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Assistance of partially reduced MoO_3 interlayer to hole-injection at iron phthalocyanine/ITO interface evidenced by photoemission study

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ABSTRACT

Molybdenum trioxide (MoO_3) has been widely used as an interlayer between electrode and functional organic layer inducing significant improvement in the performance of organic electronic and optoelectronic devices such as organic light-emitting diodes (OLEDs) and organic photovoltaics (OPVs). In this work, the electronic structures and energy level alignment at FePc/MoO_3 (3 nm)/ITO and FePc/MoO_x (3 nm)/ITO ($x < 3$) interfaces have been comparatively investigated *in situ* by means of photoemission spectroscopy (PES) in an attempt to understand the influence of MoO_x layer on the interfacial hole injection property. It is found that the electron injection barrier is only 0.45 eV for electron extraction from the highest occupied molecular orbital (HOMO) of FePc to the conduction band of MoO_x. Simultaneously, two gap states at binding energy of 1.15 eV and 2.30 eV present in 3 nm MoO_x, which extend from the valence band maximum of MoO_x to the Fermi level. These gap states are suggested to originate from the partial occupation of Mo 4d states due to the reduction of MoO_3 during the annealing process. Both lowered electron extraction barrier and presence of interfacial gap states appear to assist the hole injection from ITO anode into FePc by the insertion of MoO_x layer.

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1. Introduction

In recent years, transition metal oxides (TMOs) have been recognized as one of the most promising classes of materials that are extensively used as buffer layer between organic layer and electrode to improve the performance of organic semiconductors (OSCs) based electronic devices, such as organic light-emitting diodes (OLEDs) and organic photovoltaics (OPVs) [1–14]. The mechanism responsible for this improvement is primarily attributed to the decrease of the charge injection/extraction barrier at OSC/TMO interface. The lowering of charge injection/extraction barrier is believed to be a consequence of favorable energy level alignment at OSC/TMO interface, resulting from high work function (WF) and deep-lying conduction band (CB) of TMOs for hole injection oxides [15–17]. Thus, a facile electron extraction is allowed from the highest occupied molecular orbital (HOMO) of organic molecules to the CB of TMOs.

Recently a large amount of attention starts being paid to the effects of gap states on the charge injection or transport at OSC/TMO interface [8,11,13,18,19]. It has been realized that the chemical potential of an oxide can be decreased by introducing oxygen vacancies which practically act as n-type dopants and can raise the Fermi level (E_f), leading to the decrease of WF. MoO_3 is a typical oxide with totally empty d-bands (d^0 oxide), which is an insulator in stoichiometric form. Its conduction band minimum (CBM) is mainly composed of empty metal d-states, and valence band maximum (VBM) consists primarily of O 2p states. Oxygen deficiency in stoichiometric MoO_3 generates an obvious density of occupied defect states close to the E_f, making MoO_3 an n-type semiconductor. Further depletion of oxygen atoms forming partially reduced molybdenum oxide (MoO_x) results in a partial occupation of bonding d–d band and even antibonding d–d* band. These characteristic electronic features of MoO_x instead of MoO_3 motivate it a potential candidate as an interlayer between anode and OSCs to improve the charge injection/transportation. Greiner et al. [8] reported a metallic $MoO_{2.5}$ buffer at the $MoO_{2.5}$/N,N′-dipheny-N,N′-bis-(1-naphthyl)-1-1′-bispheny 1-4, 4′-diamine (α-NPD) interface that exhibited a favorable energy level alignment of the oxide but with the VB structure of a metal. Wang et al. [11] achieved an enhancement in the optoelectronic properties of OLEDs by treating MoO_3 the hole injection layer with slight argon ion sputtering and attributed it to the formation of gap states which made the sputter treated MoO_3 layer to show metallic characteristics. Vasilopoulou et al. [20] investigated the beneficial role of hydrogenation in tuning the electronic structure of molybdenum oxides. A large improvement in the operational characteristics of both polymer light emitting devices and bulk heterojunction solar cells

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incorporating hydrogenated Mo oxides as hole injection/extraction layers was achieved as a result of favorable energy level alignment at the metal oxide/organic interface and enhanced charge transport through the formation of a large density of gap states near the E_f.

In this study, we comparatively investigate the effects of an annealed MoO_3 layer (MoO_x) and the as-deposited one inserted between p-type organic materials (FePc) and ITO on the interfacial electronic properties, and examine how MoO_x tunes the interfacial hole injection barrier. Our choice of FePc as a representative of p-type organic semiconductors is motivated by its widespread applications in organic electronics, such as OPVs [21,22], organic thin film transistors [23] and organic sensors [24,25]. The interfacial electronic structures of FePc/MoO_3/ITO and FePc/MoO_x/ITO are derived from *in situ* synchrotron radiation photoemission spectroscopy (SRPES) measurements. By comparing the energy level alignment diagrams, it is found that the introduction of a MoO_x interlayer at the interface between p-type organic materials and ITO can effectively improve the interfacial hole injection/transportation through two independent channels, one is the electron exaction from FePc HOMO into MoO_x CB and the other is an efficient hole transport from ITO into FePc through the gap states of MoO_x locating close to the E_f.

2. Experimental details

The SRPES and XPS experiments were carried out *in situ* in an ultra-high vacuum (UHV) chamber (base pressure about 1×10^{-11} mbar) at the Surface Physics Endstation of the National Synchrotron Radiation Laboratory (NSRL), Hefei, China. The endstation was equipped with a VG ARUPS-10 hemispherical electron energy analyzer, and the total resolution of the PES spectra was about 0.15 eV. More detailed descriptions of the beamline and endstation can be found elsewhere [26]. The ITO-coated glass substrates were purchased from MTI Corporation, China. The clean surface of ITO was obtained with slight Ar ion sputtering and annealing cycles until no obvious carbon contaminations were observed by XPS. The highly purified MoO_3 (≥99.9%) and FePc (≥95%) powders were purchased from STREM CHEMICALS, INC. and TOKYO KASEI KOGYO CO., LTD., respectively. MoO_3 and FePc were sublimated onto the ITO substrate using two standard K-cells made by CreaTec Fisher & Co. Gmbh with pressure of the growth chamber better than 5×10^{-9} mbar. The growth rates of MoO_3 and FePc were estimated to be 2.0 and 4.4 Å/min, respectively by the attenuation of In 3d XPS peak intensity. In order to modify MoO_3 with oxygen vacancies, the as-deposited MoO_3 film was experienced thermal annealing *in situ* at 200 °C for 30 min then partially reduced MoO_x was yielded.

The SRPES and XPS spectra were recorded stepwise after each deposition. In the measurements of VB structure, an excitation of 70 eV was utilized. The binding energy (BE) was calibrated and referenced to the E_f of a sputtered gold foil which was spot welded on the manipulator with good electrical contact to the samples. The sample WF was determined according to the equation $\Phi = h\nu - W$, where W is the spectra width, *i.e.* the energy difference between the secondary electron cutoff and the substrate Fermi level. In order to obtain the secondary electron cutoff, a −7 V bias was applied to the sample, which accelerated all the photoelectrons with higher kinetic energy (KE) to overcome the WF of the analyzer. All the PES spectra were collected at room temperature.

3. Results and discussion

Firstly, we investigate the variation of sample WF and charging effect as a function of MoO_3 nominal thickness on clean ITO surface. Before deposition of MoO_3, the WF of clean ITO is measured to be 4.40 eV, in agreement with values in literatures [15,27,28].

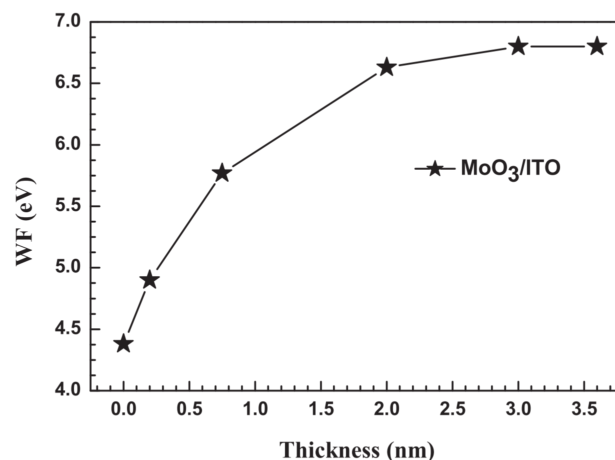

Fig. 1. The evolution of work function with the thickness of MoO_3 films deposited on ITO.

As shown in Fig. 1, the incremental growth of MoO_3 leads to an increase of the WF. The increase saturates at a nominal thickness of about 3 nm, presumably when MoO_3 forms a continuous film. Beyond this point, the WF is fixed to around 6.85 eV, in excellent consistence with the value reported previously [15]. In addition, the charging effect of such thickness of MoO_3 film was not observed in our photoemission measurements. Thus the 3 nm MoO_3 film is selected as the buffer layer between ITO and subsequently deposited FePc film in this study.

Fig. 2 displays the evolution of secondary electron cutoff and VB with the stepwise deposition of FePc on a 3 nm MoO_3 film covered ITO substrate. With increasing FePc deposition, the secondary electron cutoff shifts gradually toward lower KE, equivalent to a downward movement of the vacuum level (E_{vac}) with respect to the E_f, indicating a decrease of the WF. At the nominal thickness of 2.35 nm, the variation of the sample WF saturates and an overall WF decrease of 1.65 eV is present.

In the valence region, the pristine 3 nm MoO_3 film on ITO is mainly dominated by a representative O 2p feature at binding energy of 3–9 eV, and the VBM is located at 2.85 eV below E_f, thereby, the corresponding CB edge is at 0.35 eV above E_f by

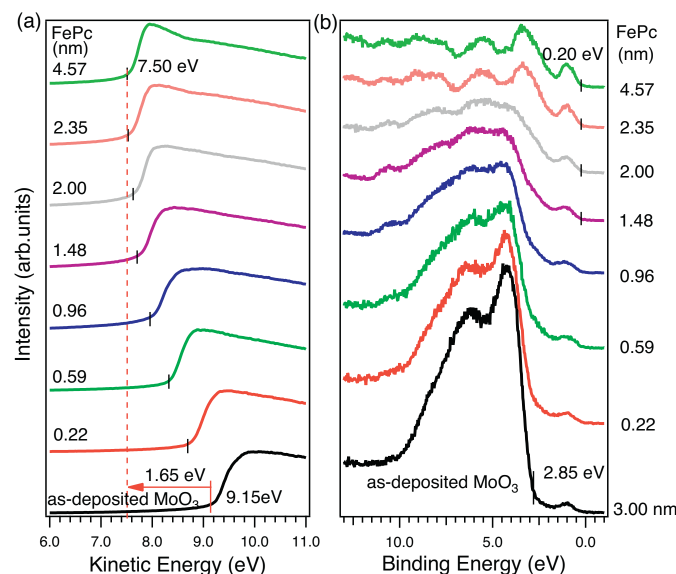

Fig. 2. (Color online) The evolution of secondary electron cutoff (a) and valence band (b) as a function of FePc thickness on MoO_3/ITO. The photon energy is 70 eV.

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