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Conductivity in nanostructured films of paramagnetic manganese phthalocyanine

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Abstract. Manganese (II) phthalocyanine MnPc is known for its interesting magnetic properties and diverse coordination chemistry, but little is known about its conductivity. In our previous work, we observed how introduction of a permanent magnetic field during deposition modifies the microcrystalline structure of the growing MnPc films. In this paper, we have shown that the magnetic field, together with the substrate temperature, is responsible for the lateral current in the two-terminal MnPc-based cells with interdigital contacts to change, while the influence of atmospheric environment and illumination is much less noticeable.

Keywords: conductivity, vacuum evaporation, film, manganese phthalocyanine

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Проводимость наноструктурированных пленок фталоцианина марганца

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Аннотация. Фталоцианин марганца известен своими интересными магнитными свойствами и разнообразием координационных взаимодействий, но о его проводимости в твердой фазе известно немного. В предыдущей работе мы наблюдали, как приложение постоянного магнитного поля во время роста меняет кристаллическую структуру пленок фталоцианина марганца. В данной работе мы показали, что магнитное поле, совместно с температурой подложки, ответственно за изменение токов в двухконтактных устройствах на основе фталоцианина марганца и встречно-штыревых контактов, в то время как влияние окружающей атмосферы и освещения гораздо менее заметны.

Ключевые слова: проводимость, вакуумный рост, пленка, фталоцианин марганца

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Introduction

Bright prospects of quantum computing and magnetic memory [1] have stimulated great interest in the physics of organometallic complexes, such as metal phthalocyanines. However, unlike inorganic (semi)conductors, these molecular materials have a more complex, two-level organization of a solid: the internal atomic structure of molecular skeleton and the arrangement of molecules in a bulk sample, each of which related to its macroscopic electro-physical and magnetic properties.

Phthalocyanines are impurity semiconductors [2, 3] whose conductivity value and even the sign depend on the sample history and the environment. In addition, the understanding of charge transport processes suffers from an uneven microcrystalline morphology of films that have several temperature-dependent polymorphs [2, 3]. It is hence desirable to find a method or experimental setup that would allow reproducibly obtaining phthalocyanine films of a certain structural quality. One of such parameters can be permanent magnetic field introduced into the growth zone during the vacuum deposition process.

Manganese phthalocyanine (MnPc) is a spin 3/2 paramagnetic complex whose molecules form crystalline phases with a herringbone motif, which is characteristic of other planar phthalocyanines. However, MnPc molecules interact more strongly with each other, which leads to an interplanar spacing of 3.2 nm [4] and ferromagnetic behavior of crystals at low temperatures. Although these facts have been known for many years [6], the microscopic transport properties of bulk samples remain practically unclear. For instance, a metastable α-phase of MnPc often mentioned in literature [5] has never been confirmed by X-ray diffraction analysis. Conclusions about its existence and properties are made based on the similarity of the intramolecular architecture of MnPc complex with copper phthalocyanine without taking into account the intermolecular (exchange) interactions [6]. This is probably why the calculations based on simple exchange models cannot predict observed effects [7]. Remarkably, that the conductivity values reported for MnPc are orders of magnitude greater than for its metal-phthalocyanine congeners [8].

The transport properties of conventional phthalocyanines have been actively studied in recent decades. The most troubling issue here is the high content of electrically active impurities reaching 10% in the commercially available materials, which is incomparable with 10^{-7}% in classical semiconductor materials like single-crystal silicon. Gas molecules, oxygen in particular, can penetrate freely into loosely packed molecular samples (films, polycrystals) and act as an electron acceptor thereby increasing the concentration of majority charge carriers, in this case, holes.

The studies on the electro-physical properties of thin MnPc films are seldom, due to widely announced instability of a molecule in air, this issue has been addressed in Ref. [9] in more detail. Here, we report some results of photoelectrical measurements on the MnPc films grown in a magnetic field applied in two different directions relative to the deposition surface.

Preparation of samples and experimental setup

The MnPc powder was recrystallized in a vacuum chamber (VUP 5M) in a crucible at 500 °C and a residual pressure less than 10^{-6} Torr before use. The handling of MnPc in laboratory conditions has been described in [9].

Glass/ITO (Merch, 25 Ohm cm) and ceramic plates equipped with photolithographically deposited interdigitated nickel electrodes (IDE) with a gap of 30 μm and a metallization height of 80 nm were used as substrates. Before being placed in the evaporation chamber, the substrates were cleaned in an ultrasonic bath with acetone and isopropyl alcohol, followed by drying in an argon flow. The deposition rate did not exceed 0.1 Å/s (according to quartz microbalancing) at a vacuum of $5 \cdot 10^{-7}$ Torr. The thickness was 100 nm for the MnPc films deposited on substrates with IDE and 100–300 nm for films on glass/ITO substrates. As a source of the magnetic field in

the growth zone, the H38 class neodymium magnets with dimensions of 55×55×35 mm providing a magnetic field strength of up to 0.6 T were used. The direction of the field lines was always parallel to the deposition surface. During the deposition on substrates with IDE, the magnetic field was oriented both parallel and perpendicular to the electrode fingers – Fig. 2, *b*.

Electrical measurements were carried out using a Keithley 4200 semiconductor characterization system in a sealed cuvette filled with argon or a synthetic air (zero gas) called "air" hereinafter. Readings were taken in a voltage sweep mode (maximum electric field was 30 kV/m, sweep time 2 minutes) or in a constant field mode at 30 kV/m. The measurement cycle was carried out as follows. The measurement started after the cuvette was purged with Ar for 10 min in the dark, 5–10 seconds after applying the bias the light was turned on for 10 min, then turned off and the measurement continued for another 10 min. Surface morphology was studied using a scanning electron microscope Carl Zeiss SUPRA 50 VP. More data on the morphology of MnPc films growth with and without a magnetic field can be found in Ref. [10].

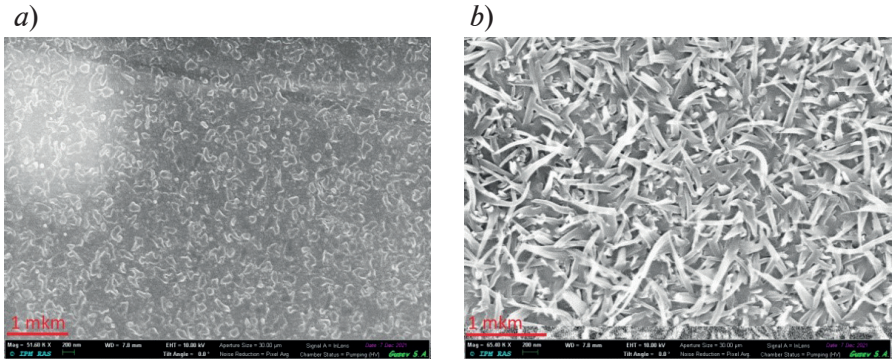

Fig. 1. SEM images of 300 nm thick MnPc film deposited onto ITO/glass substrate at zero field at 25 °C (*a*) and 200 °C (*b*)

Results and discussion

SEM images in Fig. 1, *a* show that the MnPc film grown on cold glass/ITO substrate is continuous, with irregularly shaped surface objects with typical size of 200 nm. The hot-grown MnPc consists of whisker crystals with an aspect ratio of up to 10:1 (crystal length up to 1.5 μm, width up to 150 nm), which likely do not form continuous layer on the substrate – Fig. 1, *b*. Thus, measurements of vertical conductivity give unreliable results due to leakage of the top evaporated metallic electrode and/or "burning out" of single whiskers during current flow. The in-plane (planar, lateral) conductivity measurements are discussed below.

The specific conductivity of MnPc films lies in the range $10^{-10} \div 10^{-7}$ $Ohm^{-1}cm^{-1}$ depending on the type of sample in Table 1, which significantly exceeds the value of 10^{-12} $Ohm^{-1}cm^{-1}$ indicated in [11] for copper phthalocyanine. The dark conductivity of the films grown on cold substrate (consist presumably of α-MnPc) is sensitive to the atmosphere – Table 1. It is reduced by a factor of 10 when the sample is exposed to synthetic air for 10 minutes after purging with argon, possibly due to desorption of admixtures. However, magnetic field does not remarkably affect the conductivity of cold-grown samples, so Table 1 focusses on the hot-grown samples. Their dark conductivity is low when the films are grown at zero field but largely increases when a magnetic field is applied, regardless of its direction. All hot-grown films are insensitive to the atmosphere. It should be mentioned that the synthetic air was used, which excludes the ingress of atmospheric gases other than oxygen and nitrogen (water or carbon monoxide for example). The maximum specific conductivity was measured for MnPc films deposited on a hot substrate in the presence of a 0.5T field directed parallel to the electrode fingers – Table 1.

Obviously, the reason of increase in conductivity of films grown with a field by more than two orders of magnitude is their intricate morphology with even more elongated whisker crystals than shown in Fig. 1 (not shown here). This facilitates the transport of charge carriers across the film thanks to the narrower intergrain gap. Direction of the magnetic field lines with respect the electrode fingers during the film grow does not have a clear effect on both the in-plane conductivity and the transition time, because of the large scatter of the derived values (Table 1).

The light-induced current as a constant bias (photoconductivity) is very low, as illustrated in Fig. 2.

Table 1

Dark lateral conductivity and light-induced transients for 100 nm thick MnPc films

Substrate temperature, °C	Magnetic field strength (parallel or perpendicular to the electrode fingers), T	Specific conductivity at $E = 30$ kV/m, $Ohm^{-1}cm^{-1}$		Transient time of current change, s		
		Atmosphere		Light	Atmosphere	
		Ar	Air		Ar	Air
25	0	2.5×10^{-9}	3.0×10^{-10}	On	526	588
				Off	250	116
200	0	1.0×10^{-10}	1.0×10^{-10}	On	263	161
				Off	141	161
	0.3, perpendicular	6.2×10^{-8}	6.0×10^{-8}	On	455	588
				Off	52	122
	0.3, parallel	2.4×10^{-8}	2.3×10^{-8}	On	250	182
				Off	84	93
	0.5, perpendicular	2.0×10^{-8}	3.0×10^{-8}	On	312	312
				Off	68	91
	0.5, parallel	9.4×10^{-8}	9.6×10^{-8}	On	213	133
				Off	80	82

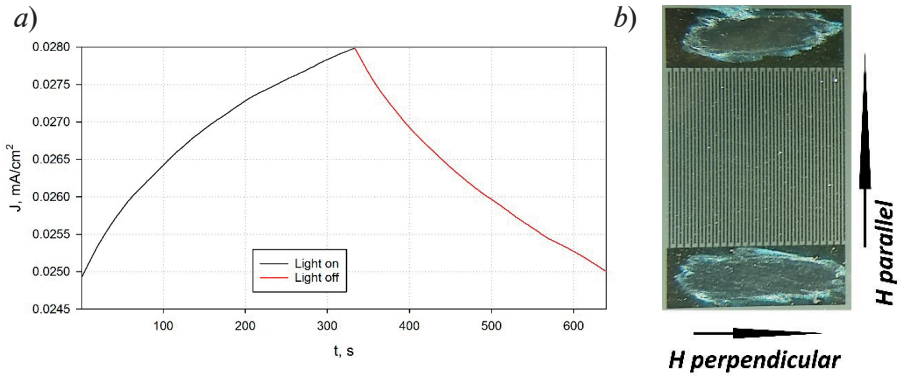

Fig. 2. Time evolution of the current density for a 100 nm MnPc film deposited at 25 °C without magnetic field (measured in Ar) (*a*); photograph of MnPc film with IDE (*b*). Parallel and perpendicular orientations of magnetic field are shown relative to contact grid

The relative rise of the signal upon illumination lies with 5%. Nonetheless, after turning the light on, a slow increase of current density is observed with characteristic exponential time from several minutes to hours (Table 1). This time scale is comparable with the processes of desorption of gaseous impurities from the samples due to evacuation or heating [11]. There are large fluctuations in the transient times with no apparent trends among samples (Table 1). However, the time during which the current decays to its initial value after light impact is shorter for all films grown in a magnetic field.

Conclusions

The magnetic field applied during the deposition of paramagnetic MnPc molecules on cold substrates has practically no effect on their dark and photoconductivity. However, the effect manifests itself with an increase in the deposition temperature up to 200 °C. As shown earlier [10], the microstructure of hot-grown films depends on the magnetic field strength but not on the direction: the stronger the superimposed field, the denser the MnPc whiskers. The samples grown in a magnetic field demonstrate faster decay of photocurrent and about two-orders of magnitude higher conductivity. Therefore, the increase in the dark conductivity of the films is associated with

field-induced morphological changes. Different in-plane orientation of the magnetic field does not lead to anisotropy of conductivity, which is consistent with the absence of in-plane anisotropy in morphology.

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