Electronic structure of buried organic-inorganic interfaces by hard x-ray photoelectron spectroscopy

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We have studied by Hard X-ray Photoelectron Spectroscopy (HAXPES) the electronic structure of deeply buried organic-inorganic interfaces composed by a top ferromagnetic layer of cobalt (15 nm), and a thin inorganic barrier (AlOₓ, NdGaO₃, SrTiO₃, 2 nm) deposited above a thick organic film (50 nm) of tris(8-hydroxyquinoline) aluminum [Al(C₉H₆NO)₃, hereafter named as Alq₃]. The multilayer was grown on a silicon (100) native oxide substrate. These hybrid heterostructures participate to the typical composition of vertical organic spin valves (OSVs) and magnetic tunnel junctions (OMTJs), i.e. spintronic devices in which two ferromagnetic contacts, applied as spin injector and spin detector, are separated by a non-magnetic organic spacer. The electronic structure of the buried interface region including a thin tunnel barrier between the organic layer and the top ferromagnetic electrode is a key issue for the understanding of the physical mechanisms involved into the charge/spin transport across such devices [1,2]. Therefore in this experiment we have collected hard x-ray core-level spectra from buried interfacial regions of samples differing for the interface layer material. In a previous work [3] we have shown that in absence of the tunnel barrier there is an effective charge transfer from cobalt to the Alq₃ in the interdiffused region forming at the interface, thus cobalt atoms or clusters donate electrons to the Alq₃. In this experiment we show that the presence of the tunnel barrier largely limits the Co-Alq₃ interaction even when STO and NGO compound are used, and that the presence of a tunnel barrier is definitively required to protect the molecular film from the overlayer deposit, avoiding both interdiffusion and strong changes in the interface electronic structure.

The measurements were performed ex-situ at the HAXPES experimental station of the P09 beamline. The incoming beam energy was set at hν = 7.52 keV to improve adequately the depth sensitivity. The x-ray beam was impinging at 5° in grazing geometry while photoelectrons were detected at normal emission. The overall resolution of the analyser combined with the photon bandwidth was 350 meV. To reduce beam damage effects and verify the interface homogeneity we measured the spectra on different sample positions and set the temperature of the samples at 150K. As a reference, we have probed the core levels for thick film samples (>50 nm) of every material used in these organic/inorganic heterostructures. Figure 1 shows a stacked overview of the 1s core level spectra detected for the Alq₃ atomic constituents, for samples with the AlOₓ, NdGaO₃ (NGO) and SrTiO₃ (STO) tunnel barriers (TBs) placed between the Cobalt and the molecules, 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 agree with the results in literature, hence molecule fragmentation or x-ray induced damage does not seem to dominate the spectra. A full interpretation of these spectra requires a careful fit analysis, currently in progress, however even without analytical data processing it is possible to identify specific spectral features differing from the case of the bare Alq₃ sample. The O1s and N1s spectra for the Co/TB/Alq₃ interfaces exhibit broad components at kinetic energy around 7067 eV and 7200 eV, respectively, which are largely attenuated for the bare Alq₃ film. The N1s spectra provide
unambiguous information about the electronic structure of the Alq₃ at the interface region, being not affected by contributions related to any other material. The O1s spectra for the oxide tunnel barrier materials will provide the reference to distinguish their contribution from the Alq₃ molecular compound and will be used for fit analysis of the spectra. C1s and Al1s signals are more intense than N1s and O1s because of the large number of carbon 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 additional contribution related to the presence of the AlOₓ layer further enlarges the peak. The C1s behaviour is qualitatively different from Al1s. We observe a loss structure at about 7310 that is usually associated to shake-up excitations. The lineshapes for the other samples are basically identical, all of them exhibiting a shift of the core-level binding energy. The spectral weight of the C1s spectrum increases around 7318 eV (low binding energy side) in close agreement of what has been observed in other studies, in particular for calcium deposition above Alq₃, and usually assigned to charge transfer effects.

Figure 1: 1s core level spectra of the buried Alq₃ with the AlOₓ, NdGaO₃ (NGO) and SrTiO₃ (STO) thin layers at the cobalt/Alq₃ interface compared to the reference spectra of a bare Alq₃ thick film (50 nm).

References