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The Role of Copper Phthalocyanine for Charge Injection into Organic Light Emitting Devices

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Abstract

We have scrutinized the charge injection efficiency from plasma treated indium tin oxide anodes into CuPc using single layer diodes fabricated under inert conditions. Current-voltage characteristics demonstrate that the hole injection from ITO into CuPc is identical for all devices, regardless of the oxide electrode surface treatment. When the devices are aged for several months in a glovebox, the current-voltage characteristics in the reverse differ in a striking way. We demonstrate that these characteristics are due to the interplay between two features, the formation of an oxygen enriched interface layer at the electrode and the doping of the CuPc film due to diffusion of oxygen out of the oxide electrode. By electro-absorption measurements and Kelvin Probe surface potential measurements we obtain a coherent picture of the most influent factors determining the characteristics of freshly fabricated and aged devices. As an important conclusion, we find that the oxygen plasma treatment of the indium tin oxide electrode produces a much more stable surface with regards to oxygen diffusion.

Introduction

The recent commercialization of organic electroluminescent flat-panel displays,[1] has definitely swept away the criticism that light emitting devices based on thin organic films would lack the stability required in technological applications. The remarkable advancement in device lifetime has been made possible due to a number of improvements including the device architecture and the use of highly stable and efficient materials but also due to the prevention of air contamination or the operation mode used to drive the devices.

Particular attention was given to the engineering of charge injecting contacts, since this approach would lead to lower driving voltages and longer lifetimes. A dramatic enhancement of the device stability was achieved by depositing a copper phthalocyanine (CuPc) layer on the indium tin oxide (ITO) anode.[2] Since then, an important number of works have concentrated on this issue. Enhancement of interface stability due to improved wetting of the organic materials on the ITO anode was reported.[3]

Recent works focussed on the injection of positive charge carriers from ITO. The role played by the thin CuPc interlayer is somewhat controversial. It appears that both injection enhancement[4] as well as injection lowering[5] are observed when using a CuPc interlayer for hole injection into the hole conducting material. Furthermore, this difference seems to depend on the pretreatment of the ITO electrode. If an oxygen plasma was used, the introduction of a CuPc interlayer between ITO and the hole transporting N,N'-diphenyl-N,N'-bis(l-naphthyl)-1-1'-biphenyl-4,4'diamine (α-NPD) deteriorates hole injection. On the contrary, if the ITO electrode was just cleaned in an ultrasonic bath using various organic solvents, the presence of the CuPc interlayer between ITO and α-NPD ameliorates hole injection. Even more, once a thin CuPc interlayer is used, current injection from ITO is no longer dependent on the surface treatment of the oxide anode[6].

In order to find an explanation to these observations, we have investigated single layer CuPc devices. Current-voltage characteristics in the forward and reverse direction were combined with electro-absorption. Using Kelvin Probe surface potential measurements we were able to observe the interface formation between ITO and CuPc layer by layer.

Experimental

The device structure we used in this study is illustrated in Fig. 1. ITO glass (Balzers, 25 Ω/square) was cleaned by ultrasonic agitation in organic solvents followed by mechanical scrubbing using a nonionic detergent. The conductive glass substrates were then thoroughly rinsed in pure water and dried. Some ITO substrates were treated by an argon or oxygen plasma for 5 minutes at a power of 10W and a gas pressure of $2 \cdot 10^{-1}$ torr. These substrates were then conveyed to a vacuum chamber where the 210 nm thick CuPc films were vapor deposited. CuPc (TCI) was purified by gradient sublimation before use. The 100 nm thick aluminum top electrode was vapor deposited in a second chamber. All thermally evaporated materials were deposited at a base pressure of $5 \cdot 10^{-7}$ torr. The device was then transferred to a glovebox for current-voltage characterization and storage. It has to be pointed out that the whole fabrication sequence including the plasma treatments was carried out under inert conditions to avoid any air contamination.

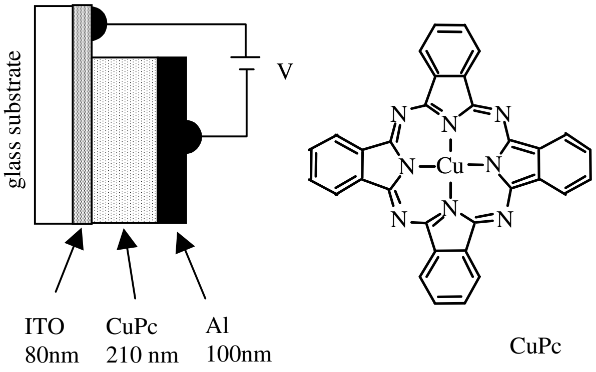

Figure 1. Single layer device structure comprising a single layer of copper phthalocyanine(CuPc) sandwiched between an indium tin oxide (ITO) and an aluminum electrode. The layer thicknesses are also indicated in the graph.

Current-voltage data were obtained from a Keithley 236 source measure unit. For the electroabsorption measurements the sinusoidal voltage output of 2.5V from a SR830 lock-in amplifier was superposed to the DC offset from the Ketihley 236 voltage source. The absorption change in the thin film due to the alternating electric field was detected in reflection mode, similarly to the method used by other groups.[6] Monochromatic light was sent through the device from the glass side and reflected at the aluminum electrode. Absorption changes in phase with the modulation frequency of the applied electric field were detected by a photomultiplier tube and measured by the lock-in amplifier. Typically, a frequency of 700 Hz was used in these experiments. All electrical and optical measurements were carried out under inert atmosphere and the devices were not exposed to air unless explicitly stated.

Kelvin probe surface potential measurements were carried out in a vacuum chamber with a base pressure of $2\cdot10^{-7}$ torr using a vibrating gold reference electrode. The special configuration of the chamber allowed to apply argon and oxygen plasma treatments to the ITO substrate and to deposit thin films of CuPc on top of ITO without breaking the vacuum.

Results and Discussion

Current-Voltage Characteristics

The current voltage characteristics are measuring the current density through the device, which is governed by both, charge injection form the electrodes and charge transport through the organic layer. Generally, by applying a voltage to the device, positive carriers can be injected form the anode into the highest occupied molecular orbital (HOMO) of the organic material while negative carriers are injected form the cathode into the lowest unoccupied molecular orbital (LUMO). In the case of CuPc the energy level of the HOMO is at -5.3 eV while the LUMO has an energy of -3.5 eV.[8] Efficient injection is only then possible, when the electrode work function matches the energy levels of the respective molecular orbitals. In our case we used ITO and aluminum as electrodes. ITO has been subject to extensive investigations. Its work function can be changed enormously by chemical and physical treatments.[9-12] In this work we were mainly interested in argon plasma and oxygen plasma treated ITO. By Kelvin Probe measurements in high vacuum, we measured work functions of 5.8 eV and 4.8 eV for oxygen plasma and argon plasma treated ITO, respectively. The as-cleaned ITO without further plasma treatment yielded a work function of 5.2 eV. Obviously ITO is an appropriate anode for hole injection into CuPc. On the contrary, aluminum having with a work function of 4.2 eV will be a very inefficient hole injecting anode. Given the large energy barrier between aluminum and the LUMO of CuPc, it is also pretty clear that neither ITO nor aluminum will be an efficient electron injecting cathode. Thus we assume that the current density through the device in Figure 1 is principally a hole current.

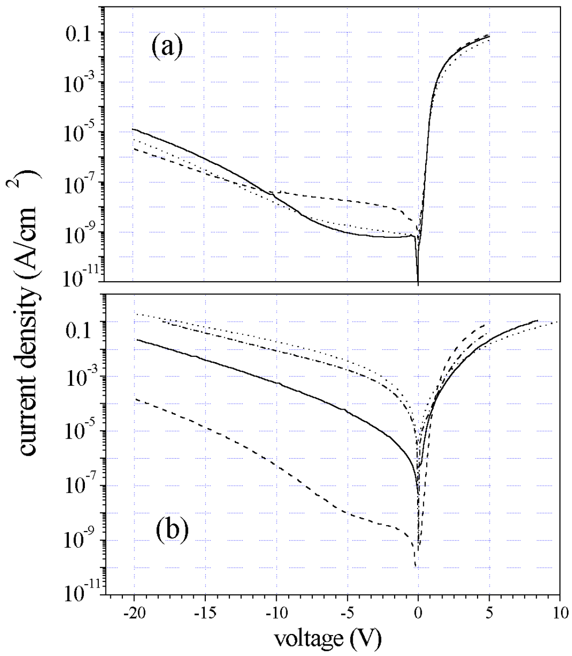

Figure 2. Current-voltage characteristics of single layer devices consisting of a 210 nm thick CuPc layer sandwiched between an ITO and an aluminum electrode. The devices differ by the treatment of the ITO electrode: as-cleaned (—), oxygen plasma (---), argon plasma (····). The devices were either measured directly after fabrication (a) or after five months storage in a glovebox (b). One device comprising an oxygen plasma treated ITO electrode was deliberately exposed to air for several days (-·-·-).

Figure 2a shows the current voltage characteristics for three devices in the forward and reverse bias direction. All devices are identical except for the treatment of the ITO electrode. The current density in the forward direction does not depend significantly on the surface treatment of the anode, despite the fact that the electrode work functions differs significantly. Furthermore, the diodes have a high rectification ratio of about 10^8 at a bias of 5V. In the reverse direction, the current densities are low for all the devices underlining the bad injection from aluminum. The device characteristics change radically with time. Figure 2b shows the current-voltage characteristics of the same devices as above that were stored for several months in a glovebox with an oxygen and water content less than 1ppm. As shown in Figure 2b, the current in reverse bias for devices using an argon plasma treated and as-cleaned ITO anode has increased by orders of magnitude. In the forward bias, however, the current has dropped considerably. These changes are much less significant in the case of the device using an oxygen plasma treated ITO electrode. Apparently, the modification in the current-voltage characteristics is related to the surface treatment of ITO. One device comprising an oxygen plasma treated ITO electrode was deliberately exposed to air for several days. After air exposure the device characteristics resemble the ones of the device having an argon treated ITO electrode. In particular, the rectifying behavior is lost (see figure 2b).

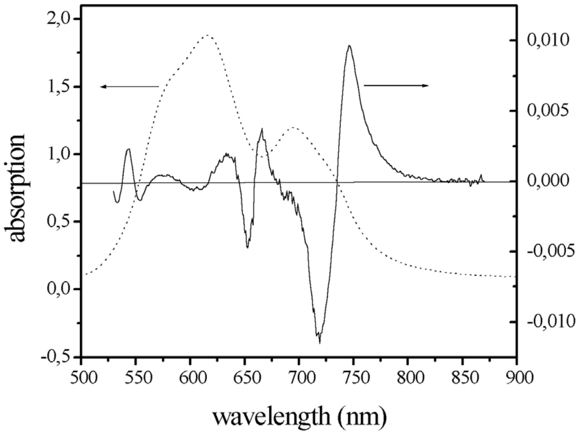

Figure 3. Electroabsorption response as a function of wavelength of a 210 nm thick CuPc film (full line). The spectrum was taken at an applied d.c. bias of –6 V. The absorption spectrum of the film is also given in graph (dotted line).

Electroabsorption Measurements

Electroabsorption spectroscopy measures the effect of an electric field on the absorption of light. The electro-absorption signal at a given photon energy is proportional to the square of the electric field and the imaginary part of the third-order nonlinear susceptibility. This technique has been applied successfully to probe the electric field inside the organic layer of a thin film device.[6] Thereby, the electric filed applied to the device consists of an alternating field added to a d.c. electric field. By varying the applied d.c. electric field, the built-in potential, i.e. the field inside the organic layer can be measured. Typically the field inside the organic layer is not only given by the work-function difference of the contacting electrode, but includes interfacial dipoles[13] and space charges.[14]

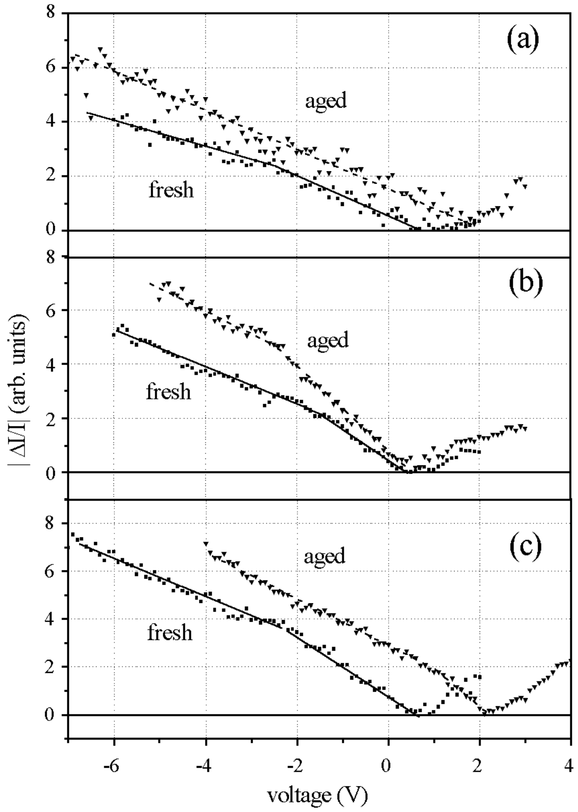

Figure 4. Electroabsorption response at a wavelength of 766 nm as a function of applied DC voltage for devices having ITO electrodes with different treatments. (a) as cleaned ITO, (b) oxygen plasma treated and (c) argon plasma treated ITO. Both measurements, taken directly after fabrication (fresh) and taken after 5 months storage in a glovebox (aged) were taken.

The electroabsorption response ΔI/I is displayed in Figure 3 together with the absorption spectrum of the CuPc film. The spectrum was taken at an applied bias of –6V and is similar to the one measured for matrix dispersed CuPc reported in the literature.[15] Two rather intense peaks at 747 nm and 714 nm can be seen. The precise nature of the nonlinear optical response in a thin CuPc film is beyond the scope of this work. The nonlinear optical properties of various metallophthalocyanines have been investigated in the literature.[16]

To investigate on the electric field inside the organic thin film, the electroabsorption signal at 766 nm was measured as a function of applied d.c. voltage. The voltage dependence of the electroabsorption response is shown in Figure 4. Again three devices were investigated differing only in the ITO electrode treatment. Two measurements are shown for each device. The first measurement was taken directly after device fabrication, the second one was taken five months later.

The built-in potential corresponds to the potential at which the electroabsorption signal vanishes. Right after fabrication, the built-in potential is about 0.7 V for all devices, regardless whether the oxide electrode was treated by an oxygen or an argon plasma. In the simplest case this value corresponds to the work function difference of the contacting electrodes. Since the aluminum electrode was deposited simultaneously on all three devices, one can assume that the aluminum/CuPc interface is the same in all three devices. In order to account for a built-in potential of 0.7 V, the effective ITO work function has therefore to be identical in all three cases. It appears that the ITO/CuPc interface is formed in such a way that the resulting effective work function is identical for all ITO electrodes, despite of the different treatments. Furthermore, the aged devices present an important increase of the built-in potential, except for the devices using oxygen plasma treated electrodes. This behavior is analogous to the current-voltage characteristics discussed above. It can also be seen that the electroabsorption signal does not vary linearly with applied d.c. voltage. It looks as if there were two slopes in the voltage dependence. This feature is dependent on the amplitude of the alternating voltage, on the modulation frequency and on temperature. It could be related to the injection of positive charge carriers and will be subject to further investigations.

Kelvin Probe Measurements

Finally, we have analyzed the effect of a thin CuPc layer on the work function of differently treated ITO electrodes. Interestingly the effective work function of the three electrodes turns out to be around 5.4 eV for all three electrodes once a layer of 5 nm has been deposited on the oxide electrode. Most of the work function shift occurs within the first nanometer of the CuPc layer. The work function of 5.4 eV coincides with the HOMO energy of CuPc and indicates that a barrierless contact is formed between CuPc and ITO:

In summary, we have observed by three independent measurements that the effective ITO work function does not depend on its surface treatment, once in contact with a CuPc layer. The Kelvin Probe measurements show that this work function is identical to the HOMO energy level of CuPc suggesting that CuPc is being doped at the electrode interface. It has been shown in the literature that metallophthalocyanine-metal contacts can be modified in a drastic way by doping the contact interface with oxygen.[17] Oxygen molecules bind strongly to metallophthalocyanines and act as p-type dopants. It was also shown by the same authors that the negatively charged oxygen atoms behave as shallow traps for the positive charge charriers. Following this model, we can get a consistent explanation of our findings. The current voltage characteristics of freshly prepared devices are extremely rectifying. After aging in a glovebox with an oxygen concentration lower than 1 ppm the current-voltage characteristics is more symmetric. In particular, the current in reverse bias is increased by orders of magnitude. This means that hole injection from aluminum has been ameliorated due to the doping of the organic layer. In the forward bias, the same doping will reduce the mobility of the charge carriers by introducing shallow traps. The increase in the built-in potential measured by electroabsorption can also be explained by the doping of CuPc. The applied electric field will be screened by the positive charge carriers and will therefore not be equal to the applied electric field. Remains the question of why devices constructed form oxygen plasma treated electrodes show much more stable behavior with time. It seems that the oxygen diffusion from ITO into CuPc is favored for argon plasma treated ITO and as-cleaned ITO while it is hindered when the oxide surface is treated with an oxygen plasma. In an atomic force microscopy study, it has been reported that an oxygen plasma lowers the surface roughness considerably while an argon plasma increases the roughness dramatically.[12] It is possible that the oxygen plasma treatment forms a smooth and compact surface layer on the electrode which prevents oxygen diffusion into the device.

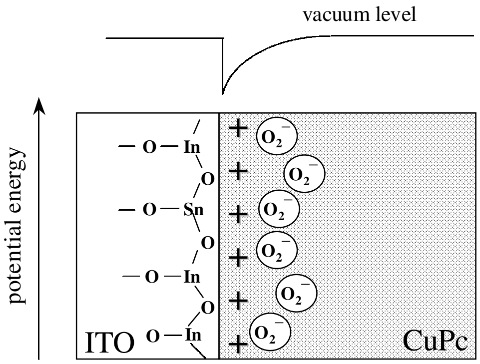

Figure 5. P-type oxygen doping at the ITO/CuPc interface. The negatively charged oxygen atoms give rise to a vacuum level shift that brings the effective work function of ITO on the same energy level as the HOMO of CuPc.

Conclusions

Utilizing current-voltage characteristics, electro-absoption measurements and Kelvin Probe measurements, we have found that ITO forms an excellent contact for hole injectioninto CuPc. The injection efficiency does not depend on the surface treatment of the oxide. Kelvin probe measurements show that the effective ITO work function is equal to the HOMO orbital energy of CuPc, meaning that hole injection is barrierless. The reason for this interface formation is doping of the CuPc interface with oxygen coming from the oxide electrode. The electron acceptor thereby forms an interfacial space charge layer as schematically shown in Figure 5. It turns out that CuPc can either lower the effective ITO work function in the case of oxygen plasma treated ITO or increase the latter in the case of argon plasma treated ITO: This picture explains the apparent contradiction in the literature concerning hole injection into organic hole conductors. It also explains why the device characteristics of multilayer organic light emitting devices is independent of the ITO treatment, once a thin CuPc layer is used at the oxide electrode interface.

When single layer CuPc devices are stored in a glovebox for several months, oxygen diffuses from ITO into CuPc. Thereby the organic layer is being doped with positive charge carriers, giving rise to an increased current density in the reverse bias. In the forward bias, the oxygen dopant acts as shallow trap and decreases the mobility of positive charge carriers slightly as compared to the undoped device. The diffusion of oxygen into the organic layer can be strongly suppressed by an oxygen plasma surface treatment. This finding is of importance in the fabrication of organic optoelectronic devices based on ITO electrodes.

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Biography

Frank Nüesch graduated in physics at the Swiss Federal Institute of Technology (ETHZ) in 1991. He moved to the chemistry department at the sister institute EPFL in Lausanne (Switzerland) to earn a Ph.D. in 1995. After several years of postdoctoral studies, he is now lecturer at the physics department at EPFL. His research on the physics of molecular optoelectronic materials and devices is focused on interdisciplinary fields such as electrode interfaces.