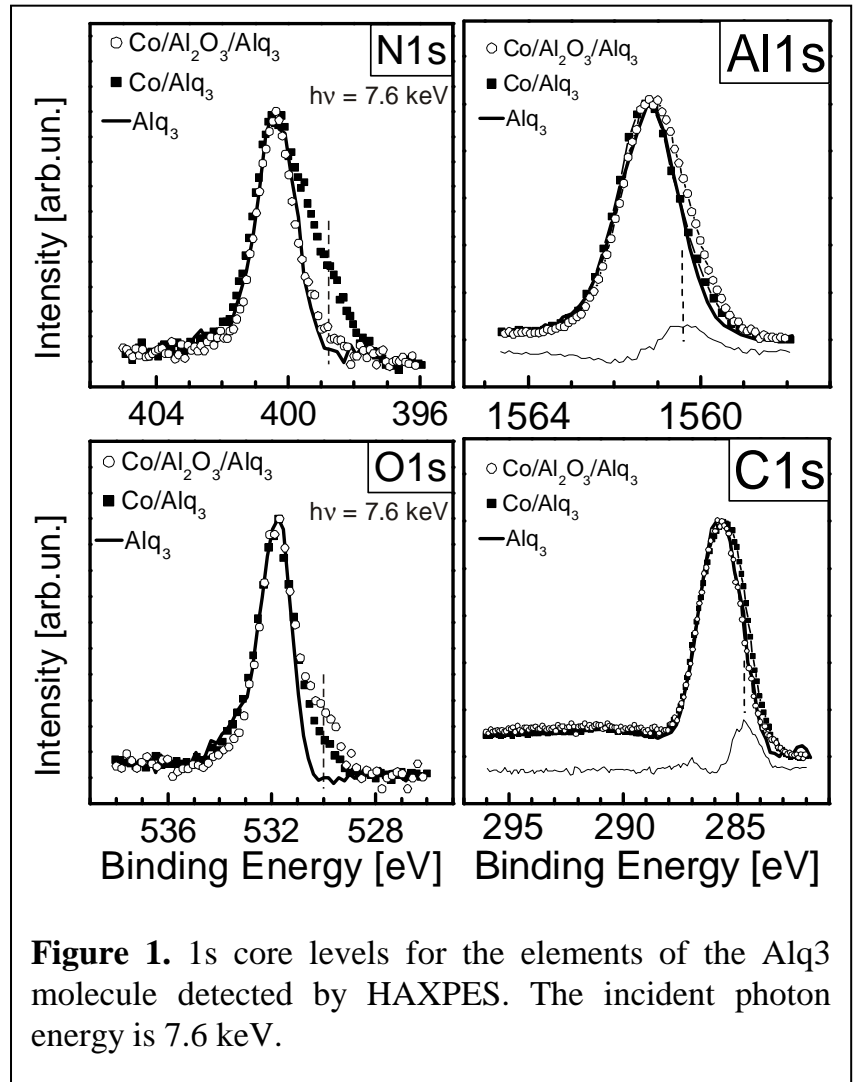


Figure 1. 1s core levels for the elements of the Alq₃ molecule detected by HAXPES. The incident photon energy is 7.6 keV.