THE CAPACITIVE CHARACTERISTICS OF THIN FILM PHOTOELECTRIC CELLS ON THE BASE OF THE MAGNESIUM PHTHALOCYANINE

M.M. PANAHOV, S.A. SADRADDINOV, J.H. JABBAROV, B.SH. BARKHALOV
Baku State University
acad. Z. Khalilov str., 23, Baku, 370145

The magnesium phthalocyanine MgPc, as well as other phthalocyanine compounds, has rather valuable physical-mechanical properties and thin film structures on its base can make a severe competition to well-known inorganic materials at application in the microtransducers. The conducted examination has demonstrated, that on the electronic processes in MgPc at alternating electric field the considerable effect can be rendered by the conditions on the contacts. In the present paper we show, that depending on a degree of doping by oxygen and the concentration of the traps in MgPc it is possible to obtain the essentially distinguished characteristics for metal - MgPc - metal structures.

The layer structures on the basis of the organic semiconductor MgPc have been obtained by a thermal evaporation in a vacuum $\approx 10^{-6}$ Torr of the MgPc layer and second Al electrode onto the quartz substrate with the previously applied transparent SnO_2 electrode. The thickness of the amorphous MgPc layer was 0,2-2,0 μm, an operating area of the structures was equal to 0,1-1,0 sm^2. Doping by oxygen was conducted by the exposure of the MgPc film in the oxygen atmosphere at the temperature 390-420 K. All measurements were conducted in a vacuum $\approx 10^{-5}$ Torr.

The examination of the dependence of the SnO_2/MgPc/Al structures capacity on the temperature and bias voltage evidenced for the presence of the depleted by holes high-resistive layer on the Al/Mg Pcinterface [1]. At low temperatures capacity of the structure is constant. With increasing of the temperature it grows and reaches the upper limiting value $\tilde{N}_n$, depending on a degree of the processing MgPc in the oxygen atmosphere (Fig.1). The values of the $\tilde{N}_n$ for the samples with different oxygen exposure differ strongly. It must be noted, that the effect of such processing on the photoelectric properties of the Al/MgPc/Ag structure was described earlier in [2]. It is easy to explain apparent growth of capacity, if one supposes, that the Al-MgPc interface is characterized by the capacity C_{sch} of the depleted by the charge carrier's layer, shunted by the resistance R_{sch}. If one accepts, that for the considered alternating-current range ($w=2pf$) a relation $R_{sch} >>(wC_{sch})^{-1}$ is valid, so the capacity of the Al/MgPc/Ag "sandwich" can be calculated by the equation [3, 4]:

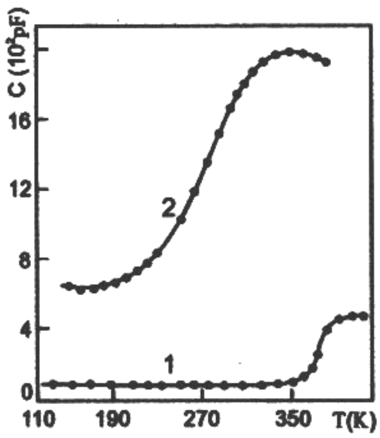

Fig.1. The capacitance versus temperature curves for SnO_2/MgPc/Al structures, proceeded in high vacuum (1) and oxygen atmosphere (2).

$$\tilde{N} = \tilde{N}_{sch}\left(1 + w^2 \tilde{N}^2_{MgPc} R^2_{MgPc}\right) \cdot \left[1 + w^2 \tilde{N}^2_{MgPc}\left(\tilde{N}_{sch} + \tilde{N}_{MgPc}\right) R^2_{MgPc}\right]^{-1} \qquad (1)$$

where C_{MgPc} and R_{MgPc} are the capacity and the shunting resistance of the MgPc layer, respectively.

At low temperatures $RMgPc \gg R_0 exp(Et/KT)$ (where E_t is a depth of the oxygen levels equal to 0,62 eV [5, 6]) is big enough, and the capacity of the Al/MgPc/Ag "sandwich" is determined by the capacity of series-connected capacitors (Fig.1, T<240K),

$$C \approx \left(C^{-1}_{sch} + C^{-1}_{MgPc}\right)^{-1} \qquad (2)$$

and for not too thin MgPc layers, that is for a case when $C_{MgPc} << C_{sch}$, it is determined by the capacity of the MgPc layer, i.e. $C=CMgPc$ (see fig. 1, T<240K). At high temperatures, when R_{MgPc} becomes small, $\left[w^2 \tilde{N}^2_{MgPc}\left(\tilde{N}_{sch} + \tilde{N}_{MgPc}\right) R^2_{MgPc} << 1\right]$, the formula (1) is reduced to:

$$\tilde{N} = \tilde{N}_{sch}\left(1 + w^2 \tilde{N}^2_{MgPc} R^2_{MgPc}\right) \qquad (3)$$

At sufficiently high temperatures $\left(w^2 \tilde{N}_{MgPc} R^2_{MgPc} << 1\right)$,

$$C = C_{sch} \; . \qquad (4)$$

Using this limiting value of the capacity for a known thickness of the MgPc layer, it is possible to find the width of a depletion layer l_s from the expression:

$$l_s = ee_0 \; S \, C^{-1}_{sch} \qquad (5)$$

Calculated by this manner a Schottky barrier width (for MgPc e=3) has appeared to be equal 115Å for a sample, proceeded in the oxygen atmosphere, and 900Å for one, proceeded in the high vacuum.

Knowing l it is possible to determine the density of the trap centers Nt from the equation:

$$N_t = 10^6(\varphi_{sch} - \varphi_i)\varepsilon\varepsilon_0 / \lambda_s, \qquad (6)$$

where φ_{sch} and φ_I are the work function, for a contact material and MgPc layer accordingly. Determined by such manner the trap centers density has appeared to be equal $3.8{\cdot}10^{16}$ and $2.5{\cdot}10^{18}cm^{-3}$, accordingly, for the samples, proceeded in the high vacuum and in the oxygen atmosphere.

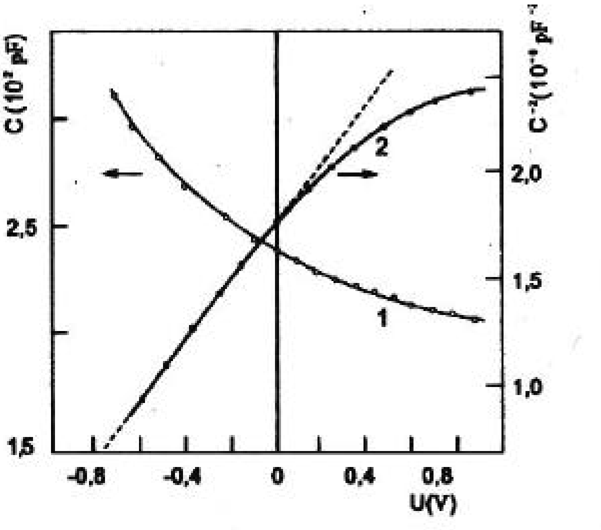

Fig.2. The capacitance versus bias voltage curves for SnO_2/MgPc/Al structures, proceeded in high vacuum.

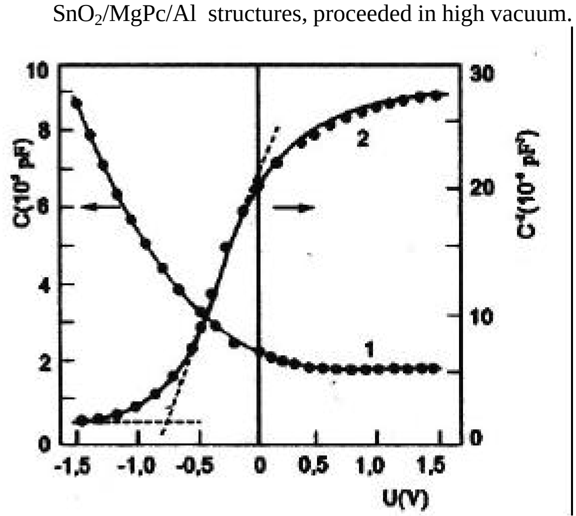

Fig.3. The capacitance versus bias voltage curves for SnO_2/MgPc/Al structures, proceeded in oxygen atmosphere.

The experimentally observed strong dependence of the capacity of the asymmetrical Al/MgPc/Ag " sandwich " on the bias voltage (Fig.2 and 3) testifies, that only up to some small value of an electric field, applied to the "sandwich", the basic mechanism of an electrical conductivity is the tunneling of the equilibrium charge carriers through a Richardson-Schottky barrier. Last circumstance determines a strong dependence of this field value on temperature (Fig.2). Beginning from this value of an electric field, at further increase of the bias voltage in the "locking" direction (negative potential is applied on Al electrode) of the Al/MgPc/Ag "sandwich", starts to prevail the charge carrier transfer through the MgPc bulk, which initially is determined by a linear growth of the transport rate of the equilibrium charge carriers through the MgPc layer (Fig. 2), and then by the velocity of the thermal-field generation of the non-equilibrium charge carriers (Poole-Frenkel effect section). The growth of the thickness of the depleted by the charge carriers layer under growth of the bias voltage (U_b>1V) is accompanied by decrease of the equilibrium capacitance of the *Al-MgPc* junction at the "locked" state of the Al/MgPc/Ag "sandwich". It is described by the relation:

$$C_{sch}^{-2} = U_{bias} \qquad (7)$$

and the slope of this linear sketch (see Fig.2 and 3) is determined, in particular, by the density of the ionized trap centers of the non-equilibrium charge carriers [5]:

$$\frac{\partial}{\partial U}\left(C_{sch}^{-2}\right) = 2\left(q\varepsilon_0\varepsilon s^2 N_t\right)^{-1} \qquad (8)$$

Determined by this manner the trap centers density N_t=$3.7{\cdot}10^{16}sm^{-3}$ for a sample, proceeded in a high vacuum and N_t=$2{\cdot}10^{18}sm^{-3}$ for a sample, proceeded in the oxygen, atmosphere are in a good agreement with the values, determined in [3].

The properties of a Schottky barrier manifest themselves self also in the photocurrent-versus-light intensity characteristics of the structure. In the Fig.4 the voltage-capacitance characteristics of the SnO_2/MgPc/Al structure has been shown. Under illumination, a separation of the non-equilibrium charge carriers on a surface barrier between Al and MgPc takes place in the MgPc, doped by the oxygen. A resistance of the barrier layer at high *L*, even at room temperature, decreases so that capacity of the barrier layer at small bias voltages decreases sharply (Fig. 4, curve 1).

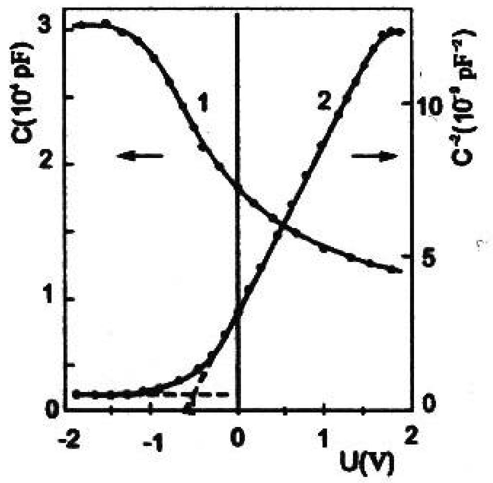

Fig.4. The barrier capacitance versus bias voltage curves for SnO_2/MgPc/Al structures, proceeded in oxygen Atmosphere, at T=298K and L=$3{\cdot}10^4$Lx light intensity (f=10^4Hz).

The intersection point of an extrapolated linear section of the $\tilde{N}^{-2} \propto U_{bias}$ dependence, under the constant illumination L=$3{\cdot}10^4$Lx with the voltage (Fig. 4, curve 2) gives the value of the diffusion potential U_d=0.4V. Using this value of U_d and taking into consideration a Schottky decreasing of the barrier [7], equal to 0.12 eV on the Al/MgPc interface, we obtain the width of the Schottky barrier $\hat{O}$=0.52 eV, that is in a good agreement with the results, observed on a direct current.

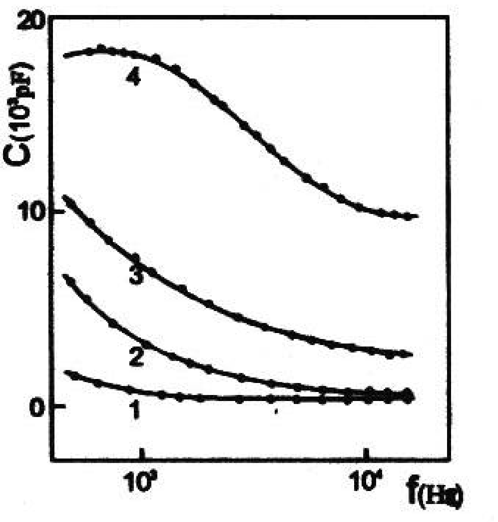

Fig.5. The barrier capacitance versus alternating current frequency curves in dark (1.3) and under steady-state illumination L=3·10^4Lx for SnO_2/MgPc/Al structures, proceeded in high vacuum (1,2) and oxygen atmosphere(3,4).

A frequency dependences of the capacity of the SnO_2/MgPc/Al "sandwich" at room temperature are given in a fig. 5. The dark capacity for undoped by the oxygen "sandwich" is high enough and does not depend on the frequency. At the same time, under illumination capacity of the structure considerably increases (Fig. 5, curve 2) at low frequency region, because of the effect of the surface electron defects on depleted by the charge carriers layer. With growth of the frequency the light increment of capacity decreases sharply. After the doping of the MgPc layer in the oxygen atmosphere, capacity of the structure sharply grows and has irreversible character (Fig. 5, curve 3). Under illumination the capacity of the *MgPc* layer, doped by the oxygen, exhibits a strong changes, promptly decreasing with the frequency growth. The apparent behavior of the capacity is completely correlated with the results of the analysis of the equation (1), from which it follows, that at high light intensities in the low frequency region the capacity of the sample should be equal $C \approx C_s$. It is seen from the Fig. 5 (the curve 4), that this limiting value of the capacity is reached at the light intensity L=10^4 Lx.

The obtained results allow to conclude, that on the basis of the magnesium phthalocyanine films it is possible to produce thin-film photoelectric cells with high enough light sensitivity. In contrast to earlier what described earlier, the photoelectric cells offered by us have more stable characteristics.

[1] *Yu. Vidadi, S.F. Sadraddinov, S.Sh. Khalilov*. Properties of film structures with a Schottky barrier on the basis of the MgPc doped by the oxygen, in: "Electronics of organic materials", Moscow, "Nauka" Publishing House, 1985, p. 179 (in Russian).

[2] Organic semiconductors (Review of the literature for 1968). The Ukrainian Academy of Sciences, Institute of Physics, Kiev, 1969 (in Russian).

[3] *B.Sh. Barkhalov, Yu.A. Vidadi*. Properties of Al /Copper Phthalocyanine/ Ag Diode Structure with the Sehottky Barriers.Thin Solid Films, 1970, V. 40, 1. 2, L5.

[4] *F.G. Simmons, G.S. Nadkarni, M.C. Lancaster*. Alterenating Current Electrical Properties of Highly Doped Insulating Films. J. Appl. Phys., 1970, v. 41, p. 538.

[5] Organic semiconductors (Review of the literature for 1969). The Ukrainian Academy of Sciences, Institute of Physics, Kiev, 1970 (in Russian).

[6] *D.D. Eley, G.D. Parfitt*. Semiconductor Character of the Electrical Conductivity of Organic Matters. Trans. Faraday Soc., 1955, v. 51, p. 1529.

[7] *S.M. Zee*. Physics of the Semiconductor Devices. Ìoscow, «Energia» Publishing House, 1973.

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