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Relation between molecule ionization energy, film thickness and morphology of two indandione derivatives thin films

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A B S T R A C T

Nowadays most organic devices consist of thin (below 100 nm) layers. Information about the morphology and energy levels of thin films at such thickness is essential for the high efficiency devices. In this work we have investigated thin films of 2-(4-[N,N-dimethylamino]-benzylidene)-indene-1,3-dione (DMABI) and 2-(4-(bis(2-(trityloxy)ethyl)amino)benzylidene)-2H-indene-1,3-dione (DMABI-6Ph). DMABI-6Ph is the same DMABI molecule with attached bulky groups which assist formation of amorphous films from solutions. Polycrystalline structure was obtained for the DMABI thin films prepared by thermal evaporation in vacuum and amorphous structure for the DMABI-6Ph films prepared by spin-coating method. Images taken by SEM showed separate crystals or islands at the thickness of the samples below 100 nm. The ionization energy of the studied compounds was determined using photoemission yield spectroscopy. A vacuum level shift of 0.40 eV was observed when ITO electrode was covered with the thin film of the organic compound. Despite of the same active part of the investigated molecules the ITO/DMABI interface is blocking electrons while ITO/DMABI-6Ph interface is blocking holes.

1. Introduction

In the devices made of organic compounds as organic light emitting diodes (OLEDs), organic photovoltaic (OPV) cells or organic field-effect transistors (OFETs) the thickness of the active organic layers, electrodes and hole or electron transport layers in most cases is only up to 100 nm [1–7]. At this thickness various surface and interface effects should be taken into account. An efficiency of the OLEDs, OPVs and OFETs directly depends on the energy level compatibility at the interface which leads to the good charge-carrier transport across these interfaces. Decrease of the film thickness can lead to the shift of molecule ionization energy and electron affinity levels due to the alignment of Fermi levels [8,9]. In that case the values obtained from bulky layers cannot be used.

Another important issue is the morphology of thin films. Surface roughness, crystal size and phase separation between two different compounds can affect the efficiency of the organic thin film devices [10]. Morphology depends on thin film preparation methods. Thermal evaporation in vacuum is mostly used for low molecular weight compounds. Usually films obtained in this way are polycrystalline [11]. It is possible to reduce the interaction between molecules by attaching bulky groups to the backbone of the molecule [12]. That leads to amorphous thin films formation by wet casting methods such as spin-coating, blade-casting or inkjet printing. Some limited influence on the morphology can be achieved by changing preparation parameters. For the thermal evaporation in vacuum these parameters are evaporation speed, substrate temperature etc. Choice of solvents or solvent additives, temperature and duration of thermal treatment can be varied in the case of the wet casting methods [13–17].

The thickness of spin-coated samples is often measured using a surface profilometer while the thickness of thermally evaporated films can be determined during the evaporation process by a precalibrated quartz resonator. Changes of the resonance frequency due to changes of quartz resonator mass are measured. It leads to a disadvantage of this method – quartz resonator doesn't give any information about the quality and the morphology of thin film as only the change of the mass is measured [18]. During the evaporation process it is impossible to determine whether separate "islands" or a continuous film has been obtained. It is especially important when preparing ultrathin (thickness < 20 nm) films.

In this work dependence of ionization energy and morphology on the layer thickness of two indandione group containing compounds was studied. Series of the samples with different preparation methods were made by taking into account the properties of the studied compounds. Sample surface images were taken by SEM to evaluate the difference in morphology between the samples of both series.

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2. Experimental

2.1. Studied compounds

In this work two organic compounds with the same chromophore were studied: 2-(4-[N,N-dimethylamino]-benzylidene)-indene-1,3-dione (DMABI) and its derivative 2-(4-(bis(2-(trityloxy) ethyl)amino)benzylidene)-2H-indene-1,3-dione (DMABI-6Ph) (see Fig. 1). Optical and photoelectrical properties of DMABI were studied previously [19,20]. It showed relatively good photoconductivity quantum efficiency which could make it a perspective candidate for OPV applications. As DMABI molecules (Fig. 1a) are flat, it tends to form a polycrystalline film which limits its use in real devices. To reduce the interaction between the molecules both methyl groups in the DMABI molecule have been substituted by bulky trityloxyethyl groups (see Fig. 1b). These added bulky groups assist in the formation of amorphous films from solutions. Quantum chemical calculations have shown that the trityloxyethyl groups are inactive and do not change the energy levels and molecular orbitals [12] meaning that any differences between the properties of thin films of DMABI and DMABI-6Ph should arise mainly from the difference in the film morphology. Both of the studied compounds were synthesized in Prof. V. Kokars group at Riga Technical University. Synthesis of DMABI and DMABI-6Ph are described elsewhere [19,21].

2.2. Sample preparation and morphology investigation

Two methods of the sample preparation were used depending on the organic compound structure: thermal evaporation for DMABI and spin-coating for DMABI-6Ph samples.

DMABI was thermally evaporated on the ITO covered glass substrates (Präzisions Glas & Optik GmbH) in a self-made vacuum system. To obtain the necessary vacuum level (better than $1{\bullet}10^{-5}$ mbar) the ILMVAC CDK250 turbomolecular pump system was used. The evaporation rate was about 1 nm/s. Thicker samples were obtained by the longer evaporation time. Nine samples with the thickness from 20 to 2500 nm were made.

DMABI-6Ph samples were made on the ITO covered glass substrates by spin-coating. Necessary amount of DMABI-6Ph was dissolved in the chloroform. Thickness of the samples was altered by changing molecule concentration in the solution. The thickest sample was obtained by using 80 mg/ml DMABI-6Ph solution in chloroform while the thinnest sample had solution concentration of only 0.5 mg/ml. Samples were made using Laurell WS–650Sx–GNPP/Lite spin-coater. Coating parameters were the same for all of the samples: rotation speed of 400 rpm, acceleration-400 rpm/s and spinning time of 40 s. Afterwards the samples were dried on a hot plate at 70 °C for 10 min. 12 samples with the thickness from 5 to 550 nm were made.

In the photoconductivity measurements sandwich type samples with the structure of ITO/organic compound/aluminum electrode were used. The thickness of the organic layer was around 500 nm. Al electrode was thermally evaporated upon the organic layer by the BOC Edwards AUTO 306 Vacuum Coater at the $9{\bullet}10^{-6}$ mbar pressure. The aluminum electrode thickness was approximately 30 nm.

The thickness of all DMABI and DMABI-6Ph samples was measured using Veeco Dektak 150 surface profilometer. The stylus tip diameter was 12.5 µm.

Images of the sample surface were obtained by the scanning electron microscope Tescan Lyra FE-FIB-SEM.

2.3. Energy level determination

Self-made photoemission yield spectroscopy (PYS) system was used to determine the ionization energy of the thin films. The sample and a golden electrode which collected the emitted electrons were placed in the vacuum chamber. During the measurement $1{\bullet}10^{-5}$ mbar pressure was ensured in the chamber. There was about 2 cm gap between the golden electrode and the sample. ENERGETIQ Laser Driven Light Source (LDLS EQ-99) was used as a light source. Wavelength with the spectral width of 2 nm was changed by MYM-1 diffraction grating monochromator. The light/darkness cycles were switched by the Newport 76993 shutter. The sample was irradiated through the 2 × 15 mm slit in the golden electrode. A short focal length cylindrical lens was placed between the monochromator and the quartz window of the vacuum cryostat providing illumination of the 5 × 15 mm large area of the sample. The voltage of 50 V was applied to the electrodes to improve the precision of the measurement as the signal was amplified by one order of magnitude comparing to the signal without applied voltage. ITO electrode under the organic film precluded charging of the sample which could have decreased signal quality. Keithley 617 electrometer with a built-in voltage source was used to apply the voltage as well as to measure the electrical current.

The adiabatic energy gap of the studied compounds was determined from the photoconductivity measurements. The setup was similar to the setup of the photoemission measurements. Instead of the electron collecting electrode, we used aluminum electrode deposited on the organic film (ITO/organic compound/Al). The method of these measurements was described previously [22].

3. Results and discussion

3.1. Sample morphology

Evaluation of the quality of thin films and the information

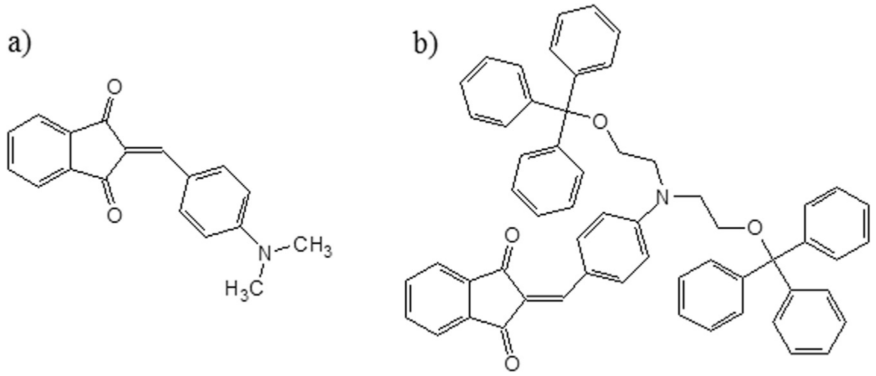

Fig. 1. Studied compounds: a) DMABI; and b) DMABI-6Ph.