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Sputter deposition of indium tin oxide onto zinc pthalocyanine: Chemical and electronic properties of the interface studied by photoelectron spectroscopy

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ABSTRACT

The interface chemistry and the energy band alignment at the interface formed during sputter deposition of transparent conducting indium tin oxide (ITO) onto the organic semiconductor zinc phtalocyanine (ZnPc), which is important for inverted, transparent, and stacked organic light emitting diodes, is studied by in situ photoelectron spectroscopy (XPS and UPS). ITO was sputtered at room temperature and a low power density with a face to face arrangement of the target and substrate. With these deposition conditions, no chemical reaction and a low barrier height for charge injection at this interface are observed. The barrier height is comparable to those observed for the reverse deposition sequence, which also confirms the absence of sputter damage.

1. Introduction

Organic light emitting diodes (OLEDs) are of great importance for future display applications [1]. Moreover they are investigated for lighting systems because of the possibility to create large area white light emitting sources [2]. Flexible and transparent OLED light sources and displays can be prepared. Thin semitransparent metal films [3] or transparent conducting oxides (TCOs) [4] are used in OLEDs as transparent electrodes. Among the TCOs, Sn-doped indium oxide (ITO) is the most widely used material, because of its outstanding optical and electrical properties [5,6]. ITO is a degenerate n-type semiconductor with a high charge carrier density in the conduction band [7]. The work function of ITO [8] allows for good injection of charge carriers (holes) into a hole conducting organic semiconductor [9–11], which is also a crucial point for the luminous efficacy of the organic light emitting diodes. The organic molecule zinc phtalocyanine (ZnPc) is a chemical stable complex well studied in literature [12,13]. The material is considered for organic solar cells [14] as well as for OLEDs as hole transport/injection layer [15].

Fully transparent OLEDs may be prepared with TCO bottom and top electrodes. Transparent top electrodes can also be used for top emitting inverted [16,17] or stacked OLEDs [18]. High temperatures are excluded for the deposition onto organic materials due to their low sublimation temperatures. While ITO with the best optical and electrical properties is commonly deposited by magnetron sputtering at elevated substrate temperature [19], preparation of ITO at room temperature may lead to amorphous film growth and electrodes with higher resistivity [20,21].

Sputter deposition is accompanied by plasma excitation leading to excited atoms and ions [22,23], which are chemically reactive and are expected to cause chemical decomposition of the organic molecules as schematically illustrated in Fig. 1. This *sputter damage* may result in formation of charged defects modifying the barrier for charge injection or to trap states in the organic material reducing carrier mobility. One strategy to reduce sputter damage is provided by using mild deposition parameters, which can be established by low deposition power, high process gas pressure and large target-to-substrate distance [24].

So far, the chemical stability of organic layers during sputter deposition of transparent conducting oxides has not yet been explicitly demonstrated. In this contribution we present a X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) study of the interface formation between ZnPc and ITO, investigated by repeated deposition and analysis cycles. The experiments provide information on chemical reactivity of the interface as well as on the energy band alignment at the interface. In contrast to the many studies reported in literature, the ITO film is not used as substrate for the growth of an organic layer but deposited onto the organic material by magnetron sputtering. Therefore the injection barrier at this interface cannot be modified by a post deposition treatment of the TCO material.

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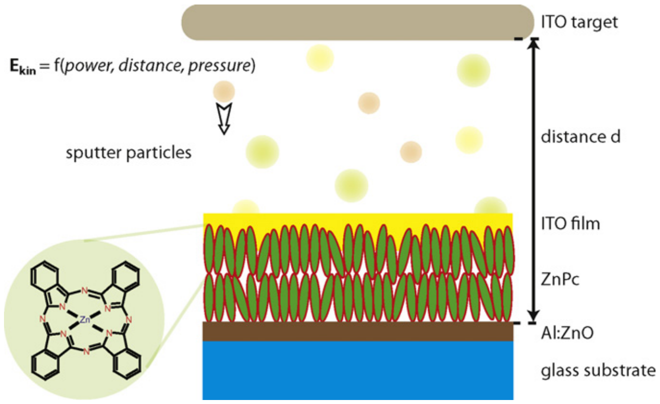

Fig. 1. Schematic representation of the r.f. magnetron sputter process of ITO on top of the organic substrate ZnPc investigated in the present work. The kinetic energy of the sputtered particles, when arriving at the surface of the substrate, depends on the sputter power density, the deposition pressure and the target to substrate distance. The particle flux contains indium, tin and oxygen atoms. Moreover also molecules can be formed during the sputter process. Argon process gas atoms are omitted for clarity.

2. Experimental

The experiments were performed in an ultra high vacuum system combining different preparation chambers with a surface analysis unit (Physical Electronics PHI 5700) for in situ XPS and UPS measurements [25]. Contamination free samples can be prepared and measured without breaking vacuum. The base pressure of the system DAISY-Mat (DArmstadt Integrated SYstem for MATErials research) was 10^{-9} mbar. X-ray photoelectron spectra were recorded using monochromated Al Kα ($h\nu = 1486.6$ eV) radiation providing an overall energy resolution of approximately 0.4 eV as determined from the Gaussian broadening of the Fermi edge of a sputter cleaned silver sample. UP spectra were measured in normal emission with He I excitation ($h\nu = 21.22$ eV) from a gas discharge lamp and a substrate bias of −1.5 V. To confirm the absence of surface contaminations, XPS emission lines of oxygen and carbon were used for the ZnPc and the ITO film, respectively. Binding energies are all given with respect to the Fermi energy of the metallic sample holder, which has been derived prior to the measurement using a sputter cleaned Ag sample. Binding energies have a typical uncertainty of ±50 meV.

The organic ZnPc substrate film was evaporated from a home made temperature controlled evaporation source with an alumina crucible and a tantalum heating wire. The source temperature was set to 360 °C resulting in a chamber pressure of 5×10^{-9} mbar during deposition. Aluminum doped ZnO coated glass was used as substrate for avoiding charging effects during the XPS measurements. The deposition time of the ZnPc film used as substrate for the stepwise ITO deposition was set to 360 s, resulting in a film thickness of 20 nm. This is sufficient to completely cover the ZnO:Al substrate and thin enough that no noticeable charging occurs during the photoemission measurement.

The ITO films (In_2O_3:Sn with SnO_2=10 wt.%) were deposited at room temperature by radio frequency (r.f.) magnetron sputtering (13.56 MHz) in a custom made chamber from an 2 in. ceramic target with a power density of 0.25 W/cm^2. The target to substrate distance was set to 10 cm and the deposition pressure to 0.5 Pa in pure argon atmosphere. With these deposition conditions, the deposition rate is determined as 0.7 nm/min. The target was conditioned by pre-sputtering with the given deposition conditions for 30 min prior to each deposition step. Deposition times can be adjusted with an uncertainty of ∼1 s by rotating the substrate with a manipulator into the region of the particle flux. After each deposition step a complete XPS and UPS characterization was performed.

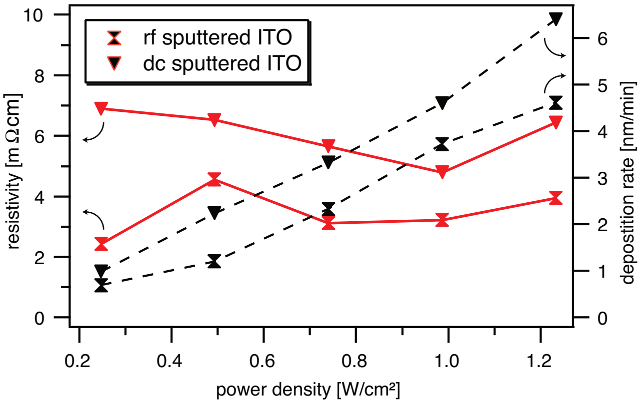

Fig. 2. Resistivity and deposition rate of ITO thin films sputtered at room temperature in argon atmosphere with various sputter power densities and plasma excitations.

For electrical, and structural characterization, ITO films were deposited onto glass substrates using mostly the same conditions as those selected for the interface experiments. The thickness of the films was 100 nm. Analysis was carried out using a Keithley 2400 source meter with a linear 4-point contact geometry (resistivity) and a PTS 3003 Seifert X-ray diffractometer.

3. Results and discussion

3.1. Properties of ITO films

The deposition of oxides onto molecular organic substrates requires mild deposition conditions including low substrate temperatures. While extensive literature exists describing the properties of ITO films deposited by magnetron sputtering at high substrate temperature (typically 400 °C) [7,19,26–28], only a few reports were dedicated to properties of films deposited at room temperature [20,26,29]. In order to identify suitable deposition conditions, ITO films were sputtered at room temperature with r.f. and d.c. plasma excitations at different power density. The lowest resistivity of ∼2.4 mΩ cm is obtained for r.f. excitation and lowest power density of 0.25 W/cm^2 (compare Fig. 2), which are the parameters used for the interface experiment. The magnitude of resistivity compares to ∼4 mΩ cm [26] and ∼0.7 mΩ cm [29] reported in literature for room temperature magnetron sputtered films. It is about one order of magnitude lower than the resistivity of films deposited from the same target at 400 °C [30]. The plasma absorption edge at longer wavelengths is not observed in transmission spectra (not shown) for the room temperature deposited films as also observed previously [26]. The films also do not exhibit the well-known blue-shift of the absorption edge (Burstein-Moss shift) of degenerately doped material. This indicates that the lower conductivity is mainly due to a lower carrier concentration.

An X-ray diffraction pattern recorded in Bragg–Brentano geometry from an ITO thin film sputtered at room temperature onto glass is shown in Fig. 3. Noticeable reflections related to the crystalline bixbyite phase of In_2O_3 [31] are observed, indicating that the film is not completely amorphous. This compares well with the dependence of the crystalline structure on the deposition pressure reported in literature for ITO by Song et al. [32]. The texture coefficient calculated according to Ref. [48] is the highest (1.7) for the (2 2 2) reflex, indicating a slightly preferred orientation of crystallites with (2 2 2) planes parallel to the surface.

This may have important consequences for the interface formation due to the dependence of the work function on crystallographic