THE MECHANISM OF ELECTRICAL CONDUCTIVITY IN THIN-FILM STRUCTURE ON THE BASIS OF THE ORGANIC SEMICONDUCTOR VANADIUM PHTHALOCYANINE

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The volt-ampere and capacitance-voltage characteristics in metal-semiconductor-metal (MSM) structures on the basis of vanadium phthalocyanine (VPc) organic semiconductor have been investigated. It is revealed that at the absence in the MSM-structure of the high-resistive interface barriers, nonlinear CVC at high electric fields is a result of the field assisted thermal emission of charge carriers from traps (Poole-Frenkel effect). It is also established that at low temperatures and high electric fields, when density of the charged traps is sufficiently high (> 10^{24} m^{-3}), Coulomb potentials overlapped and a barrier lowering becomes proportional to electric field intensity and the modified Frenkel-Poole effect becomes predominant.

INTRODUCTION

High light and thermal resistance, ability to form of a continuous film by evaporation in vacuum at moderate temperatures makes the organic semiconductor vanadium phthalocyanine (VPc) a valuable material for the solution of a number of tasks of microelectronics.

Choosing the appropriate material for electrodes, using known techniques it is possible to create ohmic [1-3] as well as rectifying [3-6] electrical contacts to a surface of metal-organic semiconducting compounds of the phthalocyanine series.

For some phthalocyanine compounds the charge transport and rectifying of an alternating current phenomena were investigated in layered structures («sandwiches»), which electrical contacts were formed by using identical or different metals [3, 5-7].

For study the structures on the basis of the phthalocyanine with non-blocking contacts more often a method of space-charge-limited currents (SCLC) is used [8]. In phthalocyanine single crystals with silver electrodes ohmic (linear) current-voltage characteristics (CVC) were observed that passes further in nonlinear one. In many experimental works, at the absence of the blocking contacts in phthalocyanine thin film structures, nonlinear CVC are interpreted by the charge carrier injections in bulk from electrodes [8, 9].

EXPERIMENTAL PART

Our studies of the electrical properties of structures on the basis of the evaporated VPc layers have shown that at absence in the structure of blocking electrodes, nonlinear CVC is a result of the field assisted thermal emission of charge carriers from traps.

Double additional cleaning of the industrial VPc powder by vacuum sublimation has ensured reproducibility of our results. Investigated structures were obtained by consecutive thermal vapor deposition in a vacuum (p $\approx 10^{-3}$ Pa) the bottom Ag electrode, the VPc layer and the top Ag electrode on a non-heated ceramic substrate. On the same substrate were obtained simultaneously eight identical on topology "sandwich" samples, distinguished only by thickness of the VPc layer, that being within the limits of 0.4-2.0 μm. All measurements were carried out in a vacuum 10^{-3} Pa.

The study of the temperature-field dependences of the electrical conductivity for VPc have shown, that nonlinear CVC of the Metal/VPc/Metal structures are stipulated by Frenkel-Poole emission, which study allows to receive the information about the charge carriers localization centers in a semiconductor [10].

For study of electrical properties of the high-resistance films it is necessary previously to establish the diagram of distribution of the applied voltage in MSM-structure, which is determined, mainly, by the basic properties of the metal/semiconductor interface. An effective way of an establishing of distribution of the voltage in MSM-structures is a study of the conduction and capacity at various temperatures and frequencies [11]. The capacity of the Ag/VPc/Ag structure in a wide temperature range practically does not depend on temperature (Fig. 1). Besides for structures with the identical electrode areas, but with various thickness of a VPc layer (d = 0.67-1.30 μm) electrical capacity $C \sim d^{-1}$ (insert in a fig. 1). These data unequivocally testify to absence of the electrical field discontinuities in the considered structure [11]. In this case equivalent circuit of a sample is represented by capacity, shunted by active volume resistance, and the applied constant voltage U totally drops in the VPc layer.

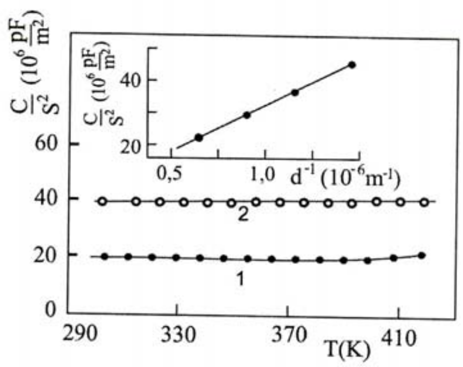

Fig.1. Dependence of capacity C on the temperature T of the Ag/VPc/Ag structure with various thicknesses d of the *VPc* layer, μm: (1 - 1.30; 2 - 0.67). Insert - C/S vs d^{-1}.

The dependence of the current I on the applied voltage U in Ag/VPc/Ag structure is given in fig. 2. At low voltages with the increase of the voltage U the current I grows linearly, and at large voltages - non-linearly. It has appeared that at the large voltages the dependence $I/U \propto exp(U^{1/2})$ takes place. At passing to rather thick VPc films the character of dependence is preserved, however inclination α of a linear part of dependence $lg(I/U)$ on $U^{1/2}$ appreciably decreases, and the value of the product $\alpha\, d^{1/2}$ practically remains constant.

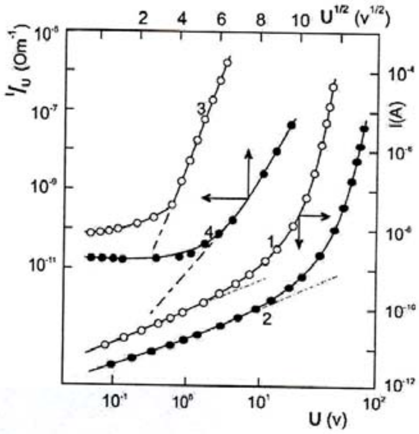

Fig. 2. Dependence of a current I on the applied voltage U in the Ag/VPc/Ag structure (1 and 2) and I/U on $U^{1/2}$ (3 and 4) at different thickness of VPc films, μm: 1- 0.67 (1 and 3) and 1.30 (2 and 4). The electrodes area S =1.15 mm^2.

At the absence a high-resistance interface barriers in the MSM-structure the linear dependence $lg\ I/U$ on $U^{1/2}$ may be connected with Poole-Frenkel emission [12, 13], when the process of thermal excitation of the charge carriers from traps is facilitated by the applied electrical field. It can be checked up by studying temperature dependence of a current at various voltages and establishing of characteristic parameters.

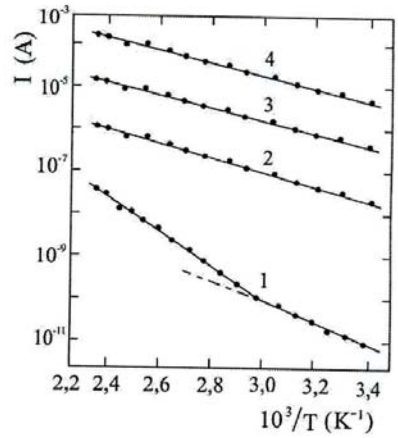

Fig. 3. The temperature dependences of the current I in the structure Ag/VPc/Ag at different applied voltages, V: 1 – 0.4; 2 – 10; 3 – 20 and 4 - 30 . Thickness of VPc film d = 0.67 μm.

In a fig. 3 are given the temperature dependence of a current at various fields in VPc film. In a weak field (F < 6 $\cdot 10^5$ V/m) current I exponentially depends on T and also is described by two activation energies: 0.56 and 0.75 eV (in account per кT). The value E_0 = 0.56 eV is a depth of the dominant trapping levels. The second value characterizes intrinsic conductivity of the VPc (1.50 eV in account per 2 кT *)* and meets to the data given elsewhere [13]. In a strong field, when ($F \geq 10^7$ V/m), an exponential increase of a current with the increasing of the temperature is described only by an activation energy E_F < 0.56 eV, and with growth of F the value of E_F decreases according to the Frenkel's theory on the ionization of the traps:

$$E_F = E_0 - e\beta F^{1/2} \tag{1}$$

where e- electronic charge, β - Frenkel-Poole constant. The value of β can be determined from the curves of the dependence of the Frenkel's barrier lowering for the traps $\Delta\Phi = E_0 - E_F$ on $F^{1/2}$ (fig. 4.), which appears equal to β= 4.25· 10^{-5} V$^{1/2}$m$^{1/2}$.

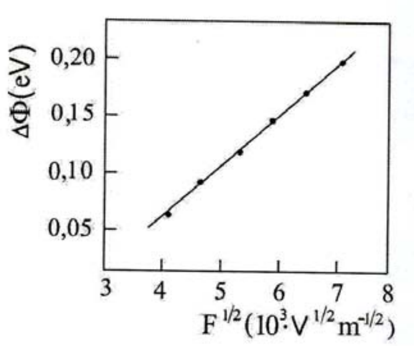

Fig. 4. The dependence of the barrier lowering $\Delta\Phi$ on $F^{1/2}$ for Ag/VPc/Ag structure.

The dependences of the conductivity σ on F in Frenkel coordinates for two temperatures are given in the Fig. 5. In a weak electric field σ does not depend on F (section *ab*) and σ= 4·10 Ω^{-1}· m^{-1} at T = 298 K. Further, with the increase of F in an interval of the several orders the conductivity grows according the law $\sigma \propto expF^{1/2}$ (section *cd*), and the inclinations of straight lines decreases with increasing of the temperature. On this section σ varies according to expression:

$$\sigma \sim \exp\left(-\frac{E_0 - e\beta F^{1/2}}{kT}\right)$$

From the inclination of straight lines on a section *cd* we find, that β = 5.1·10^{-5} V$^{1/2}$m$^{1/2}$ (at T = 298 K) and β = 5.5· 10^{-5} V$^{1/2}$m$^{1/2}$ (at T = 403 K).

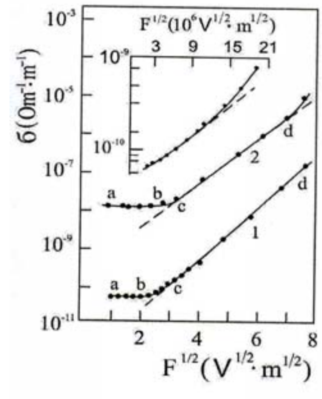

Fig. 5. Dependence of the electrical conductivity σ on $F^{1/2}$ at 298 K (1) and 403 K (2).Insert – the dependence of σ on F at 298 K.

From the theory follows, that Frenkel-Poole constant depends on the dielectric permeability ε and is determined from the formula [12]:

$$\beta_T = (e^3/\pi\varepsilon\varepsilon_0)^{1/2} \tag{3}$$

From the dependence of capacity of structure C on d^{-1} was found, that ε = 3.4 for VPc (fig. 1, insert), and from the formula (3) it is obtained $\beta = 4.12\cdot10^{-5}$ $V^{1/2}m^{1/2}$, that are in good accordance with the values found experimentally from the dependences $\Delta\Phi$ and σ on $F^{1/2}$. The ratio of the values β and β_T, experimentally determined by various ways is within the limits of 1.03-1.3.

In the σ versus $F^{1/2}$ curves a section bc (fig. 5) is observed which is narrowed with the growth of the temperature. It has appeared, that on this section σ obeys the low $\sigma \propto \exp F$. The thermally assisted field ionization, which passes to $\lg\sigma \propto F$ at rather low fields and to $\lg\sigma \propto F^{1/2}$ at high ones, is theoretically analyzed elsewhere [10]. Hence, in VPc are realized the conditions, required for the observation of such emission, and in a section bc the field dependence of conductivity is described as [10]:

$$\sigma \sim exp\left(-\frac{E_0 - \frac{1}{2} erF}{\kappa T}\right) \quad , \tag{4}$$

where r - distance between two next charged traps. As it is seen, at low temperatures and high fields, when density of the charged traps too large, Coulomb potentials are overlapped and a barrier lowering becomes proportional to F. From the expression $r = \sqrt{\frac{e}{4\pi\varepsilon\varepsilon_0 F}}$ we find, that the traps with E_0=0.56eV are separated by 76Å and have concentration $2\cdot10^{24}$ m^{-3}. Depending on films evaporation conditions, when density of acceptors in VPc exceeds 10^{24} m^{-3}, the modified Frenkel-Poole effect becomes prevailing.

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ÜZVİ YARIMKEÇİRİCİ VANADİUM FTALOSİANİN ƏSASINDA NAZİK TƏBƏQƏLİ STRUKTURLARDA ELEKTRİKKEÇİRİCİLİYİNİN MEXANİZMİ

Üzvi yarımkeçirici vanadium ftalosianin əsasında metal-yarımkeçirici-metal (MYM) strukturlarının volt-amper və volt-tutum xarakteristikaları tədqiq olunmuşdur. Müəyyən edilmişdir ki, MYM- strukturunda yüksək müqavimətə malik potensial çəpərlərin mövcud olmadığı halda, sistemdə müşahidə olunan qeyri-xətti VAX tutma mərkəzlərində olan yükdaşıyıcıların istiliyin təsiri altında, elektrik sahəsinin dəstəyi ilə güclənən azad olunması ilə (Pul-Frenkel effekti) bağlıdır. Göstərilmişdir ki, alçaq temperaturlarda və yüksək elektrik sahələrində (F>10^7 V/m), yüklənmiş tutma mərkəzlərinin sıxlığı kifayət qədər böyük olduğu halda (n >10^{24} m^{-3}), Kulon potensialları bir-birini örtür, potensial çəpərin alçalması elektrik sahəsinin intensivliyi ilə düz mütənasib olur və modifikasiya olunmuş Frenkel-Pul effekti üstünlük təşkil etməyə başlayır.

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МЕХАНИЗМ ЭЛЕКТРОПРОВОДНОСТИ В ТОНКОПЛЕНОЧНОЙ СТРУКТУРЕ НА ОСНОВЕ ОРГАНИЧЕСКОГО ПОЛУПРОВОДНИКА ФТАЛОЦИАНИНА ВАНАДИЯ

Исследованы вольт-амперные и вольт-емъкостные характеристики структур металл-полупроводник-металл (МПМ) на основе органического полупроводника фталоцианина ванадия. Установлено, что при отсутствии в МПМ-структуре межповерхностных потенциальных барьеров с высоким сопротивлением, наблюдаемые нелинейные ВАХ связаны с термическим высвобождением носителей заряда из центров захвата, облегченным электрическим полем (эффект Пула-Френкеля). Выявлено, что при низких температурах и высоких электрических полях (F >10^7 В/м), когда плотность заряженных ловушек достаточно высока (N_t >10^{24} м$^{-3}$), кулоновские потенциалы перекрываются, понижение барьера становится пропорциональным полю и начинает преобладать модифицированный эффект Френкеля-Пула.

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