

Conclusion

Samples of metal-organic framework Ni-MOF structures have been obtained. As a result of MOF material processing in a special vacuum chamber, heating to 150°C and mixing the introduced components for 30 minutes, a complex chemical compound with inclusions of iron particles with a particle diameter of 3-5 microns is formed on the substrate surface. The embedded particles act as crystallization centers and, in general, a material with ferromagnetic properties is formed. Powders consist of particles ranging in size from 10 to 50 microns, and the content of ferromagnetic metal reaches 99.16%. No extraneous impurity phases are observed, which indicates the successful formation of Ni-MOF material. Studies of the optical properties of Ni-MOF materials with ferromagnetic properties have shown that such materials have an absorption rate of more than 85%, which is important for creating efficient solar cells. There are five distinct peaks of Raman scattering in the range 600 – 1650 cm⁻¹, which are due to the main crystal structure of Ni-MOF materials. The different ratio of the intensities of the strongest lines indicates a different content of carboxyl groups in the samples.

Acknowledgment

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Cyclic thermal desorption as a mechanism for identifying conductivity in condensed films

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Abstract

The technique to study the conductivity of condensed films by cyclic thermal desorption of gaseous impurities is described. The examples of identification of the conduction mechanism in thin film fluorosubstituted copper phthalocyanine and titanium dioxide are considered based on the method of cyclic thermal desorption. It was found that the cyclic thermal desorption method is applicable for the identification of the conduction mechanism in the film with a hopping conductivity and band conductivity. It is shown that in the films of fluorosubstituted copper phthalocyanine is realized the hopping conduction mechanism. The conductivities can be carried out either by its intrinsic states or by oxygen impurity states depending on the concentration of adsorbed oxygen; impurity levels being above intrinsic levels on the energy scale. The numerical values of the localization radius of intrinsic and extrinsic states and the concentration of centers of

localization in the original materials have been defined. In the films of titanium dioxide produced by a sol-gel process the band conduction mechanism is implemented. These films are extrinsic semiconductors, in which the adsorbed oxygen is a shallow impurity.

Keywords: conduction mechanism, hopping conduction, band conductivity, phthalocyanine, titanium dioxide.

Introduction

The dependence of the conductivity of condensed films on the concentration of adsorbed impurities is determined by the electrotransmission mechanism. In thin condensed films of organic semiconductors with a hopping mechanism conductivity, including phthalocyanines and perylene pigments, adsorbed impurities affect the energy of conduction activation and the concentration of localization centers providing electric transfer, and therefore the conductivity of these films depends on the concentration of adsorbed impurities in a rather complex way [1, 2, 3]. In semiconductor films with a conduction zone mechanism, adsorbed impurities, as a rule, change the concentration of charge carriers without affecting the value of the conduction activation energy.

The purpose of this work is to study the possibility of using the cyclic thermal desorption method to identify the conductivity mechanism of condensed films. Films with deliberately different conductivity mechanisms were chosen for the study: fluorosubstituted copper phthalocyanine (CuPcF_{16}) - an organic semiconductor with a presumably jumping conductivity mechanism, titanium dioxide (TiO_2) - an oxide semiconductor with an area conductivity mechanism.

Experimental

The thick films CuPcF_{16} with a thickness of 50 nm were obtained by thermal sputtering in vacuum 10^{-2} Pa followed by precipitation on polycore substrates equipped with an interdigital system of electrodes at room temperature. Application of films TiO_2 from the film-forming composition was carried out by immersion method. Initial mix for receiving films of TiO_2 sol-gel was prepared by method according to [4]. Titanium tetraisopropoxide ($\text{Ti}(\text{OC}_3\text{H}_7)_4$) was used as the starting Ti-containing component, isopropyl alcohol ($\text{C}_3\text{H}_7\text{OH}$) was used as the solvent, and nitric acid (HNO_3) was used to catalyze the hydrolysis reaction. Molar ratios of components in initial mix for receiving films of TiO_2 are as follows: $\text{Ti}(\text{OC}_3\text{H}_7)_4 : \text{C}_3\text{H}_7\text{OH} : \text{HNO}_3 : \text{H}_2\text{O} = 0,5 : 20 : 0,1 : 0,5$. To measure electrophysical properties, either electrodes from the contact paste SrP-x-37 were used, applied to the surface of the film, or interdigital system of electrodes located under the film.

The dc conductivity of films was measured in a vacuum of 10^{-2} Pa with the aid of a V7-57/1 electrometer. The investigation was performed by the method of cyclic thermodesorption [1]. According to this technique, a sample is heated to a certain preset temperature T_0 and then allowed to cool. In the course of cooling, the conductance of the sample G is measured as a function of the absolute temperature T and described in terms of the equation

$$G = G_0 \cdot \exp\left(-\frac{E_a}{kT}\right) \quad (1)$$

where G_0 is the pre-exponential (tunneling) factor, E_a is the conductivity activation energy, k is the Boltzman constant.

The experiment consisted in a sequence of cycles, whereby the sample was heated to a stepwise increased temperature T_0 , which corresponded to a gradually decreased concentration of adsorbed oxygen. By measuring the temperature variation of conductivity in the course of cooling the sample from this temperature in vacuum, we obtained a family of curves corresponding to various concentrations of adsorbed oxygen on the same sample. Using this set of temperature

dependences, we determined the corresponding room-temperature conductance G and the parameters G_0 and E_a corresponding to various concentrations of adsorbed oxygen.

The fact that during the process of thermal desorption of oxygen the energy of activation of the conductivity of the films has CuPcF₁₆ changed significantly is confirmed by the jumping mechanism of electric transfer in this material.

Results and discussion

To explain the observed fact, use the model of a two-level hopping conduction [1], according to which the electron transfer is carried out through two parallel channels - intrinsic and impurity electron states of localization with radii a_1 and a_2 respectively. In this case, the conductance

$$G = (G_{03})_1 \exp\left(-\frac{\alpha}{a_1 n_1^{1/3}} - \frac{E_{a1}}{kT}\right) + (G_{03})_2 \exp\left(-\frac{\alpha}{a_2 n_2^{1/3}} - \frac{E_{a2}}{kT}\right), \quad (2)$$

where $(G_{03})_1$ and $(G_{03})_2$ are constants depending on the localization radius, $\alpha = 1.73$ is the percolation constant, n_1 and n_2 are the concentration of localization centers corresponding to the intrinsic and impurity states, and E_{a1} and E_{a2} are the energies of activation of intrinsic and impurity conduction, respectively.

Quantities E_{a1} and E_{a2} are defined by relation

$$E_{a1} = \frac{0,99e^2 n_1^{1/3}}{4\pi\epsilon_0\epsilon}, E_{a2} = \frac{0,99e^2 n_2^{1/3}}{4\pi\epsilon_0\epsilon}, \quad (3)$$

where ϵ_0 is the electric constant and ϵ is the relative permittivity.

Since the impurity levels are formed due to splitting-off from the intrinsic levels, the concentration of electron localization centers of intrinsic and impurity states are connected by the relation

$$n_1 + n_2 = n = const. \quad (4)$$

In this case the temperature dependence of conductivity is described by relation (1) and the experimentally observable the conduction activation energy appearing in this relation, and the quantity of the tunneling factor is calculated as

$$E_a = -\frac{d(\ln \sigma)}{d(1/kT)}, G_0 = G \exp\left(\frac{E_a}{kT}\right). \quad (5)$$

The results of comparison of experimental data obtained by the cyclic thermal desorption method with calculations according to the two-level jumping conductivity model made it possible to obtain for CuPcF₁₆ the dependence of conduction activation energy E_a on the proportion of impurity localization centers $x = n_1/n$ shown in Figure 1. The calculations used the values of $a_1 = 70$ pm, $a_2 = 92$ pm, as well as the value of the concentration of localization centers in the material without impurities $1,35 \cdot 10^{27} \text{ m}^{-3}$, which best describe the experimental data. At high and low concentrations of adsorbed oxygen (points 1 and 3 in Figure 1), conductivity is carried out according to impurity states, and at intermediate concentrations (point 2 in Figure 1) - mainly according to their own. From the fact that $a_1 < a_2$, it follows that the impurity levels lie on a scale of energies above their own.

The temperature dependencies of the conductivity of the TiO₂ films, obtained by cyclic thermal desorption, are activation in Figure 2.

In the process of oxygen desorption, conductivity decreases, however, unlike CuPcF₁₆, the energy of conduction activation does not change. The constancy of the conduction activation energy at the decreasing concentration of adsorbed oxygen is indicative of the zonal conductivity

mechanism of the sol-gel film TiO_2 . A small amount of conductivity activation energy (less than 0,25 eV) indicates that the films are TiO_2 impurity semiconductors in which adsorbed oxygen acts as a fine impurity.

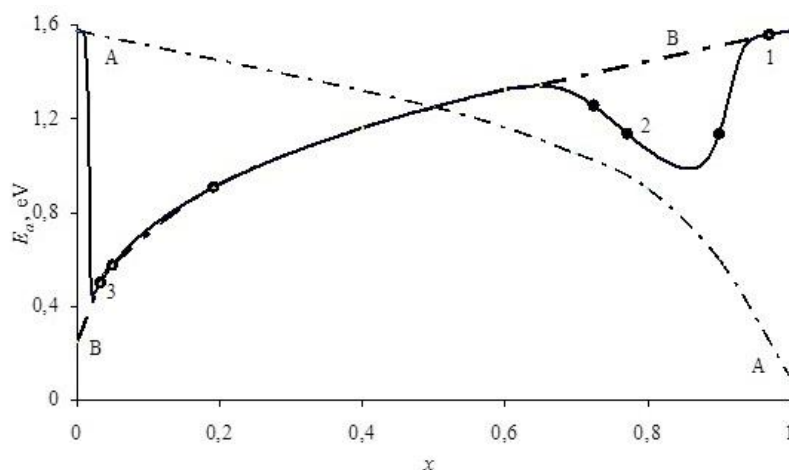


Figure 1. Relation between the conductivity activation energy E_a and relative concentration x of oxygen adsorbed on a CuPcF_{16} film. Points – the experimental data, dash-dotted line – contribution of intrinsic (A-A) and impurity (B-B) electron states, solid line – result of calculations using a two-level hopping conductivity model

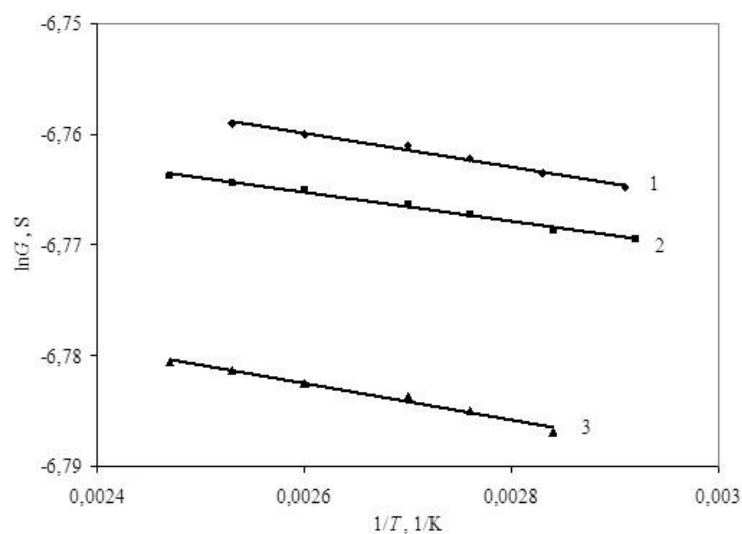


Figure 2. Temperature dependence of the film TiO_2 obtained by cyclic thermal desorption under vacuum cooling with different temperatures: 1 – cooling from 80 °C; 2 – cooling from 120 °C; 3 – cooling from 160 °C

Conclusion

It has been found that the cyclic thermal desorption method is applicable for identifying the conductivity mechanism in jumping conduction films, zone semiconductor and metal conduction. It is shown that in films of fluorosubstituted copper phthalocyanine there is implemented a jumping mechanism of conductivity, besides, depending on concentration of adsorbed oxygen, conductivity can be carried out either by intrinsic states or by impurity states of oxygen, at that impurity levels lie on the scale of energies above intrinsic ones; values of localization radii of intrinsic and impurity states and concentration of localization centers in the initial material are determined. The sol-gel

made titanium dioxide films implement a zonal conductivity mechanism, these films being impurity semiconductors in which the adsorbed oxygen is a fine impurity.

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Electrical conductivity of nanocrystalline nonstoichiometric tin dioxide films near the metal-insulator transition

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Abstract

The temperature dependence of conductivity $\sigma(T)$ of nonstoichiometric tin dioxide films were studied in the temperature range 4-300 K. The films were fabricated by reactive DC magnetron sputtering with following 2-stage temperature annealing. Samples are characterized by high electron concentration (more than 10^{20} cm^{-3}) and a high degree of disorder. Several methods used to distinguish between metallic or insulating types of conductivity were employed to interpret experimental $\sigma(T)$ dependences. These methods give opposite conclusions. Model of polaron transport in metallic systems with strong lattice disorder stimulating dynamic process of electron-phonon coupling was proposed for our samples in order to settle the discrepancies.

Keywords: metal-insulator transition, tin dioxide, metallic conductivity, localization, polaron.

Introduction

Tin dioxide (SnO_2) has attracted intense theoretical and experimental attention due to its wide applications in a variety of applications. A remarkable feature of SnO_2 is the possibility of coexistence of high n -type conductivity and optical transparency even in amorphous state. The main source of free charge carriers in undoped samples are ionized oxygen vacancies which act as shallow donors. As a result the metallic state in nonstoichiometric SnO_2 can be achieved by increasing of the concentration of oxygen vacancies without additional doping with low energy donors. As far as the concentration of oxygen vacancies can be quite easily adjusted by variation of technological synthesis parameters the SnO_2 can be considered as suitable objects to investigate metal-insulator transition (MIT).

MIT is one of the most striking physical phenomenon and has been intensively studied over the last several decades. Nevertheless existing theories of MIT (Anderson and Mott mechanisms) fail to explain some experimental results. For example, Mooij correlations phenomenon stated that the slope of the resistivity curves $\rho(T)$ for many materials near MIT is inversely proportional to extrapolated