

Beata Białek

*Pedagogical University, Częstochowa*

## THE ELECTRONIC STRUCTURE OF THE NEAR SURFACE REGION OF IRON(II) AND COPPER(II) PHTHALOCYANINE THIN FILMS - A COMPARATIVE EXPERIMENTAL AND THEORETICAL STUDY

**Abstract:** The results of the electronic structure of near surface region of iron(II) and copper(II) phthalocyanine thin films carried out with both Photoemission Yield Spectroscopy (PYS) technique and *ab initio* calculation method are presented. A comparative analysis of the experimental and theoretical results is given. It is shown that the experimental values for the ionization potentials and work functions of the investigated materials may be compared with the calculated third and second occupied molecular energy levels, respectively. \*

### Introduction

An increasing interest in the electronic properties of organic semiconductor thin films has encouraged the starting of methodical studies of iron(II) and copper(II) phthalocyanines, (Pc), which are very often used in many fields of industry. Our investigations were performed with particular reference to the application of these materials in gas sensor technology. To make our research complete we studied the electronic properties of iron and copper phthalocyanines experimentally and theoretically. Such treatment was considered to be a test for the theoretical explanation of experimentally observed phenomena in phthalocyanine thin films, especially under the influence of oxidizing agents. The results of our research, provided both by Photoemission Yield Spectroscopy (PYS) and the computational quantum chemical *ab initio* method, have already been published [1-4]. So far, however, our data obtained by the two different methods have not been compared. This paper is an attempt to correlate all the results.

### Review of results of previous studies

Although the results of our earlier studies are recorded in the literature, the most important of them are briefly recalled here. This can be helpful for the better understanding of this paper.

The investigations of the photoemission yield from vacuum evaporated copper and iron phthalocyanine thin films, of 1.6  $\mu\text{m}$  and 1.0  $\mu\text{m}$  thickness, respectively, were carried out under ultrahigh vacuum conditions ( $10^{-7}$  Pa). Photoemission yield spectra were recorded in the photon energy range 3.5 to 6.2 eV with the interval of 1 nm for samples freshly evaporated and annealed at a temperature up to 410 K. In order to examine the sensitivity of phthalocyanine thin films investigated for oxygen adsorption, the samples were exposed to oxygen ( $10^2 - 10^6$  L). The sets of photoemission yield spectra obtained were the basis for further analysis, the results of which may be shortly referred to as follows:

- thin films of copper and iron phthalocyanines obtained in the process of vacuum evaporation are the extrinsic semiconductors with the occupied acceptor electronic states in their energy gap, which probably appear due to the high concentration of lattice defects;
- the value of the work function determined for vacuum evaporated phthalocyanine thin film is 4.81 eV and, in consequence of annealing at the temperature of 410 K, decreases linearly to 4.62 eV; on the contrary, because of oxygen adsorption ( $10^5$  L), the value of the work function increases to 4.80 eV;
- the value of the work function determined for vacuum evaporated iron phthalocyanine thin film is 4.55 eV and, in consequence of annealing at the temperature of 410 K, decreases linearly to 3.80 eV; the same was observed for copper phthalocyanine thin film; as a result of oxygen adsorption ( $10^5$  L), the value of the work function of FePc increases to 4.00 eV;
- the observed reduction of the value of the work function for investigated materials during annealing is presumably related to water vapour and oxygen desorption from their surface, whilst an increase in the value is related to oxygen chemisorption on surface structural defects, which is also seen as a change in the distribution of electronic states in the energy gap of phthalocyanines.

Simultaneous theoretical investigation of the electronic properties of copper and iron phthalocyanine thin films was carried out by applying the *ab initio* computational quantum chemistry technique on the SCF level, which was available through the GAUSSIAN 92 program package [6]. As a model for phthalocyanine thin film a single phthalocyanine molecule with  $D_{4h}$  symmetry was chosen. The valid geometry for both copper and iron phthalocyanines was

taken from the literature [7,8] and has not been optimized. The investigations were performed in two stages: firstly, the electronic structures of both the copper and the iron phthalocyanine molecule as isolated were determined, then the influence of oxygen adsorption on the electronic structure changes was monitored. The electronic structure of the investigated systems was determined by the position of the occupied and unoccupied molecular energy levels.

On the basis of the results of calculations which we carried out for copper and iron phthalocyanines and in the case of their interaction with molecular oxygen, we discovered that:

- oxygen adsorption on the copper and iron phthalocyanine thin film surface is strongly localized: the oxygen molecule is preferably adsorbed onto the phthalocyanine surface in the perpendicular position to its plane, exactly over the central metal ion;
- as a consequence of oxygen interaction with the metal phthalocyanine molecule, the stable complex of phthalocyanine - oxygen is formed with the effective chemisorption bond created through 3d metal atom orbitals and phthalocyanine inner ring orbitals with  $e_g$  symmetry; in the CuPc - O<sub>2</sub> complex the bond length is equal to 2.5 Å, while in FePc - O<sub>2</sub> it is 2.1 Å;
- the interaction of the MePc (Me = Cu, Fe) molecule with oxygen causes a rearrangement of both occupied and unoccupied molecular orbitals in the investigated systems, which - as the lowest unoccupied molecular orbitals are lower in the energy scale, while the highest occupied ones are raised in the scale - may result in the formation of a new conduction band in these materials and explain the observed rise of electrical conductivity of phthalocyanines placed in an oxygen atmosphere.

The points mentioned above as a review of some facts are considered to be the most important for the experimental and theoretical results obtained and compared as defined in the title of the paper.

### **A comparative analysis of the experimental and theoretical results**

Both in the PYS experiment and in the *ab initio* calculations we determined the value of the ionization energy of investigated materials. For that we could correlate the two types of results: experimental and theoretical ones. Table I contains the values of ionization energy obtained for CuPc, FePc and CuPc - O<sub>2</sub>, FePc - O<sub>2</sub> systems from the photoemission yield spectra and *ab initio* calculations.

Table 1.  
Ionization energy values [eV] for CuPc, FePc and CuPc - O<sub>2</sub>, FePc - O<sub>2</sub> systems

CuPc		FePc	
PYS [2]	<i>ab initio</i> [4]	PYS [3]	<i>ab initio</i> [5]
5.36±0.31	2.32	5.00±0.30	3.72
	3.25		3.75
	4.93		4.73
	7.79		5.98
CuPc-O <sub>2</sub>		FePc-O <sub>2</sub>	
5.46±0.31	1.67	5.00±0.33	2.29
	2.38		4.13
	3.47		4.36
	7.03		6.38

We have found our experimental results to be in a good agreement with other results reported in the literature [9]. As is seen from Table 1, the calculated values corresponding to the energy of the third occupied molecular level in the investigated systems may be in agreement with the experimentally obtained ionization energies. This correspondence is maintained in the case of both the isolated CuPc and FePc molecules and the molecules after interaction with oxygen: all the values are constant within the error limit.

Correctness of this comparison is even more clear when the measured value of the work function is taken into account: for CuPc the value obtained experimentally is 4.62±0.03 eV and under the influence of oxygen increases to 4.77±0.03 eV, and for FePc the values are 3.80±0.03 eV and 4.00±0.03 eV, respectively. This may be compared with the calculated energy of the second occupied molecular level of each system investigated, especially when calculations are done with the STO-3G basis set. Then the energy of the second occupied molecular level calculated for the isolated CuPc molecule is 4.62 eV. For the CuPc molecule after interaction with oxygen we observe a divergence between experimental and theoretical data, since the calculated value that we suggest to be corresponding with the measured work function is as much as 1.47 eV higher. It is clear however that the trend of increasing work function of phthalocyanine under the influence of oxygen is still comparable experimentally and theoretically. We hope that the further use of better basis sets will lead to results that will be even more consistent with the experimental values.

More discerning analysis of the results obtained in our complex studies has shown that our comparative analysis is valid and useful. The results obtained experimentally with the use of Photoemission Yield Spectroscopy and *ab initio* calculations are complementary to one another. The latter method may be

successfully used in qualitative studies of the electronic structure of phthalocyanines and their changes under the influence of active gases. Respective quantitative studies carried out on the basis of photoemission yield spectra from the upper part of the valence band of the phthalocyanine thin films, though difficult, are also possible [10].

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Beata Białek

### **Struktura elektronowa obszaru przypowierzchniowego cienkich warstw ftalocyjanin żelaza(II) i miedzi(II) - analiza porównawcza wyników doświadczalnych i teoretycznych**

**Streszczenie:** W pracy przedstawiono rezultaty badań struktury elektronowej obszaru powierzchniowego cienkich warstw ftalocyjanin żelaza(II) i miedzi(II) prowadzonych metodą spektroskopii wydajności kwantowej fotoemisji (PYS) i metodą obliczeniową *ab initio*. Przeprowadzono analizę porównawczą wyników doświadczalnych i teoretycznych. Stwierdzono, że wyznaczone drogą eksperymentalną wartości potencjału jonizacji wyjścia badanych materiałów odpowiadają obliczonym wartościom energii odpowiednio trzeciego i drugiego obsadzonego poziomu molekularnego.