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ELECTRICAL PROPERTIES OF STRUCTURES BASED ON NANOCRYSTALS CdS IN GELATIN MATRIX

The electrical characteristics of composite structures based on nanocrystals of cadmium sulfide in a gelatin matrix are studied. It is shown that in the freshly prepared structures, an electric field is formed, which irreversibly increases the electrical resistance of the structures. A complicated form of the temperature dependence of the current is obtained, which is associated with the participation in the current transport of H^+ and OH^- ions in the low-temperature region and electrons arising from rupture of π-bonds in the high-temperature region.

1. Introduction

The optical and electronic properties of semiconductor nanocrystals differ significantly from those for macrocrystalpic matter and depend on the particle size. Such semiconductors, due to the quantization effect [1], make it possible to control their optical, electrical and structural properties, changing only the particle sizes.

Polycrystalline semiconductor films lose their positions in electrical engineering and they are replaced by polymer films with nanocrystals embedded in them. One of the most suitable for use in creating such structures are semiconductor compounds of the A_2B_6 group and, in particular, cadmium sulfide. This material is promising for use in light-emitting devices, since all colors can be obtained by varying the size of the nanocrystal, which makes such structures universal. The literature contains information on the preparation of structures with CdS nanocrystals in the gelatin matrix, their optical and luminescence characteristics [2-4] are described. However, there is practically no information on the electrical properties of such structures. At the same time, in the excitation of luminescence by an electric field, electronic processes play a decisive role in such structures. In this paper, a probable mechanism of electronic processes that determine the electrical conductivity of composite structures with CdS nanocrystals in a gelatin matrix is considered.

2. The film's fabrication methods and experiment

The structures studied were prepared by chemical synthesis from aqueous solutions of cadmium nitrate (0.025 M) and sodium sulphide (0.25 M). The synthesis of nanocrystals of cadmium sulphide occurred at a temperature of +40 ° C in an aqueous solution of photographic gelatin. Gelatin has all the necessary qualities for its use as matrices for semiconductor nanocrystals. Gelatin molecules consist of three polypeptide spiral chains. These chains are interconnected by a limited number of cross-links (so-called σ-bonds) that support the structure of the molecule [5]. Such a structure does not allow the formation of rigid crystalline blocks and is convenient for creating matrix systems, since it has many cells, where molecules of the most diverse substances can enter under suitable conditions. Thus, gelatin molecules in an aqueous solution form a kind of skeleton that divides the which nucleation of nanocrystals and their subsequent growth takes place. Obviously, the more the volume released (ie the less the gelatin concentration), the more reagents it will be in and the more likely will be the formation of nuclei of nanocrystals followed by their fusion. Therefore, the dimensions of CdS nanocrystals depend on the concentration of the gelatin solution.

At the end of the reaction, a solution of cadmium sulfide nanocrystals was deposited on glass substrates coated with a conductive SnO_2

layer. After drying of the gelatin with the CdS nanocrystals embedded in their bulk, an upper electrode of the In-Ga alloy was deposited onto the films. Thus, the investigated composite structures located in the interelectrode space were packed chaotically located gelatin molecules, in the space between which CdS nanocrystals are located and also water molecules, ionic products of the chemical synthesis of Na^+, NO_3^-, formed as a result of hydrolysis of polymer molecules ions $H^+$and OH^-. The films had a thickness of 20-50 μm. The concentration of CdS nanocrystals in the polymer matrix was about 5 wt%. Measurements of the optical absorption spectra showed that the with of the band gap E_g of the CdS nanocrystals studied is 2.68 eV, which is much higher than the value for single crystals ($E_g \approx 2.4$ eV) and is due to the size-quantization effect. The obtained result allowed to calculate [1] the dimensions of nanocrystals of cadmium sulfide, which turned out to be within 12-14 nm.

3. Results and discussion

Figure 1 shows the current-voltage characteristics (I-V characteristic) freshly prepared structures measured at constant voltage. Curve 1 is measured in order of increasing applied voltage, and curve 2 is in order of decreasing voltage. When measuring curve 1 on the I-V characteristic, significant instabilities and chaotic oscillations of the current were observed, which disappeared when the voltage applied to the structure was 600-700 V. After this, the I-V characteristic measured in order of decreasing applied voltage (curve 2) was stable and reproducible in subsequent measurements, regardless of whether they were made in order of increasing or decreasing the applied voltage. Thus, in the freshly prepared structure, an electric field is formed, as a result of which the resistance of the composite layer increases by more than an order of magnitude. The mechanism of current flow in similar polymer matrices can be determined both by transport of carriers by means of ions, and by "jumping" electrons through free radical bonds of the molecular skeleton of the matrix element in the direction corresponding to the polarity of the applied voltage [6]. Electric molding in freshly prepared samples can be caused by a reorientation and a change in the spatial arrangement of gelatin molecules under the action of an electric field. It is possible to polarize gelatin molecules as a result of hydrolytic destruction of some of the weak π-bonds and the formation of polar regions with uncompensated electrons. A necessary condition for rupture of π-bonds is the folding of gelatin molecules in a strong electric field. This reduces the number of current-conducting ion channels by compaction of the gelatin layer and, as a consequence, leads to an increase in the resistance of the matrix element.

A linear section is observed on the current-voltage characteristic of the formed structure at low voltages, which, in the region of stresses exceeding 100 V, is replaced by a section of the power-law dependence of the current on the voltage described by the law $I = const \cdot V^n$ $I = const \cdot V^n$, where n = 1,8-2. Since in the region of these stresses the average electric field strength in the composite layer reaches $(2-5) \cdot 10^4\ V/m$, this behavior of the I-V characteristic can be related to the establishment of a current flow regime limited by the space charge [7] in the composite layer, as was

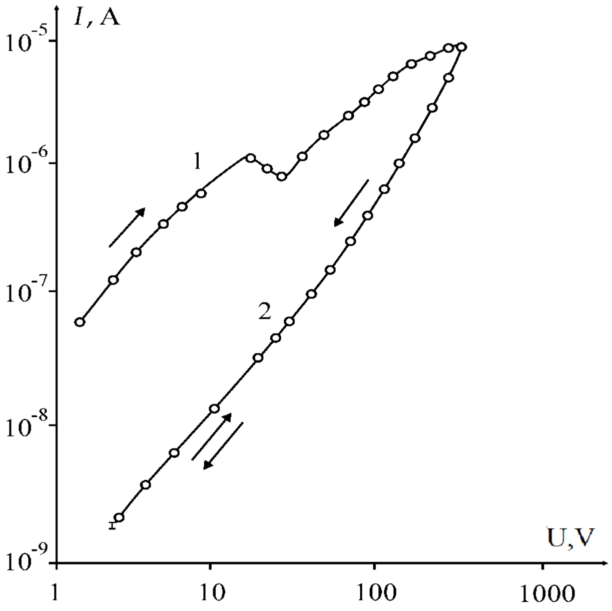

Fig. 1. The current-voltage characteristics of a nanocrystal structure CdS in the gelatin matrix. (T = 295 K).

the case in polymer films of polydiphenylenephthalide, described in [8].

In Fig. 2 shows the current-voltage characteristics of the molded structure measured at a constant (curve 1) and alternating (curve 2) voltage. It can be seen that the current-voltage characteristic measured at alternating voltage remains linear up to voltages of 600 V. This indicates that the quadratic section of the current-voltage characteristic measured at constant voltage is actually due to the flow in the composite of currents limited by the space charge, and is not related to the sample self-heating flowing current [9].

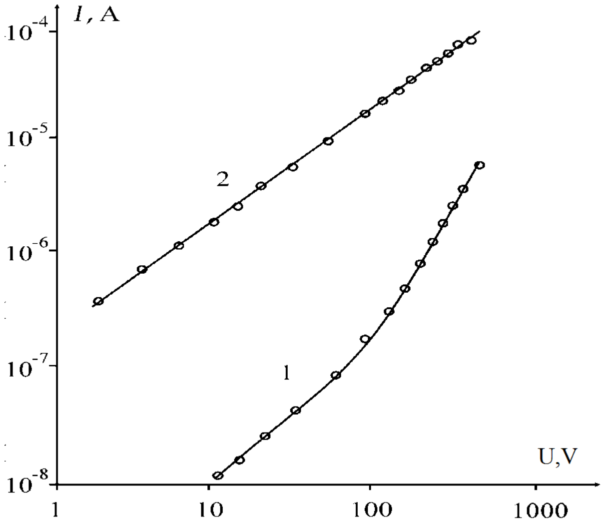

Fig. 2. Current-voltage characteristics of a nanocrystal structure CdS, measured at constant (1) and alternating (2) voltages (T = 295 K).

In Fig. 3 shows the temperature dependence of the dark current (TDDC) of the structure under study. You can see that it has a complex view. At low temperatures, the current increases exponentially with an increase in temperature with an activation energy of 0.65 eV. When the temperature reaches about 340 K, a maximum is observed on the TDDC curve. Further, there is a tendency to an insignificant decrease in the current, which, with a further increase in temperature, is again replaced by a segment of its exponential growth with an activation energy of 0.2 eV. When the temperature reaches about 380 K, a second maximum is observed on the TDDC curve. With further heating of the sample, the current begins to decrease randomly. The TDDC curve, measured in the order of cooling of the sample, shows that the current decrease also takes place exponentially. However, the activation energy of the conductivity turns out to be much larger and amounts to 1.2 eV.

This behavior of TDDC can be explained as follows. In gelatin molecules along polypeptide chains, there are a large number of weak hydrogen bonds (π-bonds), which, in the main, retain H^+ ions and also hydroxyl groups OH^-[5]. With an increase in temperature due to the energy of thermal motion, these bonds are destroyed, as a result of which the concentration of current carriers, which are H^+ and OH^- ions, increases. Then the regions on TDDC with activation energies of 0.65 eV and 0.2 eV can be associated with the liberation of H^+ and OH^- ions, respectively. At a temperature of about 420 K most of the π-bonds are destroyed. However, the broken bonds (as a result of the escape of the H^+ion) acquire a negative charge, since uncompensated, so-called π-electrons remain on them. Further, in the gelatin, the conjugation effect can be manifested, consisting in the fact that the «clouds» of π-electrons of all atoms that form double bonds on a certain section of the molecular chain are established in one plane and overlap [10]. In this case, the π-electrons are no longer localized, but belong to the entire conjugate system. In the presence of conjuga-

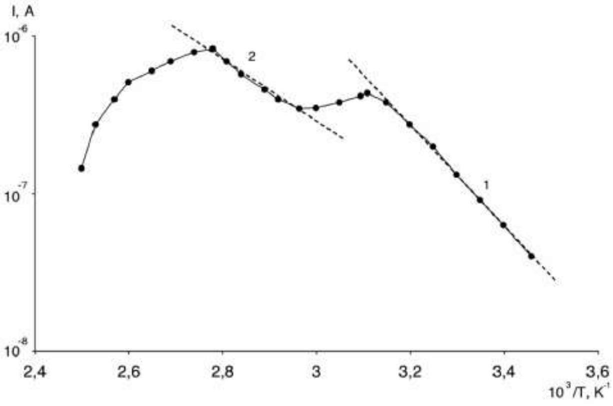

Fig.3. The temperature dependence of the dark current of the investigated structure. (V= 50 B).

tion, the length of the bonds is aligned. Therefore, such systems are characterized by higher stability than non-conjugated systems. With an increase in the length of the conjugation chain, the electrical conductivity of the polymer as a whole increases, since now within the conjugation chain the π-electrons of the macromolecule move both in a single potential well with a periodic potential determined by the structure of the chain. However, the motion of an electron along the conjugation chain is not a sufficient condition for the conductivity of the polymer. It is required that charge carriers can pass from one molecule to another, i.e. from one interface system to another. Such intermolecular transitions are realized by means of activation overcoming of potential barriers between molecules and require energy expenditure. If we assume that during the cooling of the sample from 440 K to room temperature, the predominant current flowing mechanism is the above, then the value of the activation energy of conductivity obtained from TDDC characterizes the height of potential barriers between molecules overcome by π-electrons.

4. Conclusions

The electric molding of freshly prepared structures, leading to an irreversible increase in the resistance of the composite layer, is due to the spatial reorientation of gelatin molecules under the action of an electric field. The electrical conductivity with CdS nanocrystals and its change with increasing temperature are determined by the free H^+ and OH^- ions, which result from the destruction of π-bonds in gelatin molecules. At high temperatures, conductivity is determined by π-electrons, which freely move along the conjugation chains of gelatin molecules and perform activation transitions between molecules with the overcoming of intermolecular potential barriers.

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Abstract. The electrical characteristics of composite structures based on nanocrystals of cadmium sulfide in a gelatin matrix are studied. It is shown that in the freshly prepared structures, an electric field is formed, which irreversibly increases the electrical resistance of the structures. A complicated form of the temperature dependence of the current is obtained, which is associated with the participation in the current transport of H^+ and OH^- ions in the low-temperature region and electrons arising from rupture of π-bonds in the high-temperature region.

Keywords: cadmium sulphide, nanocrystals, gelatin films, electrical conductivity.

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А. П. Чебаненко, А. В. Полищук

ЭЛЕКТРИЧЕСКИЕ СВОЙСТВА СТРУКТУР НА ОСНОВЕ НАНОКРИСТАЛЛОВ *CdS* В ЖЕЛАТИНОВОЙ МАТРИЦЕ

Резюме. Исследованы электрические характеристики композитных структур на основе нанокристаллов сульфида кадмия в желатиновой матрице. Показано, что в свежеприготовленных структурах имеет место формовка электрическим полем, которая необратимо повышает електрическое сопротивление структур. Получен сложный вид температурной зависимости тока, который связывается с участием в токопереносе ионов H^+ и OH^- в области низких температур и электронов, возникающих в результате разрыва π-связей, в области высоких температур.

Ключевые слова: сульфид кадмия, нанокристаллы, пленки желатина, электропроводность.

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А. П. Чебаненко, А. В. Поліщук

ЕЛЕКТРИЧНІ ВЛАСТИВОСТІ СТРУКТУР НА ОСНОВІ НАНОКРИСТАЛІВ CdS В ЖЕЛАТИНОВІЙ МАТРИЦІ

Резюме. Досліджено електричні характеристики композитних структур на основі нанокристалів сульфіду кадмію в желатиновій матриці. Показано, що у свіжовиготовлених структурах має місце формовка електричним полем, яка необоротно підвищує електричний опір структур. Отримано складний вигляд температурної залежності струму, який пов’язується з участю у струмопереносі іонів H^+ та OH^- в області низьких температур і електронів, виникаючих в результаті руйнування π-зв’язків в області високих температур.

Ключові слова: сульфід кадмію, нанокристали, плівки желатину, електропровідність.