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A photoemission study of interfaces between organic semiconductors and Co as well as Al_2O_3/Co contacts

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ABSTRACT

We have studied the energy-level alignment of ex situ, acetone cleaned Co and Al_2O_3/Co contacts to the organic semiconductors pentacene and rubrene by combined X-ray and ultraviolet photoemission spectroscopy. Our results demonstrate that the work function under these conditions is smaller than in the in situ cleaned, atomically clean case. Moreover, the studied interfaces are characterized by very small, short range interfaces dipoles and substantial injection barriers for holes. This represents essential information in view of their use in organic spintronic devices. Our core-level photoemission spectroscopy measurements rule out chemical reactions.

1. Introduction

Organic spin electronics, also referred to as organic spintronics, has come into focus as a new and promising research field in recent years [1]. In this context, organic spintronics comprises the application of organic materials for the transport and the control of spin-polarized information. The demonstration of the giant magnetoresistance effect (GMR) in metallic heterojunctions [2,3], as well as tunneling magnetoresistance (TMR) [4] in ferromagnetic tunnel junctions are considered important breakthroughs in the field of spin electronics. It has also initiated further applications regarding magnetic memory devices in which the active control and the manipulation of spin degrees of freedom is anticipated [5]. For the injection/detection of spin-polarized electrons in an organic semiconductor, a ferromagnetic (FM) electrode with a substantial degree of electron spin-polarization in the conduction band is required. A lot of activity is presently going on to inject spin-polarized currents in organic semiconductors [6–12]. One of the earliest reports is by Dediu et al. [13], who reported the possibility of injecting spin-polarized currents in organic semiconductors and reported room temperature magnetoresistance for α-sexithiophene as the spin transport medium between two $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) electrodes. A spin-valve effect in a vertical geometry device using tris(8-hydroxyquinolino)-aluminum (Alq_3) between a 60-monolayer thick $La_{0.7}Sr_{0.3}MnO_3$ film as bottom electrode and a top electrode of 3.6 nm Co was reported in 2004 by Xiong et al. [8]. Furthermore, Santos et al. [11] reported a tunneling of the spin across a thin layer of Alq_3 up to room temperature. All these observations can be regarded as encouraging for the field of organic spintronics in which the flexibility and variability of the organic semiconducting material is combined with a further degree of freedom for switching or controlling a device via external magnetic or electric fields. Organic materials are mainly consisting of light elements, which leads to weak spin–orbit coupling. Despite the presence of nuclear spins, the hyperfine interaction in organic materials is possibly also weak [1]. Therefore, organic semiconductors are believed to have a long spin relaxation time and consequently a large spin diffusion length λ_S. In 2008 Shim et al. [14] reported a large spin diffusion length of 13.3 nm in amorphous rubrene, showing the great potential of organic semiconductors for organic spintronic development.

Rubrene ($C_{42}H_{48}$) as well as pentacene ($C_{22}H_{14}$) are characterized by high charge carrier mobilities, for organic standards. For rubrene high hole mobilities in the range of 15–20 cm^2/Vs were reported for high-purity single-crystals [15,16]. Also pentacene exhibits high charge carrier mobilities from typical 0.4–1 cm^2/Vs for thin-film transistors (TFTs) made from good quality pentacene films [17] to 35 cm^2/Vs for high-purity single-crystals [18]. Consequently, rubrene and pentacene are promising candidates for future electronic devices as well as for the investigation of spin transport properties. The choice of Co as electrode material comes from the fact that Co is a commonly used ferromagnetic material

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for the injection as well as detection of spin-polarized electrons in spintronic devices [8,11,19] with a bulk spin-polarization of around 45% [1,20,21]. A common problem for spin injection and detection using a ferromagnetic metal (such as Co) electrode is the so-called conductivity mismatch [1,22,23]. To solve the conductivity mismatch problem two solutions are possible: (i) a fully spin-polarized FM material, e.g. a half-metal such as LSMO which is an attractive rare-earth compound characterized by nearly 100% spin-polarization of charge carriers [24] is used as the electrode material. Recently, LSMO electrodes have been applied in spintronic devices with organic semiconductor thin films [8,13,19]. (ii) The introduction of a thin tunnel barrier (e.g. Al_2O_3) as a large spin-dependent resistance in between the ferromagnetic electrode and the organic semiconductor is another possible solution for the conductivity mismatch problem [1,23]. The fabrication of a tunnel barrier, Al_2O_3 in our case, is important to overcome the conductivity mismatch between the metal electrodes and a semiconductor spacer, which is a problem in semiconductor spintronic devices [22,23]. The insertion of a thin tunnel barrier of Al_2O_3 has been successfully applied in spintronic devices [11,19].

Up to now only a few studies on interfacial properties of spintronic relevant contact materials (e.g. LSMO, Co) and organic semiconductors using photoemission spectroscopy were published. Zhan et al. have published in 2007 and 2008 interface studies for the organic semiconductor Alq_3 in contact to the electrode materials LSMO [25] and Co [26]. The interfacial properties between the two organic semiconductors α-sexithiophene (α-6T) and copper-phthalocyanine (CuPc) were published in 2008 and 2009 by our group reflecting the influence of the applied in situ cleaning [27] as well as ex situ cleaning [28] procedure to the used LSMO thin film contacts. The interface properties of the organic semiconductor pentacene in contact with Co were previously published by Tiba et al. [29] and Popinciuc et al. [30]. The influence of a thin tunnel barrier on the interfacial structure of interfaces between Co and pentacene was studied in 2007 by Popinciuc et al. [31]. In the past, the interfaces between various metallic electrodes and organic semiconductors have been studied widely [32–37]. Most of these interfaces are characterized by the presence of an interface dipole confined to a thin interfacial layer, whereas the origin of this interface dipole is not fully understood yet [38,39].

In this contribution, we present a detailed analysis of interfaces for the two archetype organic semiconductors, pentacene and rubrene, in contact with ex situ cleaned Co as well as Al_2O_3/Co thin films. We have studied the energy-level alignment of ex situ, acetone cleaned Co and Al_2O_3 contacts to the organic semiconductors pentacene and rubrene using combined X-ray and ultraviolet photoelectron spectroscopy. Our results demonstrate that the work function under these conditions is smaller than in the in situ cleaned, atomically clean case. Moreover, all studied interfaces are characterized by very small, short range interface dipoles and substantial injection barriers for holes. Our core-level photoemission spectroscopy measurements rule out chemical reactions for all three interfaces. This represents essential information in view of their use in organic spintronic devices.

2. Experimental details

The presented combined X-ray and ultraviolet photoemission spectroscopy studies were performed using a commercial PHI 5600 spectrometer, which is equipped with two photon sources. Monochromatized photons with an energy of 1486.6 eV from an Al Kα source for X-ray photoemission spectroscopy (XPS) and photons from a He-discharge lamp with an energy of 21.21 eV for ultraviolet photoemission spectroscopy (UPS) are provided. All ultraviolet photoemission spectroscopy measurements were done by applying a bias voltage of −9 V to distinguish between the analyzer and sample cutoffs and the spectra were additionally corrected for the contributions of He-satellite radiation. The total energy resolution of the spectrometer was determined by analyzing the width of an Au Fermi edge to be about 350 meV (XPS) and 100 meV (UPS), respectively.

As substrates for our organic layer, we used ex situ cleaned polycrystalline Co (40 nm) and Al_2O_3 (3 nm)/Co (40 nm) films. For the Co as well as the Al_2O_3/Co films a SiO_2 (300 nm) coated silicon wafer was used as substrate. The substrates were cleaned in a cleanroom environment with acetone, IPA, and DI-water. In an UHV chamber (base pressure 1×10^{-10} Torr) Co as well as Al were deposited via e-beam evaporation. First the Co was deposited with an evaporation rate of 0.1 nm/s. For the Al_2O_3/Co substrates Al was evaporated in a second step also with a rate of 0.1 nm/s. The Al coated samples were transferred to a load lock for the plasma oxidation without breaking the vacuum. The plasma oxidation was performed with a pressure of 100 mTorr and a voltage of 800 V, giving a current of 85 mA. The Al/Co samples with a thickness of the Al layer of max. 2.5 nm were oxidized for 30 min resulting in a 3 nm thick Al_2O_3 layer thickness. We determine the height of the Al film before the oxidation with a crystal inside the evaporator. The thickness of the Al_2O_3 layer will be about 20% larger than that of the Al film. The Co and Al_2O_3/Co substrates were exposed to ambient conditions and subsequently cleaned ex situ using acetone (2 min bath in acetone and additionally rinsing the sample for 1 min). We point out that in the fabrication of organic electronic devices, e.g. devices which used $La_{0.7}Sr_{0.3}MnO_3$ as the bottom-electrode material, such a treatment is also applied [7–10]. By applying this kind of ex situ cleaning it is possible to probe bottom contacts as they are applied. In this way we are able to provide an energy-level alignment that is of relevance for the understanding and modeling of corresponding devices. From our core-level photoemission studies we can conclude that the Co as well as Al_2O_3/Co surfaces are still covered with a contamination layer consisting of carbon and oxygen. The composition of this contamination layer was determined to be on average 70% carbon and 30% oxygen. The thickness of the contamination layer is about 1–2 nm. The thickness of the contamination layer was estimated from photoemission intensities. In previous publications it was already demonstrated that ex situ cleaning results in such a contamination layer independent on the individual details of the applied treatment [28,40,41].

Thin films of rubrene and pentacene were deposited by in situ thermal evaporation on Co and Al_2O_3/Co thin films with a typical evaporation rate of 0.1–0.25 nm/min in a preparation chamber (base pressure 2×10^{-10} mbar), which is directly connected to the analyzer chamber. Subsequently, the films were transferred to the analyzer chamber without breaking the vacuum and characterized taking a full-range XPS spectrum. The number of impurities in the films was very small and below the detection limit of the XPS due to the ultrahigh vacuum conditions during the preparation process of the organic films. To estimate the thickness of the individual organic overlayers we have monitored the attenuation of the intensity of the Co2*p* substrate peak for the Co thin films as well as the O1*s* substrate peak for the Al_2O_3/Co films [42,43] due to the organic film. Considering the procedure of Seah and Dench [43] we have calculated the mean free path of the electrons in rubrene to be about 2.27 and 2.11 nm in pentacene films, for the kinetic energy of 955.6 eV for the O1*s* signal from the contaminated substrates and a density of 1.27 g/cm^3 for rubrene and 1.32 g/cm^3 for pentacene [44,45]. We point out that this procedure to determine the thickness of the organic layer is only correct for layer-by-layer growth. If the organic film does not grow uniformly, this method underestimates the film thickness.