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Effect of oxygen plasma treatment on air exposed MoO_x thin film

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Oxygen plasma (OP) treatment on air exposed molybdenum oxide (MoO_x) has been investigated with ultraviolet photoemission spectroscopy (UPS) and angle resolved X-ray photoemission spectroscopy (AR-XPS). It was found that the work function (WF) reduction of MoO_x by air exposure can be recovered partially by OP treatment on the surface. The overall recovery was measured to be slightly more than 64%, which was adequate to provide a hole extraction layer to many hole-conducting organic materials. The incompleteness of the WF recovery could be attributed to the formation of a very thin layer of oxygen rich absorbents on top of the evaporated MoO_x film after OP treatment. AR-XPS showed that OP treatment shifted the core levels of oxygen and molybdenum about 0.1 eV toward the lower binding energy (BE), and confirmed the existence of oxygen deficiency in the evaporated MoO_x film. We also investigated the electronic energy level evolution of copper phthalocyanine (CuPc) on MoO_x/ITO by UPS. With the deposition of CuPc on OP treated MoO_x we observed band bending and the highest occupied molecular orbital (HOMO) level of CuPc was almost pinned to the Fermi level, which indicates the possibility of efficient hole injection with the OP treated MoO_x film.

1. Introduction

Molybdenum oxides (MoO_x) as well as other transition metal oxides (TMO) have been extensively used as hole injection layers in organic light-emitting diodes (OLED) [1–6] and hole extraction layers in organic photovoltaic (OPV) cells [7–10]. It is known that the extensive application of MoO_x on organic electronics can be partly attributed to its high work function (WF) [11,12]. Kröger et al. [13] reported a measurement result of 6.86 eV for the surface WF of MoO_x, which was larger than ionization potentials (IP) of most organic semiconductors. Other reports [14–16] argued that MoO_x had the ability to decrease the hole injection barrier at anode/organic interfaces due to its high WF. Furthermore, MoO_x is an n-doped material and has to rely on the high work function to improve hole extraction, in contrast to p-type oxides (like NiO). However, the WF of MoO_x film is especially sensitive to environmental conditions [17] such as air exposure, humidity, temperature and so on. Many investigations [17–19] have confirmed that the surface WF of MoO_x films reduced significantly after exposure to air even for a short time. The reduction of surface WF decreases the efficiencies of hole injection or extraction when the MoO_x films are used as anode/organic interlayers. A lot of attempts [20–22] have been made to recover the high WF of air exposed MoO_x films. In our previous work [17], we observed a substantial WF recovery of air exposed MoO_x films with vacuum annealing. The recovery of WF was measured to be over 60% at the saturation annealing temperature of about 460 °C. However, it remains to be seen if the WF

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recovery of air exposed MoO_x films by vacuum annealing is sufficient and whether other approaches exist. Given that the oxygen plasma (OP) treatment is a common method to clean surfaces in device fabrication, it is interesting to investigate whether OP treatment can be used as an efficient way to recover the WF of MoO_x films.

In this paper we report the effect of OP treatment on the electronic energy levels of air exposed MoO_x films using UPS and AR-XPS. We monitored the changes in the valence electronic structure and WF of the surface as a function of OP exposure. The vacuum deposited MoO_x film started with high initial WF values, but with air exposure the surface WF gradually reduced to much lower ones. The reduced WF was partially recovered by OP treatment, and the recovery depended on the time span of the OP treatment. Although the OP treatment could not overcome completely the effect by the thin layer of oxygen rich absorbents on the top of the evaporated MoO_x film, it surely regained a chemical environment similar to the vacuum evaporated MoO_x film. With further evaporation of CuPc, we showed that the interface was characterized by band bending in CuPc and the HOMO level almost pinned to the Fermi level, which indicated the reduction of the hole injection barrier with the OP treated MoO_x film.

2. Experimental

The UPS and AR-XPS experiments were performed using a VG ESCA Lab system equipped with a He I (21.22 eV) gas discharge lamp and a Mg Kα X-ray source (1253.6 eV). The ultrahigh vacuum (UHV) system consists of a spectrometer chamber, an in situ oxygen plasma (OP) treatment chamber, and an evaporation chamber with a precision leak valve. The base pressure of the spectrometer chamber and evaporation chamber are typically 8×10^{-11} torr and 5×10^{-8} torr, respectively. We recorded the UPS spectra with the samples biased at −5.0 V to observe the true low energy secondary cut-off. The UV light spot size on samples was about 1 mm in diameter. The substrate was a borosilicate glass from Corning, coated with 250 nm thick conducting indium tin oxide (ITO). At first the ITO substrate was treated in OP for 25 s. A 100 Å MoO_x film was then thermally evaporated in the evaporation chamber onto ITO, and the thickness of evaporated film was monitored by quartz crystal microbalance. After a 10^{12} L ($1\ L = 10^{-6}$ torr second) air exposure, subsequent 15, 30, and 45 s OP treatments were carried out. The plasma treatment was performed at an oxygen working pressure of 600 m torr with a bias voltage of −500 V. The UPS and AR-XPS spectra were recorded at each step in order to follow the evolution of both the frontier orbital and the core levels of the film. Furthermore, 0–250 Å CuPc films were evaporated on the MoO_x film and then measured by UPS at each steps. Another 100 Å MoO_x film was thermally evaporated onto ITO in order to investigate the dependence of electronic structures on the take-off angle. The instrumental resolution for UPS measurements was chosen to be 0.20 eV. The XPS resolution was ~1.4 eV. All measurements were done at room temperature.

3. Results and discussion

In Fig. 1, the UPS spectra of the MoO_x on ITO are presented as a function of the air exposure and OP treatment. Fig. 1(a) and (b) shows the cut-off and the valence band (VB) regions of the UPS data, respectively. All the spectra were normalized to the same height for visual clarity. The short vertical bars denote the peak positions of VB region of MoO_x film. The WF of the in situ OP treated ITO was measured to be 5.66 eV which increased to 6.65 eV upon the deposition of 100 Å MoO_x. For the evaporated MoO_x film, a characteristic peak could be observed at ~3.91 eV in binding energy (BE) value corresponding to a VB maximum of 2.78 eV. After a 10^{12} L air exposure the surface WF of MoO_x sharply decreased to 5.54 eV and the decrement of WF was 1.11 eV, while the VB maximum shifted toward the higher BE a bit, from 2.78 eV to 2.98 eV. With the subsequent process of OP treatment, the reduced WFs due to air exposure were recovered gradually and while the peak positions of VB region shifted back slightly toward lower BE.

To highlight the effect of OP treatment on air exposed MoO_x film, in Fig. 2, the WF and the VB maximum of MoO_x film are presented as a function of increasing span of OP treatment time. From Fig. 2(a), the WF of MoO_x after a 10^{12} L air exposure was 5.54 eV according to the previous section, which was consistent with our previous report [11]. The WFs were measured to increase to 6.07, 6.18 and 6.26 eV for 15, 30 and 45s OP treatment, respectively. It is obvious that when the span of OP treatment time is more than 30s, the increase becomes slower and more gradual, which indicates that the WF of MoO_x is close to saturation after OP treatment for 45s. From Fig. 2(b), the VB maximum of the air exposed MoO_x film was measured as 2.98 eV, which reduces with increasing the time of OP treatment and nearly saturates at 2.89 eV after 45s OP treatment. It is clear that the change of the VB maximum is much less than that of the WF, suggesting that the OP treatment affects mainly the surface instead of doping charges in the MoO_x film.

It is not surprising that air exposure of MoO_x film can reduce the WF. Meyer et al. [23] showed that exposure to

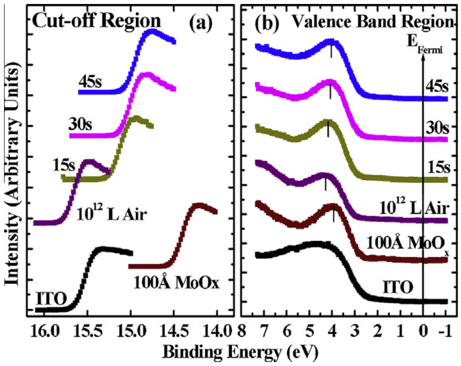

Fig. 1. Evolution of the cut-off (a) and the VB edge (b) of the UPS spectra of the MoO_x on ITO as a function of the air exposure and OP treatment. The vertical bars denote the peak positions of VB region of MoO_x.