



# Surface states and space charge layer electronic parameters specification for long term air-exposed copper phthalocyanine thin films

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## ABSTRACT

The photoemission yield spectroscopy (PYS) study of the 1-year air-exposed thin 16-nm copper phthalocyanine (CuPc) layers deposited on n- and p-type Si (111) native substrates was presented. The occupied electronic states in the band gap and in the upper part of the valence band have been identified from PYS spectra and their possible origin was discussed. Furthermore, space charge layer electronic parameters of organic thin films and their variations upon the exposure were determined. Different values of work function were received as equal 4.64 eV and 4.80 eV for copper phthalocyanine on n-Si substrate and on p-Si one respectively while ionization energies were estimated accordingly as 5.18 eV and 5.21 eV. It was found that after the long term air exposure the work function and surface band bending of CuPc increased by 0.94 eV and 0.56 eV respectively for the layers on n-Si and by 1.05 eV and 0.59 eV for those on p-Si indicated their higher gas sensitivity. Additionally, we detected the significant surface dipole effect on both phthalocyanine samples manifested by strong shift in electron affinity of 0.38 eV and 0.46 eV for layers on n-Si and p-Si substrate respectively. To explain these changes we developed the model of CuPc surface-ambient gas electronic interaction.

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## 1. Introduction

The family of metallophthalocyanines (MePc) as the group of the popular organic semiconductors presents the excellent chemical stability and electronic properties. It is widely used as the active material in optical and electronic devices like light emitting diodes, field effect transistors, solar cells and gas sensors [1–4]. Especially gas sensing properties of MePc's have been in the centre of attention due to the progressive interest in air purity monitoring and toxic gas detection. At the same time, the specific studies of the influence of ambient atmospheres on MePc layers have appeared crucial for examination of the phthalocyanine-based electronic devices stability and testing of their degradation processes [5–8].

The application of organic materials thin film in electronics or as a gas sensor is strongly dependent on the electronic properties of their subsurface area. In the case of MePc layers (i.e. organic semiconductors) there are occupied electron surface states in the band gap ( $E_g$ ) below the Fermi level ( $E_F$ ) and in the upper part of the valence band ( $E_v$ ) for organics denoted as the Highest Occupied Molecular Orbital (HOMO) peak onset energy ( $E_{HOMO}$ ). These surface states control surface electronic parameters of the space charge layer including work function ( $\varphi$ ), ionization energy ( $\Phi$ ), surface band bending ( $eV_s$ ) and surface electron affinity ( $\chi_s$ ) [9,10].

Operating in the “real world” conditions the surface of organic device is unavoidably subjected to the influence of the ambient air.

Interaction between surrounding gases and the phthalocyanine surface leads to a charge transfer which induces changes in electronic state occupation, and respectively modifies surface electronic properties. These processes finally can manifest themselves as the alterations of the electrical conductivity, which could be detected as the response of a potential CuPc-based sensor. Thus, in order to optimize the phthalocyanine-based electronic devices and to comprehend their sensing mechanism, it is necessary to analyze the changes in their electronic band structure upon ambient gas exposure.

In our previous investigations we described the electronic and chemical interaction between thin 16-nm copper phthalocyanine (CuPc) sensing layers and oxidizing gases present in ambient air during short 12-h exposure [11]. The organic films were deposited on n-type and p-type Si (111) substrates covered by  $\text{SiO}_2$  native oxide. After interface studies [12] the final fresh and air-exposed structures were probed with the X-ray photoemission and ultraviolet photoemission spectroscopies (XPS and UPS respectively) in order to determine surface chemistry and surface electronic parameters [11]. The XPS study revealed that after short term exposure, the surface chemistry of CuPc remained unaffected. However, the UPS results showed that the phthalocyanine work function increased by 0.55 eV from the initial (i.e. just after deposition) value  $\varphi = 3.70$  eV for layer on n-Si and increased by 0.25 eV from  $\varphi = 3.75$  eV for layer on p-Si. Moreover, we found upward shift in surface band bending equal to 0.45 eV and 0.30 eV for phthalocyanine on n-Si and on p-one respectively having initial surface energy difference  $E_F - E_{HOMO}$  as 1.10 eV and 1.00 eV for corresponding layers. We detected also a slight surface dipole for sample on n-Si demonstrated by small shift in surface electron affinity of 0.10 eV from initial

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$\chi_s = 2.50$  eV. For sample on p-Si the change in electron affinity was detected below the measurement uncertainty limits ( $\pm 0.10$  eV), so we treated value of  $\chi_s = 2.45$  eV obtained for fresh layer as the constant. Taking into consideration CuPc transport band gap equal 2.30 eV [13] we established the identical changes to  $\Delta\chi_s$  in ionisation energy  $\Delta\Phi$  for corresponding layers outgoing from the value  $\Phi = 4.80$  eV for layer on n-Si and  $\Phi = 4.75$  eV for layer on p-one [11].

In the next step, the XPS study was conducted for the same CuPc layers on defined silicon substrates after interaction with ambient air during long term (1-year) exposure. Stable in shapes, characteristic for bulk copper phthalocyanine, core levels peaks Cu2p, N1s and C1s confirmed integrity of the molecular film without detectable defragmentation [14]. However the uptake of oxidizing gases as a result of air exposure becomes visible during quantitative XPS analysis based on C1s, N1s and O1s detailed peak area. It revealed for CuPc on p-Si substrate about 2.5 times higher O:N and O:C elemental ratio than for one on n-Si [14]. Moreover we observed the core levels peak shift between samples on n-Si and on p-Si about 0.15 eV towards higher binding energy [15].

We interpreted the stronger interaction between ambient air components and organic layer on p-Si as the result of different morphological structure (determined with atomic force microscopy and scanning electron microscopy measurements). CuPc on p-Si presented a compact network of densely packed crystallites with lateral size in the range 50–100 nm and surface roughness equalled 0.67 nm, but on n-Si showed more open network of around 1.5 times larger crystallites and roughness [14].

In the present work we continue photoemission studies of CuPc thin films interaction with ambient air agents during prolonged time. Here we focus on the specification of the occupied electronic states in the band gap below Fermi level and in the upper part of the valence band. In order to obtain highly resolved energy spectrum for the band gap region we applied photoemission yield spectroscopy (PYS) method, the unconventional photoemission technique with photoelectron mean free path around 10 nm [9,10,16]. It bases on the measuring of the total number of photoemitted electrons per incident photon ( $Y(E)$ ) at a given photon energy ( $E$ ) usually up to 6 eV. Thanks to the large dynamic range (up to 6 orders of photoemission yield variation) and high energy resolution (up to 0.03 eV) it allows to determine directly the set of the electronic parameters of the semiconductor space charge layer like, among others, the work function and ionization energy [9,10,17]. Moreover, the derivative of the photoemission yield with respect to the photon energy  $dY(E)/dE$  is proportional to the effective density of occupied electronic states  $N(E)$  localised in the band gap below the  $E_F$  and in the upper part of the valence band. Additionally, fitting the photoemission curve in high-energy part by Kane's theoretical model [18] allows distinguishing between the surface and bulk state contribution [17]. Capabilities described above point, that the PYS method appears as a suitable tool for surface and interface electronic structure characterization and gives highly resolved complementary information to other photoemission techniques.

## 2. Experimental details

As the substrates two conductivity types of silicon wafers Si(111) (BOSCH GmbH) were used: n-type P-doped with an electron concentration of  $7 \cdot 10^{13} \text{ cm}^{-3}$ , and p-type B-doped with a hole concentration of  $1 \cdot 10^{15} \text{ cm}^{-3}$ . Substrates were covered with the native  $\text{SiO}_2$  oxide and pre-cleaned with acetone and deionized water.

CuPc thin films with the thickness of 16 nm were thermally evaporated from the sublimed powder (Sensient Imaging Technologies GmbH, Syntex Division). The deposition rate of organic was about 0.01 nm/s at the base pressure  $8 \cdot 10^{-6}$  Pa. During the whole evaporation process the Si substrates were kept at room temperature. The thickness of CuPc thin films was controlled with a quartz crystal microbalance (Inficon XTM 2).

After the CuPc deposition, the sample surface chemistry was tested by the XPS method. This method employed a SPECS system equipped with a PHOIBOS 100 hemispherical analyzer and monochromatized XR-50 Al K $\alpha$  X-ray lamp with the photon energy of 1486.6 eV and parameters described in [11]. Moreover, in order to determine the initial electronic properties, the freshly deposited CuPc underwent the UPS measurements. In these studies the photoelectrons were excited with the 21.2 eV He I line of helium discharge lamp and separated in the PHOIBOS 100 analyzer as in [11].

After the in-situ XPS and UPS investigations, the freshly deposited CuPc layers were exposed to the ambient air at the room temperature for 12 h and reinvestigated [11] and then once again exposed at the same conditions for long period of 1-year. Then, the CuPc surface chemistry was firstly checked by XPS as reported in [14,15].

As the next step, the space charge layer parameters of phthalocyanines were determined basing on the PYS measurements. In this photoemission technique the ultraviolet light from deuterium lamp was passing through a high resolution SPM-2 monochromator (Zeiss<sup>TM</sup>) and focused onto the sample kept in the base pressure  $1 \cdot 10^{-6}$  Pa. Emitted photoelectrons were collected by a channeltron oriented with an angle of 15° to the normal to the sample plane. Simultaneously part of the light beam was deflected towards the M12FQC51 photomultiplier in order to measure the spectral intensity of the incident photon flux. Photoemission yield spectra  $Y(E)$  were taken at 1-nm intervals (which corresponds to energy resolution of 0.03 eV) in the range 200–350 nm (6.2–3.6 eV). The spectra were subjected to smoothing and subsequent derivation with respect to photon energy in order to obtain the effective density of occupied electronic states  $N(E)$  localized below the Fermi level. The electronic parameters of CuPc were determined using non-commercial PYS Optimiser v2.1 software. The distribution of states  $N(E)$  in form of peaks was decomposed into Gaussian components applying CASA XPS software with a linear background subtraction.

## 3. Results and discussion

Fig. 1a shows the PYS spectra of the 1-year air exposed 16-nm CuPc thin film deposited on n-type Si(111) covered with native  $\text{SiO}_2$ . The photoemission yield spectrum  $Y(E)$  presented in the graph was divided into two energy regions for direct determination of CuPc space charge layer parameters. The low energy part of the  $Y(E)$  corresponds to the occupied surface electronic states localised in the band gap below the Fermi level. Applying the procedure described at [19,9,10] we used the Fermi-Dirac distribution as a fitting to the low energy tail of the spectrum. This processing allowed the determination of the energy distance between  $E_F$  and vacuum level energy  $E_{vac}$  (in our conditions the vacuum energy was assigned to  $E_{vac} = 0$ ) which is defined as a work function  $\phi$ . In the case of CuPc on n-Si we obtained  $\phi$  equal  $4.64 \pm 0.03$  eV. The high-energy part of a  $Y(E)$  spectrum corresponds to the occupied electronic valence band states (from bulk and surface) localised in the upper part of valence band. The energy distance between top of the valence band  $E_v$  (or  $E_{HOMO}$  for organics) and  $E_{vac}$  level is defined as the ionisation energy  $\Phi$  [9,10].

In order to estimate  $\Phi$  we fitted the high-energy part of the  $Y(E)$  spectrum by the theoretical formula developed by Kane [18]:  $Y(E) = A \cdot (E - \Phi)^m$ , where  $A$  is a constant and  $m$  is the transition/scattering coefficient. The number  $m$  describes the photoemission mechanism from the upper part of a valence band and depends on various factors like optical excitation, emission and possible scattering of photoelectron [18]. For the high-energy part of the  $Y(E)$  spectrum taken for CuPc on n-Si, the best fitting by the theoretical curve (denoted on the Fig. 1a as the  $Y(E)$  Kane's) was obtained with the  $m$  coefficient equal to 2.5. The ionisation energy determined as  $E_{HOMO}$  edge was then  $\Phi = 5.18 \pm 0.10$  eV.

According to the Kane's model, value of  $m = 2.5$  corresponds to indirect electron transition with scattering on "real" surface [18]. Similar

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