



Resident holes and electrons at organic/conductor and organic/organic interfaces: An electron paramagnetic resonance investigation



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ARTICLE INFO

Article history:

Received 28 March 2016

Received in revised form

2 June 2016

Accepted 1 July 2016

Available online 21 July 2016

Keywords:

Interface cations

Dipole layer

OLEDs

Integer charge transfer

Electron paramagnetic resonance

ABSTRACT

A number of organic/conductor and organic/organic interfaces have been examined by EPR spectroscopy to ascertain the areal concentration of organic ions at the interface. Organic hole transport materials such as NPB and TAPC at an interface with MoO_x are found to have areal concentrations on the order of 10¹⁴ cations per cm². C₆₀ at an interface with MoO_x creates ≈10¹³ cations per cm² depending on the roughness of the substrate. However, C₆₀ at an interface with Mg or Ag produces only about 4 × 10¹² anions per cm². Ion concentrations are generally in accord with the energy levels (adiabatic IP, EA etc) of the two materials at a given interface.

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1. Introduction

Numerous experiments have demonstrated that charge transfer occurs at conductor/organic interfaces under conditions typical of organic electronic devices (for examples see refs 1–16). This charge transfer creates radical cations (holes) or anions (electrons) in the organic layer. If the HOMO level of an organic material is higher than the Fermi level of the conductor then electrons can be ‘pulled’ into the conductor (holes can be injected into the organic); or if the LUMO level of an organic material is lower than the work function of the conductor then electrons can be ‘pulled’ (injected) into the organic layer – even in the absence of an applied field. A more fundamental criterion is detailed in the integer charge transfer (ICT) theory [2–4]. When the adiabatic ionization potential (IP) of the organic material is less than the effective work function of the conductor, cation formation can occur. Likewise, if the adiabatic electron affinity (EA) of the organic material is greater than the work function of the conductor then anion formation can occur. An additional driving force may be provided by image potential formation, which reduces the IP or increases the EA of the material adjacent to the conductor relative to that of the bulk material. This

charge ‘migration’ across the interface forms a dipole layer.

A related phenomenon occurs when a so called hole injection (HI) material such as 1,4,5,8,9,11-hexaazatriphenylene hexacarbonitrile (HAT-CN) is deposited between the transparent conductor indium tin oxide (ITO) and an organic hole transport (HT) layer. It has been shown that when 4,4-bis *N*-1-naphthyl-*N*-phenylamino biphenyl (NPB) is deposited over a HI layer of HAT-CN on a glass/ITO substrate that HAT-CN anions were formed [11]. It likely can be presumed that NPB cations were also formed.

Techniques such as ultraviolet photoelectron spectroscopy (UPS) have been used to measure the vacuum level shift as a function of deposited thickness of organic materials on conductors or HI materials (see for example [1–7,12,13]). This shift is caused by the presence of the dipole layer mentioned above. Charge modulation spectroscopy (CMS) has been used to investigate cations or anions in a dipole layer [9,17]. CMS makes it possible to identify cation and anion species by their characteristic absorption spectra, but it cannot provide a quantitative assay of their concentrations.

In a previous investigation the cation concentrations at representative conductor/organic interfaces were quantified by EPR measurements for several HT materials deposited onto MoO_x on a fused quartz/ITO substrate [11]. These areal ion concentrations ranged from 8 to 15 × 10¹³ per cm² of the deposited area. It is known, however, that the surfaces of as received ITO and MoO_x deposited on ITO are not planar on a nm scale and that actual areas

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may exceed the nominal planar area by 50% or more. (see for example [13,14,18,19]).

The goal of the current investigation is to examine a number of interfaces and determine the approximate areal ion concentrations formed with various combinations of conductor and organic material. Each interface is comprised of a HT material or fullerene (C_{60}) in contact with one of several conductors or the HI material HAT-CN. Additional measurements by charge modulation spectroscopy (CMS) and voltammetry (displacement current method) were used to confirm the formation of NPB cations on HAT-CN and to show that fullerene (C_{60}) cations, though formed on MoO_x , are not easily transported through the bulk of a C_{60} layer.

2. Experimental

2.1. Materials and devices fabrication

Quartz slides were obtained from Chemglass and quartz slides coated with ITO were obtained from Delta Technologies, LTD [20]. They were cut into 7 mm × 25 mm pieces for use as substrates. These substrates were cleaned by sonication for 10 min in a deionized water detergent mixture then rinsed 3 times with sonication in high purity water. This was followed by sonication in acetone and then in isopropanol followed by subsequent drying in air. The substrates were mounted on a sample holder and placed in a thermal vacuum coater. Tooling factors were obtained using profilometric measurements of NPB and MoO_x films deposited on glass slides. The depositions were monitored by a Sycon STM-100 Thickness/Rate Monitor. At pressures $1-2 \times 10^{-6}$ Torr, quartz and quartz/ITO substrates were coated with 10–30 nm of MoO_x from a tungsten boat at a rate of 1.5 Å/s. Subsequently, these substrates received a deposition of one of the organic materials at 2 to 4 Å/s. Other conductor/organic interfaces were coated in a similar fashion. It should be noted that these deposition conditions are similar to conditions used to make organic light emitting diodes (OLEDs), organic photovoltaic (OPV) and other organic devices. In addition to fullerene (C_{60}), the organic materials used were: 4,4-bis *N*-1-naphthyl-*N*-phenylamino biphenyl (NPB), tris (quinolin-8-olato) aluminum (III) (Alq₃), 1,1-bis(di-4-tolylamino phenyl) cyclohexane (TAPC), and 1,4,5,8,9,11-hexaazatriphenylene hexacarbonitrile (HAT-CN). The structures of the aromatic materials are shown in Fig. 1.

2.2. Electron paramagnetic resonance (EPR) spectroscopy

X-band EPR spectra were recorded on a Bruker EMXplus spectrometer equipped with a 4119HS cavity (TE₀₁₁). Samples were individually placed on an EPR quartz sample holder and wrapped with Teflon™ tape. For all samples care was taken to position the conductor surface along the node of the electric field in the cavity. The nominal instrumental parameters were: 0.6325 mW microwave power; 1G/s scan rate; 20 ms time constant; ~9.70 GHz microwave frequency; and 8 G modulation amplitude. EPR spectra of some C_{60} samples were also recorded with 4 or 2 G modulation amplitude. Modulation amplitude was selected to produce detectable signals, but may result in over-modulation of the signal. However, over-modulation should not affect quantitative assays (number of spins), but only the resulting line widths. It should be noted however that with smaller modulation amplitudes sharp resonances (e.g. fullerene – C_{60} ions) become more prominent and broader lines can 'fade' into the baseline [21]. This is done to help with species identification. The spectra were integrated with the Xenon software (Bruker) and the integrated intensities were compared with the intensity of an impurity in the quartz sample holder which served as a secondary standard [22]. The weak

impurity signal in the quartz sample holder was 'calibrated' with known amounts of TEMPOL. A weighed amount of 4-hydroxy-TEMPO (TEMPOL) was dissolved into *p*-xylene. A measured quantity of this solution was mixed with a known amount of melted paraffin. After solidification of the mixture, weighed amounts were melted onto the surface of quartz and quartz/ITO substrates. Any variation in cavity *Q*-values between samples will affect the internal standard as well and, thus, was compensated for by the internal standard for the spin quantitation results. EPR simulations were performed using EasySpin [23] to calculate *g*-values and line-widths. EasySpin can account for effects of modulation amplitude to obtain estimates of the natural line-width. Due to very low concentrations of ions ($\approx 10^{12}$ per cm^2) in some samples, notably those with HAT-CN, it was necessary to subtract the quartz background contributions of impurity resonances at or very close to $g = 2.003$ to determine quantitative results and approximate line-widths.

2.3. Voltammetry, charge-modulation spectroscopy and UV-Vis spectroscopy

The voltage-dependent capacitance of several devices was obtained by voltammetry or displacement current methods [15,17,24–27]. A sawtooth voltage function was applied to a device and the current through the device was monitored via the voltage drop across a load resistor. The current and applied voltage signals were recorded with a digitizing oscilloscope, and current was plotted versus voltage: a voltammogram. Voltammograms were obtained at several sweep rates to confirm that the devices were behaving properly (absence of pinholes etc.). Voltages are always reported for the bias applied to the anode with the cathode near ground potential.

Charge-modulation spectroscopy (CMS) measurements were performed on several devices to detect cation or anion motion in or out of the organic material at the dipole layer. The CM apparatus has been described previously [9,17]. Briefly, disperse light from a 150 W quartz lamp passes through a scanning monochromator. This light is then transmitted to the device by a fiber optic cable; the light passes through the glass/ITO substrate and organic layers and reflects from an aluminum cathode and passes again through the device. The reflected light exits through the substrate and is focused onto a New Focus Model 2011 photodiode with an internal amplifier. Both visible and near-infrared photodiodes can be used. A 2 kHz square wave voltage is applied to the device, resulting in a modulation of the cation concentration in the device and the intensity of the reflected light. The resulting AC component of the photodiode output is accessed by a lock-in-amplifier and the DC component of the photodiode output is monitored by a DC volt meter and is used to compensate for the wavelength-dependent variation in incident intensity and average reflectivity. The charge modulation signal from the lock-in amplifier and reflectance signal from the voltmeter are recorded and processed by a LabView™ program.

UV-Vis direct transmission experiments were performed to determine whether total cation or anion concentrations could be quantified without EPR techniques. The wavelength range was nominally 300–800 nm. A precleaned quartz or quartz/ITO substrate was used. Spectra were processed and corrected for substrate absorption and optical interference effects using Excel software. Unfortunately the characteristic cations absorption was only easily observed for 20 nm of TAPC deposited on quartz and exposed to I_2 vapor for several min. Interference effects made it impractical to observe the much lower concentration of interface ions with UV-Vis techniques. The extinction coefficient of TAPC⁺ at 700 nm has been measured to be 4.2×10^4 L/M cm in solution [28]. The

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