

METHODS TO INCREASE CONDUCTIVITY OF POLYMERS IN CONDUCTIVE POLYMER/CdS SEMICONDUCTOR NANOCRYSTAL STRUCTURES

The explanations to the processes passed in polymeric matrix of composite structures (conductive polymer)/(CdS semiconductor nanocrystals) at introduction of the varied additions is offered. The basic role in the process of carriers transfer in the investigated structures plays the radicals-ion, generated by current flowing on polypeptide molecules. The presence of section with negative differential resistance on volt-current characteristics can be explained by the increase in polymer resistance as a result of change in spatial configuration of gelatin molecules. The increase in conductivity of polymer at introduction of acetone addition is explained by diminishing in polymer resistance at the expense of the increase in concentration of bound water and in amount of the possible ionic paths. In the case when sodium chloride is added the increase in conductivity of polymer is explained by the raise in amount of charge carriers.

The studies in the properties of nano-dimension objects and the composite structures on their basis are one of the actual directions in development of modern science. The group of composite materials that based on semiconductor nanocrystals incorporated into conducting polymer is interesting from the practical point of view. Optical properties of such composites are defined, first of all, by properties of clusters but their electrophysical and mechanical properties directly depend on those for polymer [1]. As electrophysical features of a matrix (conducting polymer) define electroluminescent properties of a composite, and by change in parameters of polymer one can influence on luminescent characteristics of structures. We investigated structures on the basis of cadmium sulfide nanocrystals, introduced in photographic gelatin. The purpose of the present work is to study the processes of charge transfer, occurring in polymer, and also the search of the ways to increase conductivity.

To obtain cadmium sulfide nanocrystals, the method of chemical synthesis was used. According to this method, the solution of cadmium nitrate with concentration of 0.025 M was mixed up with 5% solution of photographic gelatin. Then sodium sulfide solution was added into the obtained mixture. The reaction was carried out within 15 minutes at temperature 40 °C and with continuous intermixing of reagents solution. After this, glass substrates with SnO₂ layer preliminary put on them were watered by the identical amount of solution (0.5 ml) and then were located then in drying case. The obtained samples were differed in color depending on concentration of sodium sulfide in the initial solution: from pale yellow for low concentration of sulfur ions up to bright orange for high concentration.

To increase the conductivity of polymer, during preparation of samples, the various additives

were introduced to the solution after passage of the basic synthesis reaction. As additives we used: acetone, 5% solutions of NaCl and KCl, and also graphite powder. Thus, the investigated structures represented the layers of gelatin with introduced cadmium sulfide nanocrystals. The top electrode to them was indium, applied by the method of thermal spraying in vacuum.

We will notice that gelatin is albuminous material that represents the polydisperse mixture of polypeptides (molecular weight 50—70 thousand) and their aggregates (molecular weight up to 300 thousand). Gelatin space construction has the complicated configuration. The change in any physical and chemical parameter of a system leads to changes in spatial configuration of fiber and, and consequently, in the change of electrophysical characteristics of polymeric film [2]. Exactly this feature of polymer explains differences in volt-current characteristics (VCC) of samples with different type of additions in Fig. 1. Gelatin concentration in solution, such as concentration of reagents and temperature of heating, is the basic factor influenced on the process of growth and the final sizes of nanocrystals. Long molecules of gelatin complicatedly oriented in space form the original frame dividing all solution into the elementary volumes, in each of these volumes the formation of nanocrystals nucleus and their subsequent growth takes place. Therefore, the larger allocated volume (i. e. concentration gelatin is less), the higher concentration of reagents in it will be, and the higher probability to form nucleus with their subsequent coalescence. In result, the distribution in sizes of nanocrystals will be wider, that leads to complication in the analysis of experimental results and their subsequent treatment [3].

The central place in conductivity of polymeric matrix is borrowed with ionic processes in

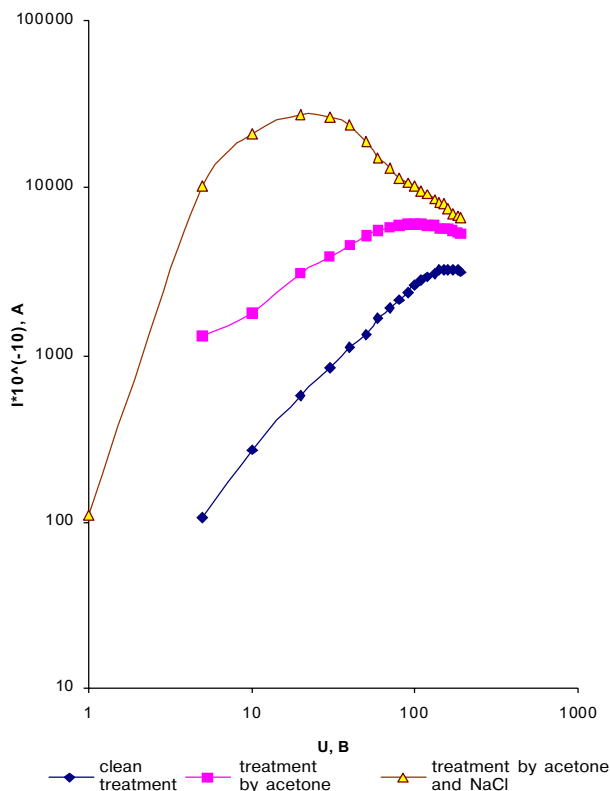


Fig. 1. Volt-current characteristics (VCC) of composites at stationary bias depending on type of additive

electrolyte consisted of products from synthesis reaction of nanocrystals and the active ionic rests, obtained as the result of hydrolysis of polypeptide molecules. The presence of free radical bounds in molecules of polymer results in constant reorientation depending on changes in the external field. Therefore, the size, mobility and concentration of radicals — ions has direct importance for conductivity. The basic ions participating in transport of charge carriers for researched structures are: H^+ , Na^+ , Cd_2^+ , OH^- , NO_3^- and Cl^- (at introduction of NaCl). Ions H^+ , Na^+ , Cd_2^+ participate in electrons transport to the centers of luminescence, and OH^- , NO_3^- and Cl^- in holes transport. We notice, that mobility of H^+ ions is in 4,5 times more than mobility of Na^+ ions [4]. Such distinction in ions mobility is connected to the go-ahead mechanism for movement of hydrogen and hydroxyl ions by means of jumping from hydroxonium to water, or from water to hydroxyl.

Excitation of luminescence centers (nanocrystals) in the polymers impregnated by colloidal solution, depends on the degree of structures hydration and quantity of radical-ions generated in them. Therefore, the increase in amount of water remained in the bound condition after sample drying, and also the increase in amount of the readily soluble ionic compositions included in polymer, are natural to increase efficiency of electroluminescence.

Let's consider in details the typical VCC of the explored structures, represented in Fig. 1. The characteristic feature is the presence of negative differential resistance section, which be-

comes more expressed when the additions of acetone, and also chloride of sodium are introduced to the samples. This specificity of VCC can be explained in the following way. Coming from dielectric properties of pure gelatin, the conductivity of sample is directly defined by volume concentration of polypeptide in polymeric tape. As, in contrast to the electrons of «bypass» current, radical-ions move directly in water solution with which a polymer is impregnated, not rely on the molecules of albumen, any change in resistances of polymer, including the local one (the change of gelatin concentration) leads to the sharp change in local flux of carriers and to the change in current through a sample in whole. Such change in local concentration of gelatin can be explained by interaction between the active, uncompensated radical bounds of albuminous molecules generated as a result of processes of polypeptide hydrolysis and electrolysis. To balance these bounds, the molecule of gelatin changes its spatial configuration so that to decrease the interaction surface, closing free radical bounds inside original globule (Fig. 2). Because molecules of polypeptide are not isolated from each other, and are in the permanent contact, interlacing between them, such change of configuration leads to the mass compression of polymeric «grid». The sequence of this is the increase in resistance of this polymer area and it explains the presence of negative differential resistance section on VCC (Fig. 1). When acetone was introduced in the process of sample preparation, current strength value in the maximum of VCC has increased in 2 times, and, the voltage corresponding to peak has decreased from 160 V up to 90 V. The noted change in VCC can be explained by the fact that at introduction of gelatin hydrophilic into solution the additive (acetone) concentration in the water, remained on a sample after its drying, increases.

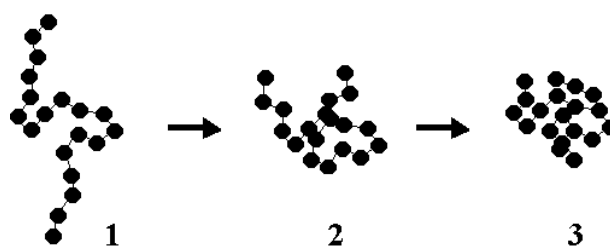


Fig. 2. Change in spatial configuration of gelatin molecule with the increase in voltage: 1 — the external field is absent; 2 — at low values of the field strength; 3 — at high strength of the field

The increase in concentration of the bound water leads to increase in number of ionic channels due to reduction in volumetric concentration gelatin. As result, the resistance of polymer falls and the smaller displacements are necessary to achieve the maximal value of current.

The voltage corresponded to the maximum of current through a sample, decreases up to 30 V, when the solution is added not only acetone, but

NaCl too. Current rises thus more than in 10 times, in comparison with pure sample. The latter is connected with the fact that besides the increase in concentration of the bound water (decrease in resistance of polymer) in sample, as a result of NaCl introduction the amount of the radical-ions, took the direct participation in processes of energy-transfer, increases. That is, the concentration of charge carriers increases. Hence, the stationary density of current is observed to be reached at the smaller value of displacement.

Let's notice, that at introduction of acetone, a molecule of bound water under action of a current, flowing through polymer, decomposed to ions of hydrogen and hydroxyl-ions. Therefore not only the resistance of matrix decreases, but also the amount of ions participated in energy-transfer increases. The result of additional introduction of sodium chloride to the solution at preparation stage is the addition of the new carriers to the existed ones. The number of radical-ions in polymer renders the basic influence on speed of current decay in VCC (Fig. 1). The internal field of a sample will change, as the result of ions movement and their redistribution in time, at the fixed value of displacement. Owing to constant change in the field affected on polypeptide molecules, they will change ceaselessly the position in space, thus closing old ionic channels and opening the new ones. This fact explains the observed appreciable fluctuations of the registered current.

Thus, the increase of current through polymer, in general case, is explained by the sharp increase in amount of radical-ions as a result of

electrolytic dissociation of polypeptide molecules and ionic bounds, and the section of negative differential resistance on VCC can be explained by the increase in resistance of polymer, because of change in spatial configuration of gelatin molecules. Radical-ions appeared when «bypass» current flowed through the polymer act the basic role in the energy transfer processes.

The increase in polymer conductivity at introduction of acetone as the additive, is explained by the reduction in polymer resistance due to increase in concentration of the bound water and number of possible ionic channels. The increase in polymer conductivity, in case of sodium chloride addition, explains the increase in number of charge carriers.

The study in influence of ions type and their characteristics on the feature of energy-transfer, and also the development of the model for electronic processes in polymeric matrix is the subject of the further research.

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СПОСОБЫ УВЕЛИЧЕНИЯ ПРОВОДИМОСТИ ПОЛИМЕРОВ В СТРУКТУРАХ ПРОВОДЯЩИЙ ПОЛИМЕР/ПОЛУПРОВОДНИКОВЫЕ НАНОКРИСТАЛЛЫ CdS

Предложены пояснения к процессам, проходящим в полимерной матрице композитных структур (проводящий полимер)/(полупроводниковые нанокристаллы CdS) при введении разнообразных добавок. Основную роль в процессе переноса носителей в исследуемых структурах играют, порождаемые проходящим по молекулам полипептида током, радикал-ионы. Наличие участка отрицательного дифференциального сопротивления на вольт-амперных характеристиках можно объяснить увеличением сопротивления полимера вследствие изменения пространственной конфигурации молекул желатин. Увеличение проводимости полимера при введении добавки ацетона, объясняется уменьшением сопротивления полимера за счет увеличения концентрации связанной воды и количества возможных ионных каналов. В случае добавления хлорида натрия повышение проводимости полимера объясняется увеличением количества носителей заряда.

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СПОСОБИ ПІДВИЩЕННЯ ПРОВІДНОСТІ ПОЛІМЕРІВ У СТРУКТУРАХ ПРОВІДНИЙ ПОЛІМЕР/НАПІВПРОВОДНИКОВІ НАНОКРИСТАЛИ CdS

Запропоновані пояснення до процесів, що проходять в полімерній матриці композитних структур (провідний полімер)/(напівпровідникові нанокристали CdS) при введенні різноманітних добавок. Основну роль в процесі перенесення носіїв в досліджуваних структурах грають, породжувані струмом, що проходить по молекулах поліпептиду, радикал-іони. Наявність ділянки негативного диференціального опору на вольт-амперних характеристиках можна пояснити збільшенням опору полімеру унаслідок зміни просторової конфігурації молекул желатини. Збільшення провідності полімеру при введенні добавки ацетону, пояснюється зменшенням опору полімеру за рахунок збільшення концентрації зв'язаної води і кількості можливих іонних каналів. У разі додавання хлориду натрію підвищення провідності полімеру пояснюється збільшенням кількості носіїв заряду.

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