Interfacial electronic structures in an organic light-emitting diode

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Direct measurements of electronic properties have been made for the metal/organic and organic/organic interfaces in a multilayer organic light-emitting diode (LED) using ultraviolet photoemission spectroscopy. The device configuration considered is indium–tin oxide (ITO)/copper phthalocyanine (CuPc)/N,N'-bis-(1-naphyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamne (NPB)/8-hydroxyquinoline aluminum (Alq)/Mg. For the material interfaces considered here, our result indicates that the traditional concept of vacuum-level alignment, though not valid for metal/organic interfaces, still holds at organic/organic interfaces. This implies that little charge transfer occurs at the interfaces due to the small interaction between organic molecules. The largest band offsets are observed between the lowest unoccupied state levels of the organic molecules. Based on the directly measured energy-level alignments, a model is proposed to explain the improved efficiency of multilayer organic LEDs, as compared to those with a single organic layer structure. © *1999 American Institute of Physics.* [S0003-6951(99)04705-1]

Organic light-emitting diode (OLED) devices have received wide spread interest due to their potential applications in multicolor flat panel displays.[1–8] In recent years, considerable efforts have been directed at developing more power efficient devices based on thin films, which can be driven by a low dc voltage, typically, below 10 V. To a large extent, this depends on improving carrier injection efficiency from both electrodes, and on obtaining balanced and controlled electron–hole recombination within a well-defined zone. The charge-carrier injection characteristics of both small organic molecule- and polymer-based light-emitting diodes (LEDs) have been explained using a band-structure model.[9] In such a scheme, carrier injection efficiency is affected by the energy barrier height at the interfaces between thin layers in the device. The energy relation among the frontier levels at the interface is, therefore, crucial in determining interfacial phenomena such as carrier injection and rectification. From this point of view, an accurate picture of the energy-level alignments at the interfaces is critical to a good device design, particularly in relation to optimizing the device efficiency. Despite such importance, the energy-level alignments have seldom been measured directly up until now. Instead, they were often estimated by lining up separately observed electronic structures of organic materials and the electrode metal, under the assumption of a common vacuum level at the interface. However, photoemission studies by Seki and co-workers[10] have shown that the vacuum levels do not align at the interface between metal and a number of organic molecules including 5,10,15,20-zinc tetraphenylporphyrin (ZnTPP), 5,10,15,20-tetraphenylporphyrin (H$_2$TPP), and Alq. Similar results have also been obtained for the phenylene vinylene oligomer/Ca interface.[11] Their works thus raised doubt about the assumption of a common vacuum level at metal/organic interfaces. On the other hand, whether the concept of vacuum level alignment holds true for organic/organic interfaces still remains to be examined.

In order to clarify the uncertainties noted above, we have undertaken direct measurements of electronic structures for the metal/organic and organic/organic interfaces involved in an organic light-emitting diode. ITO/CuPc/NPB/Alq/Mg is chosen for the study because it represents the prototypical organic LED whose performances have been well characterized. Furthermore, the small organic molecule-based LED is well suited for surface science study since organic layers can be deposited under ultra-high-vacuum (UHV) condition and characterized *in situ*. The detailed results for metal/Alq interfaces have been reported in a previous letter.[12] The present letter focuses on the measurements at organic/organic interfaces. In addition, an energy diagram is constructed based on the determined energy-level alignments in the organic LED and used to explain the improved performance of such a multilayer OLED as compared to the device with a single-layer configuration.

The experiments were carried out in an UHV facility, which is composed of three interlinking chambers for sample entry, analysis, and thin-film deposition. Metal and organic thin films were deposited onto an indium–tin oxide (ITO)-coated glass substrate from resistively heated tungsten baskets or tantalum boats. The thickness of the deposited layer was monitored by a quartz-crystal microbalance. The ITO substrates were cleaned following Ref. 1. Ultraviolet photoemission spectroscopy (UPS) measurements were performed with the HeI radiation ($h\nu = 21.21$ eV) and the photoelectrons were collected by a double-pass cylindrical mirror analyzer with an energy resolution of 0.08 eV. To ensure the collection of low-energy electrons, samples were biased at negative 4 V. The ionization potentials (IP) of organic materials can be readily determined by subtracting from the

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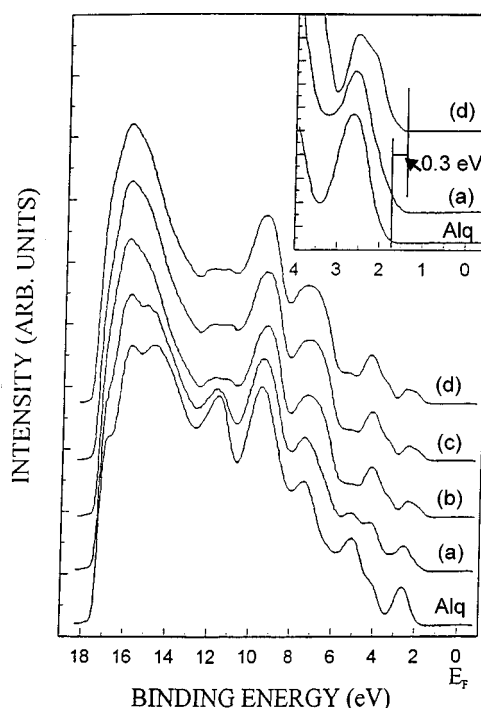[b)]On leave from Surface Physics Laboratory, Fudan University, Shanghai 200433, China.

FIG. 1. HeI UPS spectra as a function of incremental NPB deposition on Alq. The thicknesses of NPB layers are (a) 0.2 nm, (b) 0.6 nm, (c) 1.2 nm, and (d) 8.8 nm.

FIG. 2. HeI UPS spectra as a function of incremental CuPc deposition on NPB. The thicknesses of CuPc layers are (a) 0.2 nm and (b) 5.3 nm.

energy of the HeI radiation the width of the UPS spectrum. The latter is the energy difference between the intensity thresholds at the highest and lowest binding energy. In the spectra of ITO, the difference between the energy of HeI radiation and the spectral width gives the work function of ITO. The work function of ITO thus determined is 4.30 eV, in good agreement with the value (4.4 eV) reported by Park *et al.*[13] The former value was checked using Kelvin probe measurement, which determines the contact potential difference between the tip and the ITO surface. The work function of the Kelvin reference probe was calibrated using an *in situ* deposited gold film, the work function of which was determined by UPS. The Kelvin probe measurement gave a value of 4.34 eV for the work function of the ITO surface, which confirmed the value measured by UPS. The energy-band lineup at the organic/organic interface was determined by measurement of the superimposed valence-band spectra of both materials with a thin layer (a few Å) of organic molecules having a smaller IP on top of the other material. This way, the highest occupied molecular orbital (HOMO) positions of both materials can be identified simultaneously in the spectrum. The vacuum-level offsets are obtained from the shifts at the intensity thresholds at the highest binding energy sides.

　　Figure 1 shows the HeI UPS spectra of the NPB/Alq interface with different NPB overylayer thicknesses. The bottom spectrum was measured from a 10 nm Alq layer deposited on the ITO substrate. Deposition of the NPB overlayer at increasing thickness results in a progressive attenuation of the characteristic emission features of Alq. The top spectrum corresponds to a 8.8 nm thick NPB layer and represents typical emissions from the surface of NPB. In both spectra, the very distinguishable peaks, close to Fermi levels, are the HOMOs of the organic molecules. Two peaks located
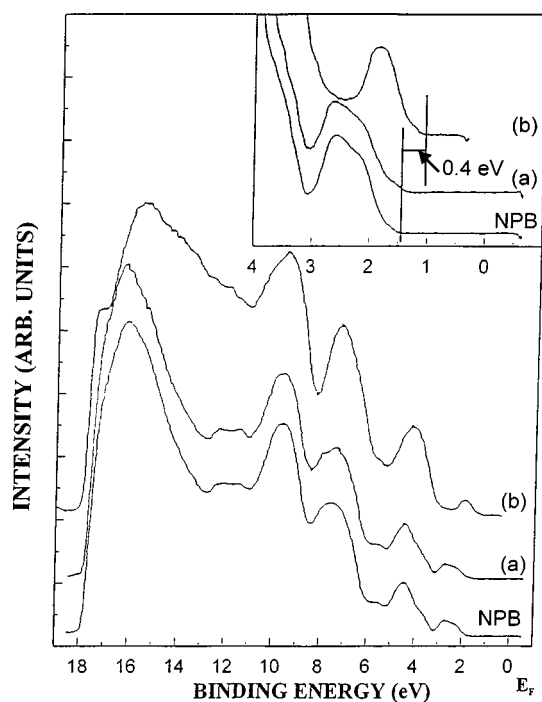
between 7 and 10 eV appear to be the common photoemission features of NPB and Alq and are probably associated with the benzene rings contained in both molecules. The IP value for Alq is found to be 5.7 eV. The value agrees with that (5.66 eV) obtained by Hamada *et al.*,[14] and is comparable to the values reported in other works.[15–19] The ionization potential for NPB is found to be 5.2 eV, which is 0.5 eV lower than that reported by Rajagopal, Wu, and Kahn.[15] The difference may be due to the critical dependence of the IP value on the specific morphology of the surface, although the exact origin of this discrepancy is not yet clear. The band offset between HOMO levels of NPB and Alq is about 0.3 eV (see the inset of Fig. 1).

　　The HeI UPS spectrum of NPB is displayed in Fig. 2, together with those from CuPc overlayers at different thicknesses. From the spectrum of a 5.3 nm CuPc layer, we obtain an ionization potential value of 4.8 eV for CuPc. Detailed features from the HOMO levels of NPB and CuPc are shown in the inset of Fig. 2 and the band offset between NPB and CuPc is found to be at about 0.4 eV. The two peaks located between 7 and 10 eV, similar to those observed in Fig. 1, can also be identified in the spectrum of CuPc.

　　Using the results from UPS spectra and taking the observed optical band gaps of organic materials as HOMO–LUMO (lowest unoccupied molecular orbital) band gaps, a diagram of energy-band alignment for the multilayer organic LED is obtained and depicted in Fig. 3. As shown in the energy diagram, there is a vacuum-level difference of −0.33 eV at the Mg/Alq interface.[12] To compensate for the vacuum energy difference, an interfacial dipole layer has to be established, presumably from the charge transfer between Mg and Alq. The voltage drop across the metal/organic interface corresponds to a barrier height for electron injection into an organic layer. These dipole barriers are especially important when a negative bias is applied to the metal side. The dipole
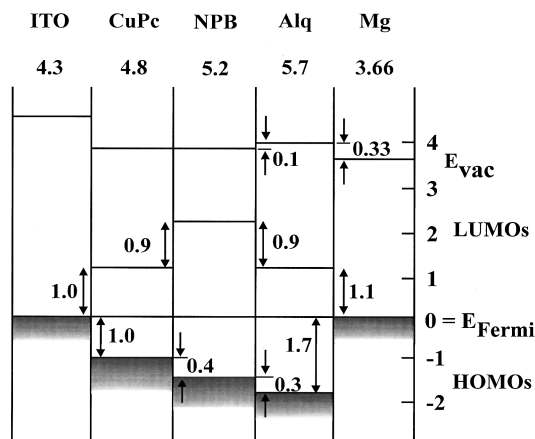
FIG. 3. Schematic diagram showing the energy-level alignment for the organic LED (ITO/CuPc/NPB/Alq/Mg). All the values shown in the diagram are in units of eV. The values shown on the top of the diagram are ionization potentials of organic materials and work functions of Mg and ITO.

mechanism for metal and organic contact has been discussed in detail in a previous letter.[12] To simplify comparison of energy barriers at various interfaces, the existence of the interfacial dipole layer is not considered in the present letter. At the organic/organic interfaces, the band offset occurs dominantly at the unoccupied state levels; the band offsets at the HOMO levels are relatively small. No difference in the vacuum levels was found between NPB and CuPc, while there is a small 0.1 eV difference between vacuum levels of NPB and Alq. In support of this, it is noted that the photo-emission study of the Alq/TPD interface also indicated a negligible difference at the vacuum levels of Alq and TPD.[17] This demonstrates that the traditional concept of vacuum-level alignment can still be applied at those organic/organic interfaces where interactions between organic materials are weak and the organic molecules remain unaffected during interface formation. However, we note also that vacuum-level shifts of 0.5 and 0.25 eV have been reported for Alq/PTCDA and Alq/NPB interfaces, respectively.[15] Currently, we have no explanations for the discrepancy found at the Alq/NPB interface. Nevertheless, it is worth noting that vacuum-level shifts can exist at the interfaces between the organic materials in some special cases.

From the band offsets determined, the improved performance of the multilayer OLED device can be understood. First, due to a large energy barrier for electrons of about 0.9 eV between the LUMO levels at the NPB/Alq interface, electrons injected from the cathode are prevented from moving into the hole transporting layer (i.e., the NPB layer). While electrons are piling up at the NPB/Alq interface, the holes, once injected into CuPc, can travel readily towards and across the NPB/Alq interface since the energy barriers for holes at CuPc/NPB and NPB/Alq interfaces are small (0.4 and 0.3 eV, respectively). Accordingly, the electron–hole recombination takes place effectively in the Alq layer near the NPB/Alq interface. This is consistent with the observation that the electroluminescence in the organic LED (ITO/CuPc/NPB/Alq/Mg–Ag) occurred within 50 Å of the NPB/Alq interface in the Alq layer.[20] Such a device modification gives improved efficiency since it keeps the electron–hole recombination away from the metal/organic interface, where a

large amount of carrier traps is present. Another device modification is the insertion of a thin CuPc layer as the hole injection layer (HIL) between ITO and NPB. Here, the energy barrier for hole injection from ITO into the organic layers (CuPc or NPB) can be estimated from the energy difference between the HOMO of organic material and the Fermi level of ITO (without considering the interfacial dipole layers). Thus, the injection barrier at the CuPc/ITO interface is 1.0 eV, which is lower than that at the ITO/NPB interface (1.4 eV). For this reason, adding CuPc between ITO and NPB layers has a ladder effect, which makes hole injection into the organic layer easier, leading to improved injection efficiency. Overall, the determined energy-level alignments have provided direct evidence to reveal the origins of the improved device performance due to the incorporation of NPB and CuPc layers into the device structure. Further studies on other prototypical organic LED devices are planned in order to develop a broader mechanistic model with the view of providing useful reference for device design.

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