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XPS study of air exposed copper phthalocyanine ultra-thin films deposited on Si(111) native substrates

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Results are presented of XPS characterization of ultra-thin copper phthalocyanine (CuPc) (16 nm-QCM controlled) films thermally deposited under UHV conditions on p- and n- type Si(111) substrates covered by native oxide. Our attempt has been focused on comparative studies of thin films in terms of the stability and durability of CuPc layers after one year of aging in ambient atmosphere. The impact of the type of the substrate doping was also explored. Our results clearly prove that CuPc layers are chemically stable and durable after one year exposure to air. We also demonstrate the existence of the substrate doping impact on the CuPc ultra-thin film what might be caused by dipole effects.

Key words: *copper phthalocyanine; CuPc; thin films; surface chemistry*

1. Introduction

Copper phthalocyanine (CuPc) is an organic semiconductor with a high thermal and chemical stability suitable for thin film technology processing [1–3]. It belongs to metal phthalocyanines (MePc), a class of metal-organic compounds possessing a metal atom surrounded by aromatic rings in the centre of the molecule [4]. It is an important material widely used in optical and electronic devices, among others light emitting diodes, field effect transistors [5], solar cells and, particularly, gas sensors [6]. The sensor mechanism bases on changes in the electrical conductivity of phthalocyanine thin films induced by the presence of small gaseous molecules [7, 8]. It has to be noted as well that the sensing properties of phthalocyanines are determined by the electronic properties of their space charge layer [9]. Following, highly ordered and defined MePc films might be of great importance for sensor device purposes [10]. Such sensors usually work in ambient air and other unfavourable environment. Thus

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stability and durability of MePc layers are in attention due to cost reduction and longevity of designed devices.

Up to now, the studies have been focused on the properties of a CuPc sensing layer under strictly controlled conditions, i.e. a sensing layer on strictly defined atomically clean substrate has been exposed to a given dose of a given gas without the presence of other gases [11, 12]. On the other hand, in the last few years an increasing attention has been paid to study layers deposited on real (covered with native oxide) substrate surfaces because oxidized Si wafers have been used as substrates in the so called organic electronics, in technology of organic field-effect transistors (OFET), where the oxide layer serves as the insulating layer between one electrode and a semiconducting film [13]. Furthermore, if the oxide layer does not affect the active CuPc film it may turn out that there is a possibility of further cost reduction (in device preparation) by partially abandoning the expensive substrate cleaning process. That is why the examination of the influence of Si substrate covered with native oxide on the surface chemistry, morphology and electronic properties of CuPc thin films is of great importance. There are not too many papers describing the quality (including durability and stability) and properties of organic layers deposited on real substrate surfaces. There is also a necessity to investigate if the electronic properties (i.e., type of conductivity) of such substrate surface, even covered with native oxide, have the influence on the organic ultra-thin film surface chemistry.

In our recent paper [14], a correlation between morphology and electronic properties of CuPc thin films (500 nm) was determined with use of atomic force microscopy (AFM) and photoemission yield spectroscopy (PYS) methods. In this work, the x-ray photoelectron spectroscopy (XPS) investigations of CuPc ultra-thin (16 nm) layers deposited on Si(111) covered with native oxide are reported. Our original attempt includes a comparative examination of thin films due to long term of air exposure (including the chemical quality of the layer) and type of the substrate doping. We suspect that difference in the type of substrate conductivity can affect the chemistry and electronic properties of deposited layers even after long-lasting exposure. That is why the XPS examinations of the chemistry of the CuPc ultra-thin layers after one year of exposure were performed.

The aim of this note is to examine the durability and stability of the CuPc layer in such a period of time. Additionally, the influence of the substrate doping on the ultra-thin CuPc films chemistry has been checked.

2. Experimental

Two types of Si(111) substrates covered with native oxide (Bosch, GmbH) were used in this experiment: the n-type (phosphorus-doped with a carrier concentration of 7×10^{13} cm^{-3}) and p-type (boron-doped with a carrier concentration of 1×10^{15} cm^{-3}). The substrates were degreased with acetone in an ultrasonic bath, rinsed with deionized water and then dried with dry air.

CuPc thin films (16 nm) were thermally evaporated in a UHV preparation chamber. For deposition, the CuPc complex sublimed powder was used (delivered by Sensient Imaging Technologies GmbH, Syntex Division). The pressure during the process (evaporation of CuPc) was better than 8×10^{-8} mbar.

The film thickness was controlled with a quartz crystal microbalance device (deposition rate was about 0.1 Å/s) and verified with XPS by monitoring the attenuation of the intensity of the substrate Si2p peaks due to the organic overlayer [15, 16].

The Si/SiO_2 substrate was examined by XPS and angle-resolved XPS (ARXPS) methods at the Silesian University of Technology, Gliwice. The ARXPS method was used to determine the native oxide layer thickness. Angle resolved XPS measurements (and the XPS measurements done for chemical analysis of the substrate) were performed with a SPECS PHOIBOS 100 hemispherical analyzer equipped with a HSA 3500 power supply unit. The XPS system base pressure was $2\cdot10^{-9}$ mbar. Spectra were taken using AlK_α source with energy of 1486.6 eV, the analyzer was set to a pass energy of 10 eV. Aquired XPS spectra were calibrated with the silver Ag3d peak at the binding energy of 368.2 eV [17]. The samples were aged in ambient air for one year and then investigated by imaging and photoemission methods.

To obtain high resolution XPS spectra, the CuPc samples were examined at the University of L'Aquila. XPS measurements were performed with a home designed system having a monochromatized AlK_α source and a PHI hemispherical analyzer. The XPS system base pressure was 8×10^{-10} mbar. XPS spectra were calibrated with respect to gold peak with energy of 84.0 eV [18].

3. Results and discussion

The XPS survey spectra of both types of Si substrates are shown in Fig. 1. The upper line corresponds to Si/SiO_2 substrate with a p-type conductivity while the lower one to n-type doped sample. All expected peaks were found. The examination of the spectra reveals the existence of a contamination layer including oxide (O1s) peak and adventitious carbon related species (C1s peak). However, there are not any substantial compositional differences between the substrates. In both cases the ratio between O1s and Si2p peak areas, corrected for atomic sensitivity factors, is close to 2 which entails that the oxide overlayer is composed primarily of a stable SiO_2 layer.

In order to determine the exact substrate bonding configuration between silicon and oxygen, the Si2p peak region was recorded at higher resolution and is shown in Fig. 2 for both types of substrate. The spin-orbit split contributions from Si substrate and oxide layer shifted by about 4 eV are seen. The latter one corresponds to SiO_2 [19] which confirms that it is the main component of the oxide layer; other silicon suboxides are not visible.

The native oxide thickness may be determined using XPS measurements under different take off angles. The method is based on changing the relative angle between the sample and the analyzer entrance slit and monitoring the signals emerging from examined substrate and its overlayer. Under the assumption that an overlayer is uniform, its thickness can be calculated with use of the Beer–Lambert equation [16]:

$$d = \lambda_A \cos\theta \ln\left[1 + \frac{R}{R^{\infty}}\right] \tag{1}$$

where: λ_A is the attenuation length of electrons emitted from a substrate in an overlayer, θ is the electron take-off angle, R is the ratio of overlayer (SiO_2 component) to substrate (Si) peak areas, R^{∞} is the ratio of overlayer to substrate sensitivity factors.

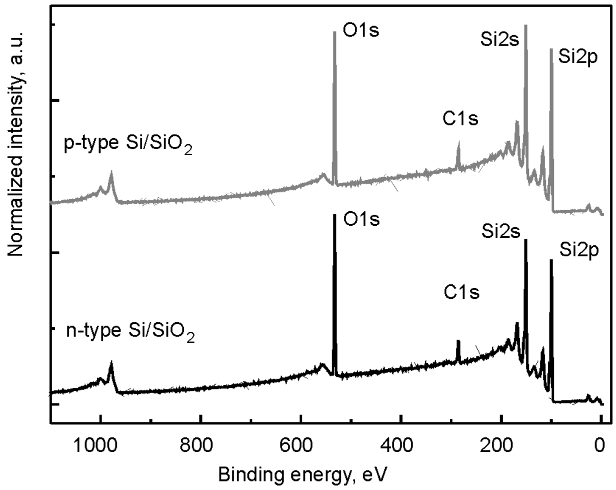

Fig. 1. Survey spectra of p-type doped Si/SiO_2 and n-type doped Si/SiO_2; all main spectral lines have been identified

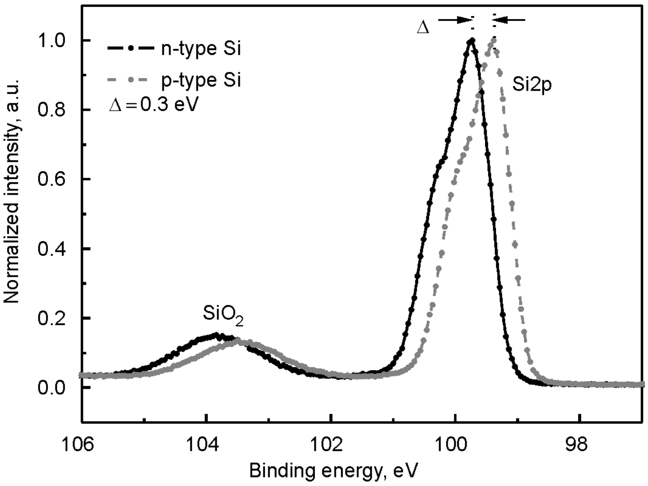

Fig. 2. Si2p peaks of n- and p-type substrates. An evident energy shift caused by doping is visible; shape of the spectral line clearly shows that the oxide layer contains only silicon dioxide

It follows from Eq. (1) that the dependence of ln($R + R^{\infty}$) on 1/cosθ should yield a straight line. The slope of the line is then the thickness divided by the attenuation length. Figure 3 presents the transformed ARXPS data for the p-type substrate. For calculations, the value of $\lambda_A = \lambda_{SiO_2} = 3.5$ nm was taken [16]. The oxide thickness for the p-type substrate is 0.77 nm; a similar analysis for the n-type one gives 0.80 nm. Auxiliary AFM investigations were done in order to check the surface structure of the used substrates. In both cases, the surface roughness was determined as 0.15 nm (data to be published elsewhere). Besides the energy shift of about 0.3 eV, there are no other qualitative and quantitative differences between the spectra. The origin of the energy shift can be related to various substrate dopings which manifests itself in various Fermi level positions.

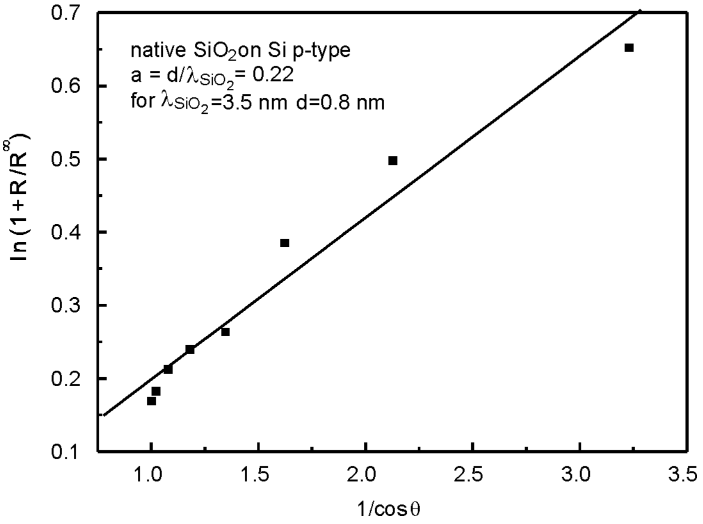

Fig. 3. Compositional depth profiling for p-type Si sample via angle dependent core level XPS

In Figure 4, the XPS survey spectra of examined 16 nm CuPc layers deposited on n-type (upper line) and p-type (lower line) substrate are shown. The samples were aged for one year in the ambient atmosphere before the examination. The spectra are characteristic of CuPc films; N1s and Cu2p peaks appeared and the C1s peak intensity drastically increased due to C=C and C–N contributions inherent in CuPc. Simultaneously, the substrate peaks diminished indicating that all the substrate is covered with CuPc film and the layers did not erode during the exposure period. The O1s peak can be treated as the contamination caused by coexistence of molecular oxygen and water vapours from the atmosphere; no other contaminants were detected.

The observed difference in intensities of O1s peaks can be related to a stronger (in the case of a p-type substrate) interaction between deposited layer (affected by substrate) and oxidizing ambience (oxygen and water vapours). This could be the reason why the O1s peak exhibits a higher intensity in the case of the p-type sample. No other explanations are likely, as the two Si substrates have almost the same oxide thickness and composition (only SiO_2) and they have been prepared under identical conditions (substrate temperature and evaporation rate).

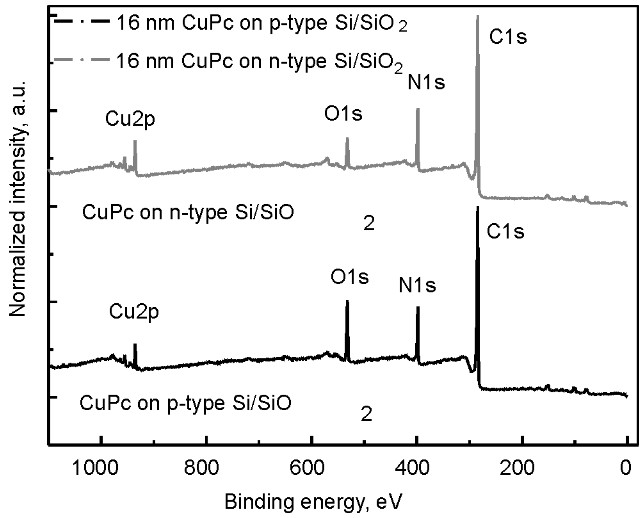

Fig. 4. Survey spectra of 16 nm CuPc films obtained from n-type and p-type samples

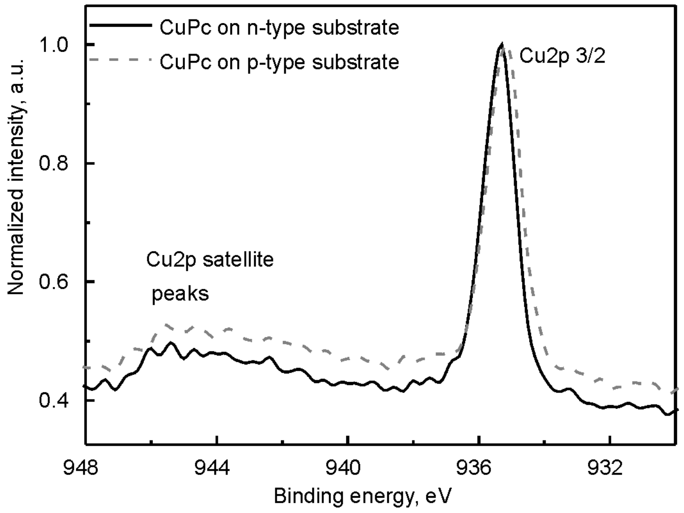

Fig. 5. Cu2p 3/2 XPS peak obtained for 16 nm CuPc film evaporated on n- and p-type Si/SiO_2 substrate

Auxillary XRD investigations showed that CuPc thin films were in the α-phase on both types of substrates and the number of CuPc monolayers was also the same (data not shown for brevity). The exact morphological information is currently under an analysis and will be published elsewhere.

For better characterization of the CuPc layer, the Cu2p$_{3/2}$, N1s, and C1s spectral windows were taken at higher resolutions. In order to determine chemical stability of the the CuPc layer after long term exposure in atmosphere, we verified the shape of Cu2p$_{3/2}$ XPS peak (due to its highest surface sensitivity). Figure 5 presents Cu2p spectra taken from both types of samples. One can observe a characteristic shape of Cu2p peak as well as satellite peaks very typical of stable CuPc layer [20, 21]. This confirmed our expectations that CuPc ultra-thin films are extremely robust even after long term aging. A more precise analysis of the Cu2p$_{3/2}$ XPS peaks energy positions points that the energy shift between n- and p-type samples is about 0.15 eV (for the n-type samples the energies are greater than for the p-type ones).

A similar effect was observed for N1s XPS peaks (not shown for brevity). It seems that the substrate doping causes the energy shift (the 0.3 eV shift originating from substrate is reduced by the phthalocyanine layer, however it still exists). We can assume that for thicker layers the effect will diminish but the assumption has to be verified by additional investigations.

4. Conclusions

Based on the XPS examination of both the Si/native oxide substrate and CuPc thin film (16 nm) one can conclude that CuPc layer is stable and durable after long term (one year) air exposure. It was proved by the unchanged characteristic chemical bonds which are clearly seen in the XPS spectra. Furthermore, the shapes of Cu2p$_{3/2}$ and N1s peaks characteristic of phthalocyanine have not been corrupted by any additional component resulting from undesired surface reactions. The only influence of the conductivity type of the substrate is clearly visible in the energy shift of the main XPS components of CuPc spectra. This is probably caused by dipole effects (we suspect that copper phthalocyanine creates surface dipole with oxygen and water vapours on p-type substrate) but the origin of such phenomena remains unrecognized and further investigations are currently in progress.

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