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## ВИВЧЕННЯ БАР'ЄРНИХ СТРУКТУР НА ОСНОВІ ТОНКИХ ПЛІВОК ФТАЛОЦІАНІНУ НІКЕЛЮ У РАЗІ ВЗАЄМОДІЇ З ГАЗОВИМ СЕРЕДОВИЩЕМ АМІАКУ

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## STUDY BARRIER STRUCTURES ON THE BASE OF NICKEL PHTHALOCYANINE THIN FILMS DURING INTERACTION WITH AMMONIA MEDIUM

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Методом термовакuumного напилення наносилися на прозорі електропровідні підкладки (Indium tin oxide (ITO)) тонкі плівки органічного молекулярного напівпровідника фталоціаніну нікелю (NiPc), а поліморфної модифікації, що володіють високою чутливістю до дії газових середовищ. На основі цих плівок були сформовані бар'єрні структури ITO/NiPc/Al та ITO/NiPc/Ni. Виявлено та досліджено ефект електрогенерації в структурі ITO/NiPc/Al під дією газового середовища аміаку. Показано, що виникнення струму короткого замикання та напруги холостого ходу спостерігається тільки в структурі ITO/NiPc/Al, що може бути зумовлено перебігом окисно-відновних реакцій в ній. Це підтверджується відсутністю електрогенерації в структурі ITO/NiPc/Ni, в якій перебіг таких окисно-відновних-реакцій є неможливим. Показано, що наявність вологи в аміачній атмосфері призводить до істотного відгуку електричного опору структури ITO/NiPc/Ni.

The barrier structures on the base of organic molecular semiconductor nickel phthalocyanine (NiPc) thin films are studied. Interaction of the thin films with gaseous ammonia medium leads to change in their electrical conductivity. Short circuit current and open circuit voltage in the barrier structure result from oxidation-reduction reactions with gaseous ammonia.

### Introduction

The development of new high-efficiency non fossil-based energy sources is a big goal of contemporary electronics. Fuel cells constitute one of the most important directions towards it [1–3]. These devices directly convert the energy of fuel into electrical energy. Recently, conductive polymers and organic semiconductors attracted much attention due to their possible use in fuel cells [4–6]. Some of the most promising organic

semiconductors for this application are phthalocyanines (Pc), for example nickel phthalocyanine (NiPc). This material exhibits p-type conductivity in the air due to the absorption of atmospheric gases [7]. Moreover, it is sensitive to other gases [8–10] and solar radiation [11–12]. Finally, NiPc has a high thermal and chemical stability and can be used as a catalyst [13]. It was shown that this material can be used in gas sensors, solar cells and other electronic devices [7–13]. For example, NiPc is used as a in systems of chemical identification and these systems are based on the effect of conductivity change due to selective absorption of O<sub>2</sub>, NO, NO<sub>2</sub> and HCl [8, 10, 14, 15]. On the other hand, there are very few reports on the influence of ammonia (NH<sub>3</sub>) on electrical conductivity and optical properties of NiPc thin films. Finally, to the best of our knowledge, electrical properties of NiPc-based barrier structures in the presence of ammonia have not been reported up to this date.

The goal of this study is to investigate the influence of ammonia on electrical properties of barrier structures based of NiPc thin films.

### Experimental

NiPC thin films were deposited by the thermal evaporation method. Indium tin oxide (ITO) continuous thin films ( $R_s = 40 \Omega/\text{square}$ ) on the glass were used as substrates in this experiment. The base pressure in the chamber was less than  $10^{-5}$  Pa. Dispersive NiPc powder (Sigma Aldrich Ltd.) was placed in the molybdenum boat, which was resistively heated to  $(400 \pm 10)^\circ\text{C}$ . Substrates were heated to  $100^\circ\text{C}$  during the thin film deposition process. These deposition parameters provide thickness uniformity of the film, and assure that molecular content of the film is equivalent to that of the powder [16]. The thickness of the resulting films was measured using interference microscope MII-2. X-ray diffraction (XRD) analysis on the samples was performed on Rigaku Rapid diffractometer. The x-ray beam was incident on the sample at  $3^\circ$  angle. Diffracted pattern of Cu K $\alpha$  radiation ( $\lambda=0.154 \text{ nm}$ ) was registered by a cylindrical detector. To achieve the best signal-to-noise ratio for NiPc reflections (marked by “x” in Fig. 2, inset), the obtained pattern was integrated in the narrow range of angles  $\Delta\chi$  which also increased intensity of NiPc peaks compared to other reflections. Aluminum (Al) and nickel (Ni) contacts were deposited on ITO/NiPC stacks by thermal evaporation and had thickness of less than 200 nm. The surface of the ITO/NiPC/Al structure was investigated using Zeiss Ultra scanning electron microscope (SEM) in secondary electron mode.

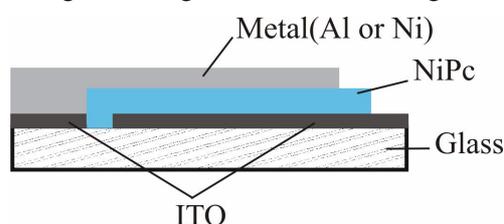


Fig. 1. Crossection of ITO/NiPc/metal structure

The crosssection of ITO/NiPc/metal structure is shown in Fig. 1. The gaseous medium was provided at room temperature in a closed volume using 10% aqueous solution of ammonia. Samples were exposed to ammonia saturated vapor pressure of 11.7 KPa. Time dependence of the resistance of a ITO/NiPc/Ni structure exposed to ammonia was measured at room temperature using VA38 DMM digital multimeter. The upper limit of the resistance

that can be measured using this device is 50 M $\Omega$  and the time response of it is 0.5 second. The electrical properties (load curves) of ITO/NiPc/Al and ITO/NiPc/Ni structures were measured using galvano-static electronic block.

### Results and discussion

Deposition conditions of NiPC thin films define their molecular orientation which in turn influences optical and electrical properties of the film [9, 16–19]. It was shown that  $\alpha$ - modification of nickel phthalocyanine ( $\alpha$ -NiPc) has higher sensitivity to gaseous media compared to other polymorphs [9]. Thus, it was important to verify the crystal structure of as-deposited NiPc thin films.

The x-ray diffraction pattern of NiPc thin films on ITO substrates has a set of low-angle reflections ( $2\theta < 20^\circ$ ) and a set of peaks at higher  $2\theta$  angles (Fig. 2). The position of the first and the most intense peak is consistent with that of 100 peak for tetragonal crystal structure of  $\alpha$ -NiPc. The second peak can be

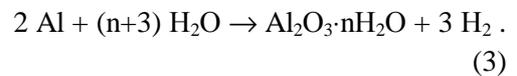
identified as a 200 reflection of the monoclinic crystal structure of  $\alpha$ -NiPc. The other low-angle peaks represent 200 and 300 reflections of tetragonal structure. All the other peaks at higher angles originate from polycrystalline ITO thin film. A broad hump in the region  $2\theta = 20 - 30$  degrees is caused by amorphous glass substrate [20, 21]. From the XRD analysis, it can be concluded that as-deposited thin films consist mostly of  $\alpha$ -modification of NiPC with tetragonal crystal structure. The size of NiPc crystallites was calculated based on the position  $\theta$  and full width at half maximum  $\beta$  of the first reflection using Scherrer's formula  $L = K_s \lambda / \beta \cos(\theta)$  where  $\lambda$  is x-ray wavelength and  $K_s=1$  is Scherrer's constant [23]. The size of the crystallites was found to be 30 nm in agreement with values reported for other phthalocyanine thin films [24, 25].

The electrical properties of the ITO/NiPc/Al barrier structure exposed to ammonia vapor are shown in Fig. 3. Experimental I – V and I – P curves have characteristic shapes of fuel cells. The output voltage as a function of the current starts at 600 mV at 0  $\mu$ A , decreases with an increasing current and reaches the value of to 0.05 V at 120  $\mu$ A. The maximal power that can be achieved at the output of the barrier structure is 22  $\mu$ W at 80  $\mu$ A current.

The generation of electrical energy in the ITO/NiPc/Al structure in the presence of ammonia may be caused by electrochemical reactions that involve Al and NiPc. As ammonia and water vapor are adsorbed on the Al surface, they form a basic solution. The base causes dissolution of the thin alumina layer on the top of Al contact. The subsequent activation of Al results in the oxidation of its atoms and the reduction of Ni<sup>2+</sup> ions described by equations (1) and (2)



Corrosion happens on the surface of Al contacts along with an oxidation reaction (1). In this process activated Al<sup>3+</sup> ions interact with water vapor which results in the formation of Al<sub>2</sub>O<sub>3</sub>·nH<sub>2</sub>O surface layer according to the reaction (3)



The initial step of the process of generation of electrical energy in ITO/NiPc/Al barrier structure is the ionization of Al contact according to reaction (1). It mostly happens on the high surface energy areas, such as particulates, pores and other surface nonhomogeneities (Fig.4, a). The exposure of ITO/NiPc/Al surface to ammonia vapor causes the area around the surface defects to change (Fig. 4, b).

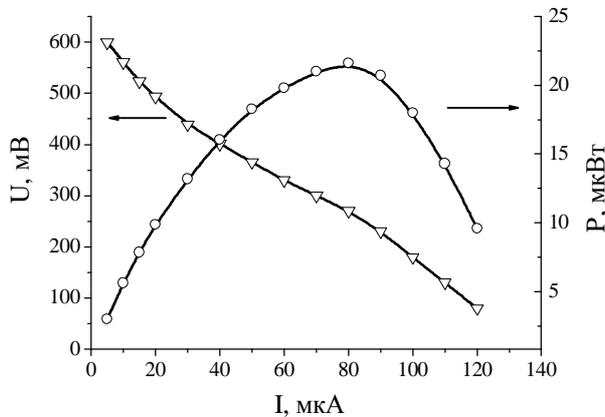


Fig. 3. Voltage and power as a function of current in ITO/NiPc/Al barrier structure exposed to ammonia

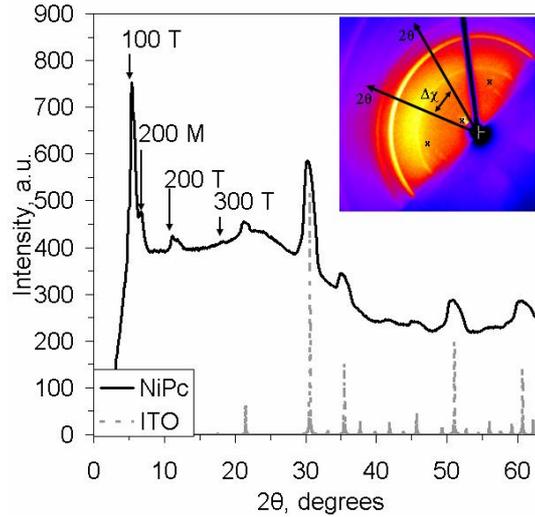


Fig. 2. X-ray diffraction pattern of NiPc thin films on ITO substrates. Inset: Intensity map obtained after XRD scan. NiPc peaks are marked by "x"

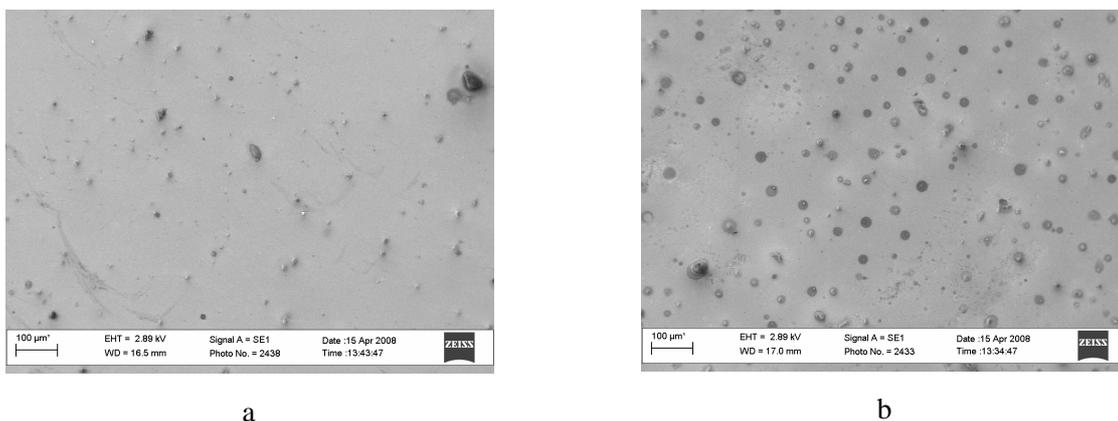


Fig. 4. SEM images of Al contact surface before (a) and after (b) exposure to ammonia for 60 min

The intermediate step between reaction (1) and (2) is the transport of electrons across the NiPc/Al interface. It is known that most of the metals form blocking barriers with phthalocyanines. In the case of NiPC, it was earlier shown by investigation of Au/NiPc/Al structures [17, 18].

The last step of the process of generation of electrical energy in ITO/NiPc/Al barrier structure is the reduction of  $\text{Ni}^{2+}$  ions in the NiPc structure. It leads to the formation of atomic nickel according to the reaction (2) and decreases the bond strength between  $\text{Ni}^{2+}$  ions and phthalocyanine molecules. This process may also induce the decomposition of NiPc molecules with the subsequent migration of Ni atoms and formation of the nickel nanoclusters and nanoparticles. Decrease in number of  $\text{Ni}^{2+}$  ions may also cause a decrease in the rate of the reduction reaction (2)

Dynamics of the reaction that leads to generation of electrical energy was studied under the periodic exposure of the ITO/NiPc/Al barrier structure to ammonia vapor. Fig. 6 shows resistance of the structure as a function of time. The value of the resistance in the “off” state was larger and response time of it was smaller than corresponding measurement limits of the VA38 DMM multimeter.

To summarize, we propose that the generation of electrical energy in ITO/NiPc/Al barrier structure can be explained in the following way. The exposure of Al contact surface to ammonia and water vapor result in the activation of aluminum. Released electrons can overcome NiPc/Al barrier, and reduce  $\text{Ni}^{2+}$  ions in NiPc molecules. It leads to the formation of excess negative charge which is supplied to the external circuit. Due to the interaction of ammonia and water molecules,  $\text{NH}_4^+$  and  $\text{OH}^-$  ionic groups are created in the NiPc thin film. It leads to significant increase in the conductivity of the system

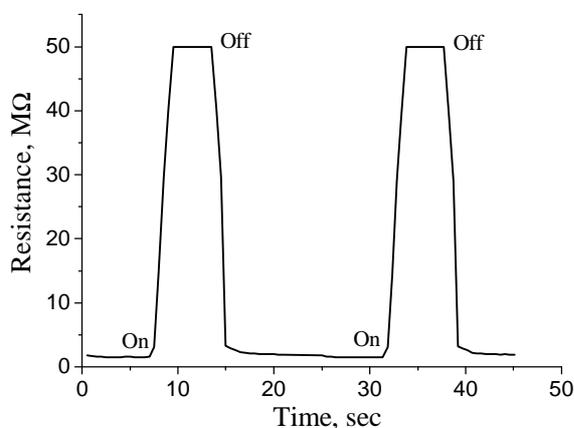


Fig. 5. Resistivity of the ITO/NiPc/Al barrier structure under the periodic exposure to ammonia medium

According to the proposed reaction mechanism, using Ni contacts instead of Al should prevent redox reaction with NiPc from happening. This fact is experimentally confirmed by the absence of electrical energy generation in the ITO/NiPc/Ni barrier structure in gaseous ammonia medium. It makes us believe that the proposed mechanism of generation of electrical energy in ITO/NiPc/Al barrier structure is correct.

### Conclusions

Thin films of organic molecular semiconductor  $\alpha$ -NiPc were deposited on ITO coated glass substrates by the thermal evaporation method. Exposure to ammonia vapor leads to the increase of the films' electrical resistance. The exposure of ITO/NiPc/Al barrier structure to the ammonia medium resulted in the generation of electrical power of 22  $\mu$ W. The optimal open circuit voltage and closed circuit current values were found to be 0.6 V and 120  $\mu$ A respectively. The generation of electrical energy in the structure is caused by a redox reaction. First, aluminum atoms are activated by absorbed ammonia and water vapor, then electrons overcome NiPc/Al energy barrier and reduce molecules of nickel phthalocyanine. It was shown that the presence of water vapor in ammonia medium leads to significant response of the electrical resistance of the ITO/NiPc/Ni barrier structure caused by ionic conductivity in the NiPc thin film.

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