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OHMIC AND SPACE-SHARGE LIMITED CONDUCTIVITY IN DIHYDRODIBENZOTETRAAZA[14]ANNULENE THIN FILMS

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The electrophysical properties of thermally deposited thin films of dihydrodibenzotetraaza[14]-annulene were investigated applying ohmic gold electrodes to them. The volt-ampere characteristic of planar thin films symmetric structure Au – dihydrodibenzotetraaza[14]annulene – Au under dark condition was measured. The direct current conductivity in this structure at room temperature and at a small applied voltage was ohmic, carried out by thermally generated carriers, and the conductivity, limited by space charges carried out by the injected carriers, was observed at a higher applied voltage. The transition from ohmic conductivity to conductivity limited by space charges occurred at an electric field strength in a thin film of $E \sim 4 \times 10^4$ V/m.

Keywords: organic semiconductors, dihydrodibenzotetraaza[14]annulene, thin films, electrical conductivity, ohmic conductivity, space-charge-limited conductivity.

ОМИЧЕСКАЯ И ОГРАНИЧЕННАЯ ПРОСТРАНСТВЕННЫМ ЗАРЯДОМ ПРОВОДИМОСТЬ В ТОНКИХ ПЛЕНКАХ ДИГИДРОДИБЕНЗОТЕТРААЗА[14]АННУЛЕНА

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Исследовали электрофизические свойства термически нанесенных тонких пленок дигидродибензотетрааза[14]аннулена с использованием золотых омических контактов к ним. Измеряли темновую вольт-амперную характеристику планарной тонкопленочной структуры Au – дигидродибензотетрааза[14]аннулен – Au. Проводимость в этой структуре на постоянном токе при комнатной температуре и при небольшом приложенном напряжении была омической, осуществляемой термически генерированными носителями, а при более высоком приложенном напряжении наблюдалась проводимость, ограниченная пространственными зарядами, осуществляемая инжектированными носителями. Переход от омической проводимости к проводимости, ограниченной пространственными зарядами, происходил при напряженности электрического поля в тонкой пленке $E \sim 4 \times 10^4$ В/м.

Ключевые слова: органические полупроводники, дигидродибензотетрааза[14]аннулен, тонкие пленки, электропроводность, омическая проводимость, проводимость, ограниченная пространственными зарядами.

ОМІЧНА ТА ОБМЕЖЕНА ПРОСТОРОВИМ ЗАРЯДОМ ПРОВІДНІСТЬ В ТОНКИХ ПЛІВКАХ ДИГІДРОДИБЕНЗОТЕТРААЗА[14]АНУЛЕНУ

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Досліджували електрофізичні властивості нанесених термічним методом тонких плівок дигідродибензотетрааза[14]анулену з використанням золотих омічних контактів до них. Вимірювали темнову вольт-амперну характеристику планарної тонкоплівкової структури Au – дигідродибензотетрааза[14]анулен – Au. Провідність в цій структурі на постійному струмі при кімнатній температурі і невеликій прикладеній напрузі була омічною, що забезпечувалась термічно генерованими носіями, а при більш високій прикладеній напрузі спостерігали провідність, обмежену просторовими зарядами, що забезпечувалась інжектованими носіями.

Перехід від омічної провідності до провідності, обмеженої просторовими зарядами, відбувався при напруженості електричного поля в плівці $E \sim 4 \times 10^4$ В/м.

Ключові слова: органічні напівпровідники, дигідродибензотетрааза[14]анулен, тонкі плівки, електропровідність, омічна провідність, провідність, обмежена просторовими зарядами.

INTRODUCTION

At the present time there is a great interest in development of organic (molecular) electronics (OE or ME), based on using of various organic molecular materials (organic dielectrics, organic semiconductors or organic «metals») for creating electronic devices. OE is now often referred to as the next-generation electronics that will enable to implement a number of significant advantages over the traditional electronics based on using inorganic semiconductors, Si being the main of them. The unique properties of organic materials create possibilities for many new applications simply impossible with standard inorganic materials. The main advantages of organic materials and, consequently, electronic devices based on it, are as follows: solubility in many solvents, the possibility for a relatively simple and inexpensive manufacturing of flexible elements on a large area at a low temperature, a light weight, opportunities for obtaining materials with desired electronic properties by purposeful chemical synthesis or physicochemical modification of already synthesized materials, a low cost of manufacturing, environmental friendliness etc. [1].

At present, macro-, micro- and nanoelectronic devices, such as various displays (big panel displays, computer displays, mobile phones, iPads, iPhones, TV sets), thin-film transistors, light-emitting diodes, photovoltaic solar cells, electronic memory devices, chemo-, bio- and physical sensors, etc. have already been created on the basis of organic semiconductors [2, 3]. Therefore, over the past years, many aspects of organic electronics research, production and market have progressed, and the pace of progress has continued to accelerate. According to IDTechEx the global market for printed and potentially printed electronics, including organics, inorganics and composites, is forecast to rise from $1.92 billion in 2009 to $57.16 billion in 2019 (see Fig. 1) [4], while the Organic Electronics Association (OE-A) predicts market growth to 200 billion over a decade [5].

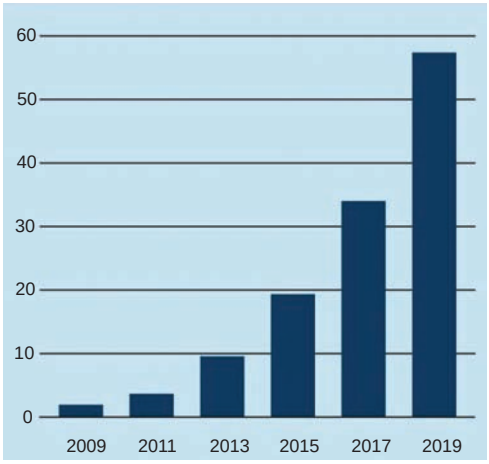

Fig. 1. Global market for organic and printed electronics (US $ billions)

There are two basic classes of organic semiconductors (OS): low molecular weight compounds and polymers [6]. The first of them is the OS class with a low molecular weight, based on the individual molecules (often called «small molecule organic semiconductors»), and it can contain from tens to hundreds of atoms. The second of them is the OS class with a high molecular weight (polymer, i. e., forming a long chain polymer). The common feature of both groups is the presence of a conjugated system of π bonds formed of p-orbitals of carbon atoms. The σ bonds, which form the backbone of the molecule, are more stable than the π bonds (fig. 2). As a result, conductivity in the OS is provided mainly by the π-electron system under ordinary conditions.

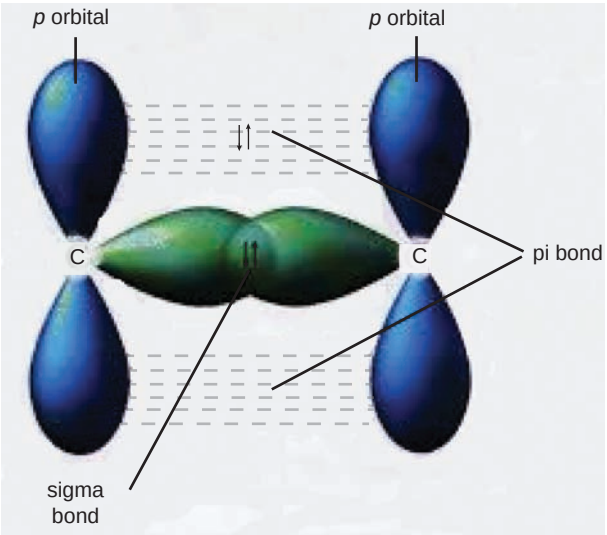

Fig. 2. Schematic image of σ and π bonds in molecules of organic semiconductors

The molecules with different atomic composition and molecular structure are synthesized and used when creating OS-based electronic devices. The low-molecular organic semiconductors, based on the molecules with macrocyclic structure, for instance such as phthalocyanine (Pc, Fig. 3) and dihydrodibenzotetraaza[14]annulene (TAA, Fig. 4), provoke special interest of researchers. These OS have a high thermal and chemical stability, π-conjugated electronic system as well as good sensitivity of electrical properties for various parameters of chemical and physical nature due to the nature of their molecular structure and the presence of the so-called macrocyclic effect in the closed macrocyclic structures. This provides wide opportunities of their application for creation of various micro- and nanoelectronic devices, where they are used usually as thin films that can be deposited by thermal evaporation. Phthalocyanines are now the most commonly used in organic electronics based on small molecule of OS and the mechanism of electrical conductivity in its thin films has already been well studied [7–9].

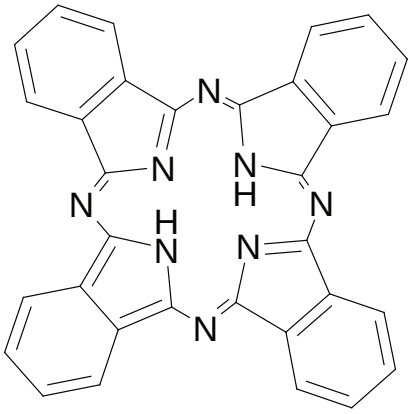

Fig. 3. Phthalocyanine

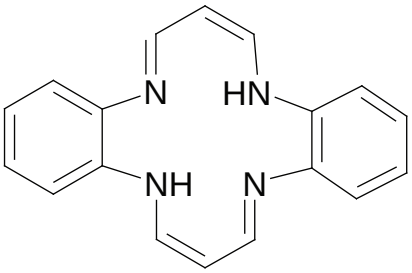

Fig. 4. Dihydrodibenzotetraaza[14]annulene

Until recently, the TAA and materials based on it have been studied and used mainly in chemistry, medicine and pharmacology, however, in the last few years the study of this OS use in engineering and electronics is proceeding vigorously. Chemical gas sensors, thin film transistors, compact discs etc. based on TAA have already been created. Questions, concerning the properties and use of substances and materials based on TAA, were highlighted in our review [10], but now there are new interesting publications related to the study of magnetic properties and applications of such materials for spin filters creation [11, 12]. They open new perspectives for using this OS in actively evolving now spin electronics and in other fields of electronics. The TAA are generally *p*- type semiconductors; they can be sublimed easily, as well as Pc, resulting in high purity thin films without decomposition.

The charge transport characteristics in thin films of OS represent a key foundation for the field of molecular electronics and development of novel organic-based electronic devices. Therefore, it is a fundamentally and practically important subject for investigation. In the present investigation the current — voltage measurements (on direct current) were carried on a planar symmetrical structure of the type: metal (Au) – thin film TAA – metal (Au), further – Au – TAA – Au – structure, to study conduction mechanism in thin films of TAA at various electric fields in the sample.

EXPERIMENTAL PART

The TAA powder, used in this work, was synthesized and purified in the chemical laboratory of the V. Karazin Kharkiv National University (Department of Organic Chemistry, thanks to Prof. V. Orlov and Prof. N. Kolos). The TAA thin films were prepared through thermal sublimation and condensation of the substance of the TAA in vacuum (at pressure ~10^{-5} Torr) with a VUP-5M setup. The TAA thin films were deposited on a polished ceramic substrate with an interdigital Au-electrode and this way the planar structure of M-TAA-M was obtained (Fig.5). The distance between the metal electrodes was 10^5 nm. The thickness of the TAA films was about 100 nm and it was regulated by the weight of the sublimed substance or duration of the period of the open shutter position. Monitoring of the thin films thickness was carried out by a

quartz resonator and additionally determined by their optical transparency.

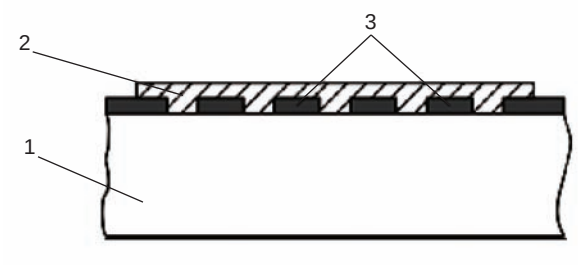

Fig. 5. Planar symmetrical thin films structure Au – TAA – Au: 1 — substrate, 2 — thin film of TAA, 3 — Au electrodes

RESULT AND DISCUSSION

Fig. 6 demonstrates the volt-ampere characteristic of planar thin films Au – TAA – Au – structure under dark conditions, obtained by us.

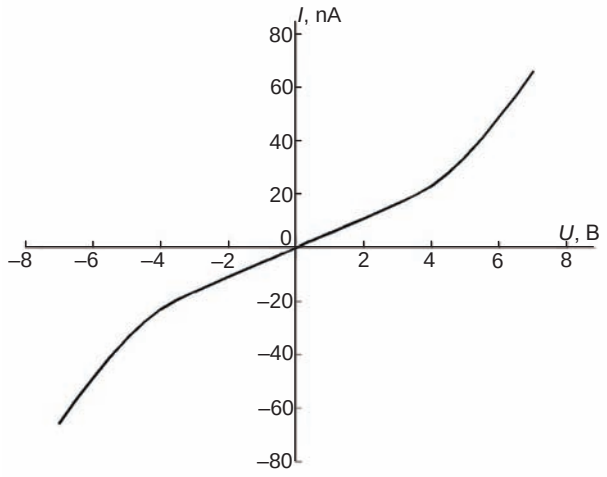

Fig. 6. Volt-ampere characteristic of planar Au – TAA – Au – structure

It can be seen that this volt-ampere characteristic is symmetric with respect to the center of coordinates and has two sections with different slopes. Charge transport in organic semiconductor thin films with ohmic contacts, as is known, depends on the electrical field strength. Charge transport by thermal carrier dominates at the low electrical field. The injected carriers are compensated by dielectric relaxation process and no net charges build up in the film. At the high electrical field, however, the injected carrier density exceeds the thermal carrier density. The injected carriers form space charges to limit the current flow. Therefore, the conduction mechanism is called space-charge-limited conduction (SCLC). The volt-ampere characteristics, obtained by us, as can be seen from the Fig. 6, have two regions. In region I (at a lower voltage) conduction follows Ohm's law and I–V characteristic in this region can be described by equation [13]:

$$J = qp_0\mu_p \frac{V}{d} = qp_0\mu_p E, \qquad (1)$$

where J is the current density, q is the elementary charge, p_0 is the thermal carrier density, μ_p is the hole mobility and d is the electrode spacing. E is electrical field strength.

In region II (at a higher voltage) conduction is SCLC and can be described by the Geurst equation [14], which is valid for metal-organic semiconductor-metal structures of the planar type:

$$J = \frac{2\mu_p\varepsilon}{\pi} \cdot \frac{V^2}{d^2}, \qquad (2)$$

where ε is dielectric permittivity of an organic thin film.

The transition from ohmic to SCLC conductivity in this investigation takes place at a voltage of 4 V i. e. at an electric field strength $E \sim 4 \times 10^4$ V/m. Our results obtained for the TAA films agree well with the results obtained in [15] for nickel phthalocyanine thin films, in which the authors also observed the ohmic conduction at lower voltages followed by space-charge-limited current at higher voltages.

CONCLUSION

In the present work the volt-ampere characteristic of planar thin films symmetric structure Au – dihydrodibenzotetraaza[14]annulene – Au is investigated. Conductivity on direct current in this structure at room temperature reveal an ohmic conduction due to thermally generated carriers in the lower voltage range, followed by SCLC conductivity due to injected carrier in the higher range. The transition from ohmic to SCLC conductivity takes place at electric field strength $E \sim 4 \times 10^4$ V/m.

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