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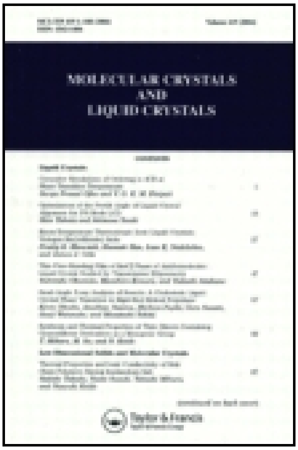

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V. V. Cherpak [a] , P. Y. Stakhira [a] , O. I. Kuntyy [a] & A. Zakutayev [a b]

[a] Lviv Polytechnic National University, Lviv, Ukraine
[b] Oregon State University, Corvallis, OR, USA

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Study of Barrier Structures on the Base of Nickel Phthalocyanine Thin Films During the Interaction with the Ammonia Medium

V. V. Cherpak[1], P. Y. Stakhira[1], O. I. Kuntyy[1], and A. Zakutayev[1,2]
[1]Lviv Polytechnic National University, Lviv, Ukraine
[2]Oregon State University, Corvallis, OR, USA

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Thin films of the α polymorphic modification of a nickel phthalocyanine (NiPc) which possess a high sensitivity to actions of gaseous media are deposited by the thermal vacuum deposition method. Indium tin oxide (ITO) continuous thin films on glass are used as substrates. On the basis of these films, the barrier structure ITO/NiPc/Al has been formed. We have found that there exists the electrogeneration effect in the ITO/NiPc/Al structure under the action of the gaseous ammonia medium. The appearance of a short circuit current and an open circuit voltage is observed only in the ITO/NiPc/Al structures that can be explained by redox reactions.

Keywords: ammonia; electrogeneration effect; nickel phthalocyanine

INTRODUCTION

The development of new high-efficiency non-fossil-based energy sources is a big goal of contemporary electronics. Fuel cells are among the most important directions toward it [1–3]. These devices directly convert the energy of fuel into the 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 the *p*-type conductivity in air due to the absorption of atmospheric gases

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Address correspondence to P. Y. Stakhira, Lviv Polytechnic National University, Lviv, Ukraine. E-mail: stakhira@polynet.lviv.ua

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[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 in systems of chemical identification; these systems being based on the effect of conductivity change due to the selective absorption of O_2, NO, NO_2, and HCl [8,10,14,15]. On the other hand, there are very few reports on the influence of ammonia (NH_3) on the 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 the 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 ($R_s = 40\,\Omega$/square) on glass are used as substrates in this experiment. The base pressure in a chamber was less than 10^{-5} Pa. Dispersive NiPc powder (Sigma Aldrich ltd.) was placed in a molybdenum boat which was resistively heated to 400 ± 10°C. Substrates were heated to 100°C during the thin film deposition process. These deposition parameters provide the thickness uniformity of films and assure that the molecular content of a film is equivalent to that of powder [16]. The thickness of the resulting films was measured using an interference microscope MII-2. X-ray diffraction (XRD) analysis of the samples was performed on a Rigaku Rapid diffractometer. The x-ray beam was incident on the sample at a 3°-angle. The diffracted pattern of Cu Kα radiation ($\lambda = 0.154$ 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 the intensity of NiPc peaks as compared with 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 a Zeiss Ultra scanning electron microscope (SEM) in the secondary electron mode.

A cross-section of the ITO/NiPc/Al structure is shown in Figure 1. The gaseous medium was provided at room temperature in a closed volume, by using a 10% aqueous solution of ammonia. Samples were exposed to ammonia at the saturated vapor pressure of 11.7 kPa.

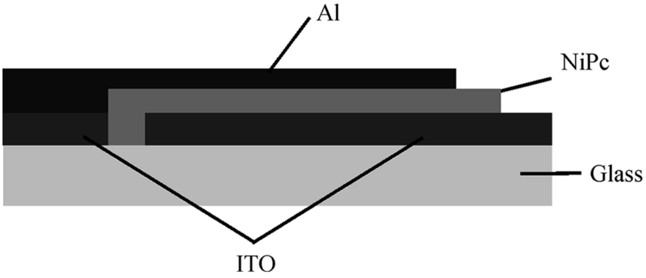

FIGURE 1 Cross-section of the ITO/NiPc/Al structure.

The electrical properties (load curves) of the ITO/NiPc/Al structure was measured using a galvano-static electronic block.

RESULTS AND DISCUSSION

Deposition conditions of NiPC thin films define their molecular orientation which then affects optical and electrical properties of a film

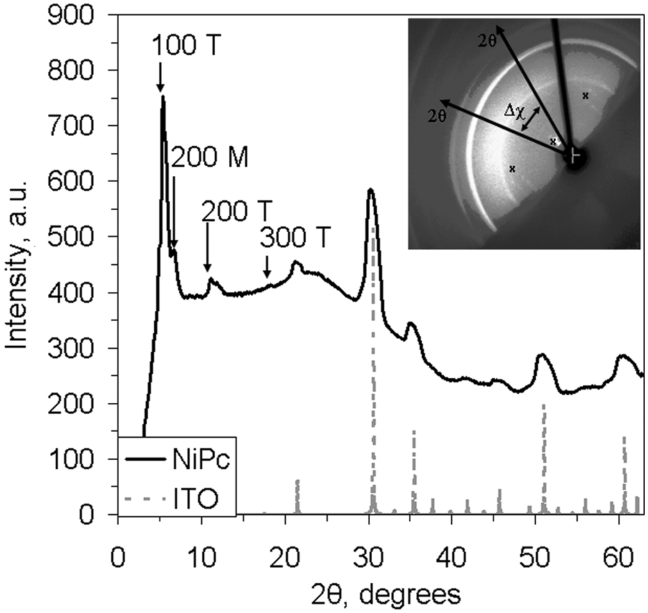

FIGURE 2 X-ray diffraction pattern of NiPc thin films on ITO substrates. Inset: intensity map obtained after XRD scan. NiPc peaks are marked by "x".

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[9,16–19]. It was shown that the α-modification of nickel phthalocyanine (α-NiPc) has higher sensitivity to gaseous media as compared with 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 2θ angles (Fig. 2). The position of the first and most intense peak is consistent with that of the 100 peak for the tetragonal crystal structure of α-NiPc. The second peak can be identified as a 200 reflection of the monoclinic crystal structure of α-NiPc. The other low-angle peaks represent 200 and 300 reflections of the tetragonal structure.

All the other peaks at higher angles originate from a polycrystalline ITO thin film. A broad hump in the region $2\theta = 20$–30 degrees is caused by the amorphous glass substrate [20,21]. From the XRD analysis, it can be concluded that as-deposited thin films consist mostly of the α-modification of NiPC with the tetragonal crystal structure. The size of NiPc crystallites was calculated on the basis of the position θ and the full width at half maximum β of the first reflection using Scherrer's formula, $L = K_s\lambda/\beta \cos(\theta)$ [22], where λ is the 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 Figure 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 μA, decreases with increase in the current and reaches the value of 0.05 V at 120 μA. The maximal power that can be achieved at the output of the barrier structure is 22 μW at the 80-μA current.

The generation of electrical energy in the ITO/NiPc/Al structure in the presence of ammonia can 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 the dissolution of the thin alumina layer on the Al contact top. The subsequent activation of Al results in the oxidation of its atoms and the reduction of Ni^{2+}ions described by Eqs. (1) and (2)

$$2\ \mathrm{Al} \longrightarrow \mathrm{Al}^{3+} + 3\ \mathrm{e}, \tag{1}$$

$$3\ \mathrm{Ni}^{2+} + 2\ \mathrm{e} \longrightarrow \mathrm{Ni}. \tag{2}$$

This process has high electromotive force, because $E^0_{Al^{3+}/Al} = -1.67V$ for aluminum and $E^0_{[Ni(NH_3)_6]^{2+}/Ni} = -0.48V$ for nickel in the ammonia

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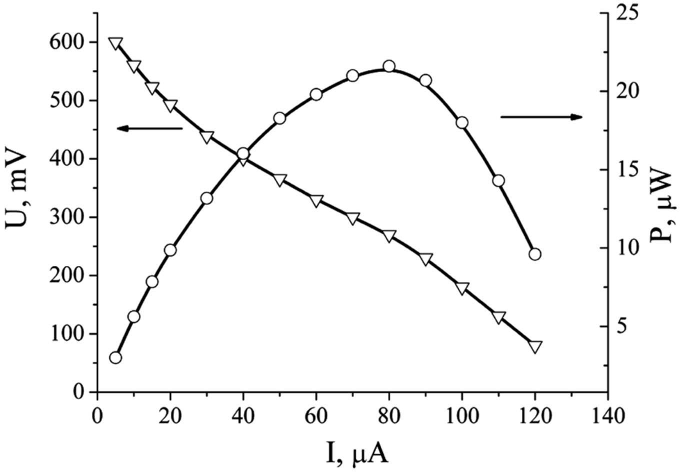


FIGURE 3 Voltage and power as functions of the current in the ITO/NiPc/Al barrier structure exposed to ammonia.

complex (analog of nickel phthalocyanine). The obtaining of nickel by the electrochemical cementation with aluminum in ammonia solutions [26] can prove that the nickel reduction happens exactly in this way.

During this process, Ni(0) stays most probably in the structure of a phthalocyanine molecule. However, taking into account that the environment contains oxygen of air, the regenerated (reduced) nickel is oxidized again to the oxidation level (+2). Therefore, it is possible to assume the inversion of the oxidation-reduction process with nickel ions Ni(+2) ↔ Ni(0).

The following concurrent reactions are possible in the volume of phthalocyanine films:

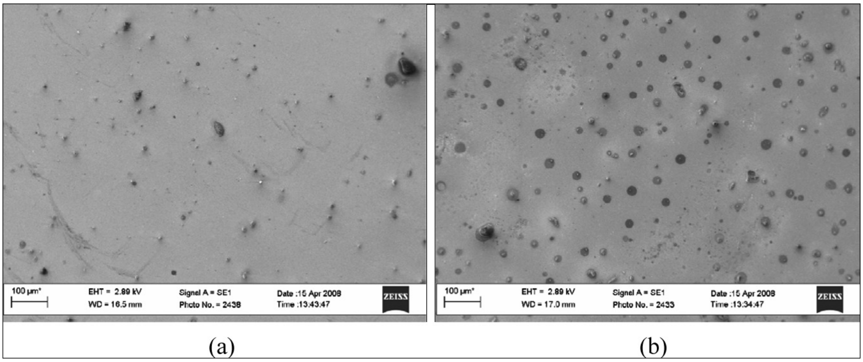
$$O_2 + 2H_2O + 4e \longrightarrow 4OH^-(E^\circ = 0.401V), \qquad (3)$$

$$2H_2O + 2e \longrightarrow H_2 + 2OH^-(E^\circ = -0.828V). \qquad (4)$$

Corrosion happens on the surface of Al contacts along with the oxidation reaction (1). In this process, activated Al^{3+} ions interact with water vapor which results in the formation of an $Al_2O_3 \cdot nH_2O$ surface layer according to the reaction

$$2Al + (n+3)H_2O \longrightarrow Al_2O_3 \cdot nH_2O + 3H_2. \qquad (3)$$

The initial step of the process of generation of electrical energy in the ITO/NiPc/Al barrier structure is the ionization of Al contacts



(a) (b)

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

according to reaction (1). It mostly happens on the areas with high surface energy, such as particulates, pores, and other surface nonhomogeneities (Fig. 4a). The exposure of the ITO/NiPc/Al surface to ammonia vapor causes changes in the areas around surface defects (Fig. 4b).

The intermediate step between reactions (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 the ITO/NiPc/Al barrier structure is the reduction of Ni^{2+} ions in the NiPc structure. This leads to the formation of atomic nickel according to reaction (2) and decreases the bond strength between Ni^{2+} ions and phthalocyanine molecules. This process can also induce the decomposition of NiPc molecules with the subsequent migration of Ni atoms and the formation of nickel nanoclusters and nanoparticles. A decrease in the number of Ni^{2+} ions can also cause a decrease in the rate of the reduction reaction (2).

CONCLUSIONS

Thin films of the organic molecular semiconductor α-NiPc were deposited on ITO substrates by the thermal evaporation method. The exposure of the ITO/NiPc/Al barrier structure to the ammonia medium resulted in the generation of an electrical power of 22 µW. The optimal open-circuit voltage and the closed-circuit current values were found to be 0.6 V and 120 µA, respectively. The generation of

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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 the NiPc/Al energy barrier and reduce molecules of nickel phthalocyanine.

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