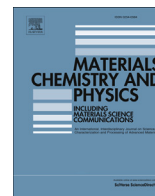




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# Quantitative correlation between air induced changes of electronic parameters and morphological features of copper phthalocyanine thin film surfaces



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## HIGHLIGHTS

- PYS study of 16 nm-CuPc/RCA-SiO<sub>2</sub>/n-Si(111) electronic properties after air exposure.
- eV<sub>s</sub>, χ<sub>s</sub>, φ changes due to oxidation process compared to the other CuPc results.
- Electronic parameters shift correlated with morphological features obtained by AFM.

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## ABSTRACT

In this work, utilizing fine-resolved photoemission yield spectroscopy (PYS) method, the set of electronic parameters of the space charge layer of 16 nm-copper phthalocyanine (CuPc) thin films deposited on n-type Si(111) substrate covered with modified SiO<sub>2</sub> was determined after long term air exposure. The PYS investigation revealed that work function and surface band bending increased upon gas adsorption by 0.64 eV and 0.32 eV respectively for organic layer and surface dipole effect appeared as the shift in electron affinity of 0.32 eV. Obtained results were compared with photoemission data received for corresponding CuPc films on different types of silicon Si(111) substrate. Collected parameters were correlated with the morphological features of the CuPc's surfaces measured applying atomic force microscopy (AFM) ability. Results of compiled PYS and AFM studies indicated particular electronic tendency for oxidation processes for certain shapes of phthalocyanine crystallites. It may suggest that by manipulation of the initial films' morphology it would be possible to control the air stability of the CuPc-based electronic devices and their vulnerability to degradation processes.

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## 1. Introduction

The copper phthalocyanine (CuPc) is a representative of wide family of metal phthalocyanines (MePc). Due to their chemical and physical attributes as well as their high stability MePc's are used as active material in optical and electronic thin films devices technology like light emitting diodes, field effect transistors, solar cells and gas sensors [1]. Particularly, gas sensing properties of phthalocyanines have been in the centre of consideration because of the emerging interest in air purity monitoring and toxic gas detection. Alternatively, the advanced studies of the ambient atmosphere influence on MePc layers have appeared important for

determination of the phthalocyanine-based electronic devices stability, reliability and for examinations of their degradation processes [2–5].

The use of organic thin film in electronics or in gas sensor technology is strongly dependent on the electronic properties of their subsurface area like work function ( $\phi$ ), ionization energy ( $\Phi$ ), surface band bending (eV<sub>s</sub>) and surface electron affinity ( $\chi_s$ ). All these parameters are determined by space charge layer controlled, in turn, by 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 ( $E_v$ ). It has to be reminded that in the case of MePc layers (i.e. organic semiconductors) the top of the valence band is synonymous to the Highest Occupied Molecular Orbital (HOMO) peak onset energy ( $E_{\text{HOMO}}$ ) [6,7].

The surface of organic electronic device (or sensor) working in the “real world” conditions is unavoidably subjected to the

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influence of the ambient air. Interaction between a 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 can demonstrate themselves among others as the alterations of the electrical conductivity, which in turn can be detected as the response signal of a potential CuPc-based sensor. Therefore, in order to optimize the phthalocyanine-based devices and to understand their sensing mechanism, it is essential to analyze the changes in their electronic band structure upon ambient gas exposure.

Our last studies were focused on the electronic and chemical interaction between thin 16-nm copper phthalocyanine (CuPc) sensing layers and oxidizing gases present in ambient air during short and long term exposures [8–11]. The organic films were deposited in the stepwise manner on n-type and p-type Si (111) substrates covered by SiO<sub>2</sub> thin native oxide. The interfaces and final surfaces of our structures were examined applying X-ray photoemission and ultraviolet photoemission spectroscopies (UPS) [12,13]. Then samples were subjected to prolonged air exposure and investigated by photoemission yield spectroscopy (PYS). This unconventional photoemission technique, with photoelectron mean free path around 10 nm, allows direct determination of the semiconductor space charge layer electronic parameters like work function, ionization energy and others. It bases on the measurement of the total number of photoemitted electrons per incident photon  $Y(E)$  at a given photon energy  $(E)$ . The energy is usually up to 6 eV with high energy resolution (up to 0.03 eV). Method operates within large dynamic range of response signal (up to 6 orders of magnitude) [5–7,11,14].

Conducted photoemission studies revealed the stronger interaction between ambient air components and CuPc organic layer on p-Si during long term exposure [8,9,11]. It was suggested that disposition for prolonged oxidation was caused by different morphological structure determined by atomic force microscopy (AFM) and scanning electron microscopy [9,15].

In this work we continued PYS studies of CuPc thin films interaction with ambient air agents over prolonged (1 – year) time. Such time period for gas interaction, without denser time scale, can provide the saturation state and is more useful for engineering application.

We investigated the 16-nm CuPc thin film deposited on n-type Si(111) substrate covered by SiO<sub>2</sub> oxide modified by procedure developed at Radio Corporation of America (RCA) [15]. Photoemission results were compared to ones obtained for 16-nm CuPc layer on Si(111) native substrates [11]. Moreover air exposed thicker film of 500-nm CuPc on native p-type Si(111) was re-examined by means of fine-resolved PYS method.

For whole set of the samples the standard morphological parameters have been recalled but first of all the specific morphological characterisation approach was developed basing on AFM image processing ability.

Finally, the goal of this paper is to check whether it is possible to predict the behaviour of the electronic structure of the CuPc layers by analysis of their initial morphology. It was performed by collecting electronic parameters response due to long term air exposure of the CuPc layers on different Si substrates and morphological features of the corresponding films in order to find the direct, quantitative relation between them. This correlation could clearly indicate the special electronic inclination for prolonged oxidation processes for certain shapes of phthalocyanine crystallites and could be helpful to predict the air stability of CuPc-based electronic devices and their degradation processes.

## 2. Experimental details

As the substrate the silicon wafer Si(111) (BOSCH GmbH) was used with n conductivity type P-doped with an electron concentration of  $7 \cdot 10^{13} \text{ cm}^{-3}$ . For previous investigation recalled in this work the p-type Si(111) B-doped was applied with a hole concentration of  $1 \cdot 10^{15} \text{ cm}^{-3}$ . Substrates were covered with the native SiO<sub>2</sub> oxide (with the thickness 0.8 nm) and pre-cleaned with acetone and deionized water. In current study SiO<sub>2</sub> native oxide were modified according to the RCA wet cleaning procedure described in Refs. [16,17] reaching the thickness of 1.3 nm.

CuPc thin films with the thicknesses of 16 nm and 500 nm were thermally evaporated from the sublimed powder (Sensient Imaging Technologies GmbH, Syntec Division and Sigma Aldrich respectively). The deposition rate of organic was about 0.01 nm/s at the base pressure  $8 \cdot 10^{-6} \text{ Pa}$ . During the whole evaporation process the Si substrates were kept at room temperature or at 330 K. The thickness of CuPc thin films was controlled with a quartz crystal microbalance (Inficon XTM 2).

The freshly deposited CuPc layers underwent the in-situ UPS measurements in order to determine the initial electronic properties. 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 described in [10].

After the in-situ photoemission investigations, the freshly deposited CuPc layers were exposed to the ambient air at the room temperature and the atomic force microscopy investigation were carried out using PSIA XE-70 microscopy in non contact mode with details referred at [9,15]. The scans were performed in several places at each sample in order to check reproducibility of the results. Acquired images were processed using image processing software (XEI<sup>®</sup>, PSIA and Gwyddion<sup>®</sup> software [18]) to correct sample inclination and distortions caused by stage. Quantitative AFM analysis was made applying Gwyddion<sup>®</sup> software capabilities.

Subsequently, after long term of 1-year air exposure, the space charge layer electronic 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>™</sup>) and focused ( $\sim 1 \text{ mm}^2$  spot size) onto the sample kept in the base pressure  $1 \cdot 10^{-6} \text{ Pa}$ . 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 PYSoptimiser v2.1 software. The data fitting procedures and quantifications were conducted using OriginLab<sup>®</sup> v8.5 software.

## 3. Results and discussion

Fig. 1a presents the PYS spectrum of the 1-year air exposed CuPc thin film deposited on n-type Si(111) covered with RCA-prepared SiO<sub>2</sub> with the thickness of 16 nm. Photoemission yield spectrum  $Y(E)$  shown in the graph was divided into two energy regions for direct specification of CuPc space charge layer parameters.

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