Electrical measurements on two-layer phthalocyanine films

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Modification of electrical properties of thin films of the low molecular weight organic semiconductors is an important stage in the development of devices employing these functional materials, e.g., diodes, photoreceptors, sensors etc. Therefore, new approaches to variation of the conditions of injection, generation and transport of the charge carriers are desirable. The present work is aimed at electrical characterization of two-component layered structures based on the phthalocyanine (Pc) type metalloorganic complexes in open cells with a constant metal/semiconductor interface (Fig. 1a and b).

The organic semiconductors under consideration are copper phthalocyanine, PcCu (**I**) and peripherally chlorinated copper phthalocyanine, ClPcCu (**II**) (Fig. 1a). As known, the substitution for halogen atoms in Pc-ligand leads to severe alteration in both the electronic system of molecule and the crystal structure of the solid (see, e.g., [1]). A downward shift of the LUMO and HOMO energy levels and hence increased ease of reduction generally result in the n-type conduction of thin films [2]. To prove this change, the so-called gas-test method is useful [2, 3]. It showed, in particular, that exposure of the films of (**II**) to the ppm level NH_3 concentrations led to an increase of conductivity, whereas for the films of (**I**) under the same conditions a decrease caused by the initial p-type conductivity was observed (cf. [4]). One can therefore assume that by bringing these two films into contiguity a contact potential (or surface dipole [5]) may arise. To compensate for this potential the electrons from (**I**) will pass to (**II**), which facilitates formation of the interfacial layer with a definite configuration. It could in turn alter the conductivity in the lateral direction, i.e., along (and near) the interface.

The samples consisted of insulating Al_2O_3 supports (3.5 × 3.5 × 0.5 mm polycorundum plates) with lithografically patterned thin Ni interdigital electrodes, where number of finger pairs was 30, interfinger spacing and finger wide 30 μm, and metallization height 0.08 μm. Molecular films were evaporated on these substrates (schematically shown in Fig. 1b) in a conventional VUP-5(SU) vacuum station. The process was carried out under vacuum ca. 10^{-4} Torr with deposition rate 0.1–0.2 nm/min. First, the ca. 100 nm thick layers of (**I**) or (**II**) were deposited, thereafter referred to as the "basic" layers. Then, the layer of a second component {(**I**) for the basic layer of (**II**) or (**II**) for basic layer of (**I**)} was evaporated at the substrate temperature of 450–460 K without breaking the vacuum. The thickness of the latter (top) layer varied from ca. 10 to 100 nm (measured by quartz resonators, atomic force microscopy and interferometry). The *I/V* curves at the voltages in the range of 0.2–20 V were recorded, their ohmic regions were used to determine the specific conductivity, σ and its thermal activation energy, E_a in the temperature range of 300–430 K. Some parameters are listed in Table I. The samples were *ex situ* characterized by various instrumental techniques (see, e.g., [8]).

*In both cases, i.e., for **II** on **I** and **I** on **II** structures, an increase of conductivity was clearly observed*, thus no depletion layers in the line of applied voltage are formed. As follows from Table I, the conductivity of the basic film rises with an increasing thickness of the top layer, while E_a decreases. On the other hand, $\Delta\sigma$ and ΔE_a do not correlate in such a manner with an increase in the thickness of the basic layer. For the basic films thicker than those used in this experiment the described trend vanishes; for thinner films the continuousness becomes markedly worse. This suggests formation of some space charge region, whose profile depends, to some degree, on the top layer thickness.

The conductivity of structures with a similar total thickness of 200 nm {i.e., 100 nm of (**I**) and 100 nm of (**II**)} but inverse alternation of layers is different (Table I): the highly resistive films of chlorinated phthalocyanine still govern the overall conductivity of the heterostructure. Therefore, the conductivity of the basic film having a direct contact with metallic electrodes keeps playing the key role.

As microscopic investigations show, the surface of the basic film is composed of wavy clusters (the substrate is by far smoother), which is typical of sublimed polycrystalline Pc films [6]. The top layer therefore has interfaces of a granular character, especially for thinner films. This can impede the transport along the **I**/**II** (or *vice versa*) interface from the upper side due to formation of "diodes connected in series opposition." The rectifying properties of Pc/halogenated Pc heterojunctions are reported elsewhere [2, 7]. This is a likely reason why the currents leaking through the top layer can be

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TABLE I

Type of the basic layer	Thickness of the top layer (nm)	Before annealing σ_{300}^{a} (ohm cm)$^{-1}$	Before annealing E_a (eV)^b	After annealing σ_{300} (ohm cm)$^{-1}$	After annealing E_a (eV)^b
I	0	6.4e−11	0.63	8.1e−9	0.47
I	10	1.4e−6	0.44	4.2e−7	0.31
I	30	2.2e−5	0.32		
I	100	2.4e−5	0.31	1.5e−5	0.21
II	0	9.5e−10	0.46	1.2e−12	0.55
II	10	7.7e−8	0.45	1.1e−8	0.49
II	30	1.0e−7	0.41		
II	100	8.2e−7	0.31	3.4e−8	0.44

[a] Specific conductivity at 300 K in air.

[b] The well-know dependence of the $\sigma = \sigma_o \exp(-E_a/kT)$ type was used, where σ_o is coefficient, E_a the activation energy, k the Boltzmann constant and T the absolute temperature. The high T sections were taken for calculations for non-linear curves in Fig. 2.

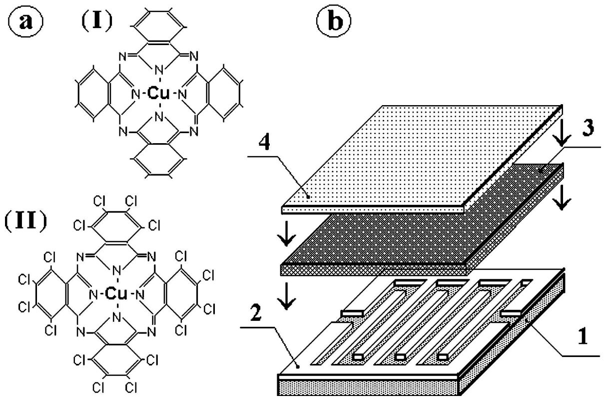

Figure 1 (a) Molecular structures of PcCu, **I** (left) and ClPcCu, **II** (right) compounds; (b) scheme of the sample fabrication: 1—insulating substrate; 2—thin metallic contacts; 3—basic layer (**I** or **II**); 4—top layer (**II** or **I**).

neglected. Further making the top layer thicker does not practically improve the conductivity, more clearly for (**II**) as "top" layer (Table I). It can be explained by a growing contact area between the layers until the islands merge into homogenous top film of any thickness (the largest possible contact).

The temperature dependencies of σ were measured on multiply treated samples at decreasing temperatures (due to some hysteresis effect). The accuracy in temperature control was ±2 K. The readings were taken when the current leaking through the samples reached a constant value. The data so obtained are presented in Fig. 1 both for air and air/ammonia mixture. Note that the curves practically coincide at higher temperatures where full desorption of NH_3 occurs. For a thicker top layer, both the basic film and the **I**/**II** interface are better screened from the ammonia impact, consequently, the curves have a nearly linear profile (Fig. 2). For a thinner top layer, the sign of the conductivity change $\Delta\sigma$ in the presence of ammonia is the same as for a single initial layer of an individual component: σ decreases for (**I**) and increases for (**II**) (Fig. 1).

Subsequent annealing in air (Table I) does not affect the above trends. However, whilst the films of (**I**) exhibit lower E_a and higher conductivity, the films of (**II**) become even more dielectric. This may be attributed to an enhanced incorporation of oxygen that is the major admixture determining the p-type semiconductivity of (**I**) films [5]. For (**II**) its role is obviously different. It should be said however, that the possibility of

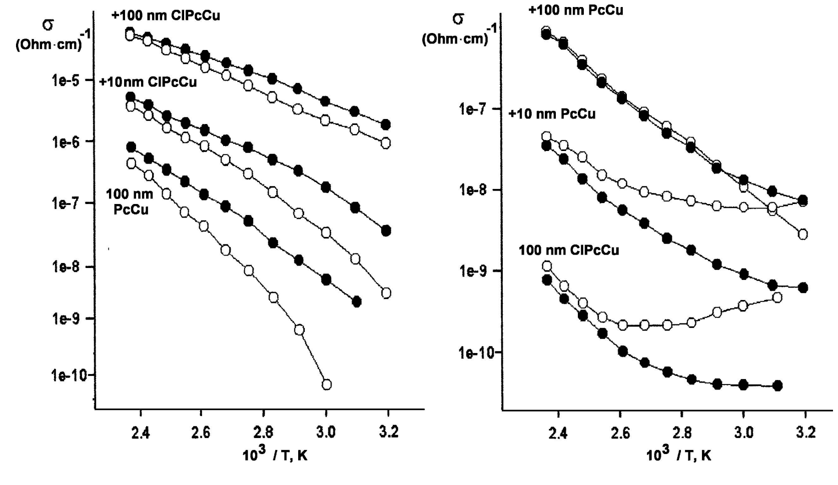

Figure 2 The dependencies of the film conductivity on the temperature for mono- and bi-layered samples (see, text and Table I for parameters): PcCu basic layer (**I**) (left), ClPcCu basic layer (**II**) (right); ●—in air; ○—in the air/100 ppm NH_3 mixture.

interlaminar diffusion of admixtures (or defects) has not been properly estimated.

We continue the study of multi-component molecular films based on substituted phthalocyanine compounds with a focus on targeted modification of their physical properties. This field includes such systems as Pc/dopant (e.g., introduced by ion-beam implantation), mixed Pc(1)/Pc(2) and bi-layered Pc(1)/Pc(2) heterostructures [8].

Here, an approach to control the conductivity of a bulky functional phthalocyanine layer with underlying planar electrodes by depositing the top phthalocyanine layer with different redox and conducting properties is reported. The experimental procedure is extremely easy. An increase by orders of magnitude in specific conductivity in the direction perpendicular to the assumed gradient of interface potential was achieved, which is a significant effect for poorly conductive phthalocyanine materials. This phenomenon can be also interesting for (photo-)electrical measurements in nontrivial schemes (such as transistors).

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