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Composite film structures containg ZnS, CdS nanoparticles prepared by MOC pyrolysis at low temperatures

G.S. Svechnikov, L.V. Zavyalova, N.N. Roshchina, I.V. Prokopenko, L.I. Berezhinsky, V.S. Khomchenko, O.S. Lytvyn

V. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine
41, prospect Nauky, 03028 Kyiv, Ukraine, Phone: +380 (44) 265 64 77, (44) 265 73 51, (44)265 62 66,
fax: +380 (44) 265 83 42, E-mail: vsk@isp.kiev.ua

Abstract. New composite structures containing ZnS, CdS nanoparticles were prepared with bright light-blue colour of luminescence. The structures were formed by spraying organic solution of zinc or cadmium ditiocarbamate onto substrates at temperatures within the range 40…120°C. It was established that the film emission maximum monotonously shifts into short-wave spectral region at the decreasing substrate temperature: from 590 nm (T_s = 120°C) to 500 nm (T_s = 50°C) for ZnS and from 510 nm (T_s = 120°C) to 450 nm (T_s = 40°C) for CdS. This fact can be explained by the quantum size effect: X-ray analysis has shown that researched films contain crystalline particles of 1…5 nm size.

Keywords: nanocrystallite, ZnS, CdS, polymeric matrix, MOC pyrolysis, luminescence.

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1. Introduction

The development of new directions in semiconductors physics and microelectronics based on size reduction of crystallites in semiconductor materials down to several nanometers has resulted in increase of light sources efficiency for the given wavelength set and can be used at a creation of more powerful computing devices.

In this connection, it seems very actual to solve the task of developing new technologies for fabrication of composite nanocrystal structures, the research of their electrophysical and optical characteristics, creation of photosensitive and electroluminescent devices with improved parameters in a wide range of spectral sensitivity on their basis.

Several basic techniques are known to form nanocrystals and composite layers containing them [1–5]. The most widely known techniques are as follows: preparation of colloidal solutions of nanocrystals by the condensation method from a solution containing the semiconductor components [3]; filling the nanosize cavities in ceolite by semiconductor clusters [4]; and also the method of a consecutive ion implantation of semiconductor elements in Al_2O_3 matrix [5].

At the same time, the chemical method is known for fabrication of semiconductor polycrystalline films of ZnS and CdS, in particular. The method is based on pyrolysis of chelate metalorganic compound (MOC) of zinc or cadmium at the substrate temperature in the range 200–340°C [6].

The purpose of the given work is the research opportunities to prepare composite layers based on ZnS and CdS from chelate MOC of zinc and cadmium at the temperature lower than 200°C. The morphology of film surface, the X-ray spectra and photoluminescence spectra were investigated to confirm nanocrystalline structure of the composite film structures based on ZnS and CdS prepared at various conditions.

2. Experimental procedure

Researched composite film structures were prepared by a chemical method of spraying an ethanol solution of chelate Zn- or Cd- MOC at the presence of polar solvent (PS) on the heated substrate.

Chelate Zn- or Cd- MOC concern to a class MOC with complex anion-ligands [7]. In this work, the following compounds were used: with ligands containing sulfur, zinc and cadmium ditiocarbamates (dtc) [9], which were applied by us in works [6,8,10], and later by authors of work [11] for obtaining of CdS and CdZnS film.

The deposition of a ZnS- or CdS- based composite film structures was carried out at atmospheric pressure in a flowing non-sealed system. The substrates are placed on a flat horizontal heater. The deposition was made by compressed air at the pressure (0.6…1.2) $\cdot 10^5$ Pa using a spraying device fixed above the substrate. Films were deposited for 5 to 20 minutes, and the film thickness was 0.5…1.0 microns depending on the deposition rate and substrate temperature. The concentration of basic substance, dtc_2Zn, $[(C_2H_5)_2NCS_2]_2Zn$, or dtc_2Cd, $[(C_2H_5)_2NCS_2]_2Cd$, consisted of 4 weight percents. It corresponds to solution of 0.1 M. The spraying rate was 1…2 ml/min. and the substrate temperature varied within the limits 40…120°C.

The surface morphology of the films was examined with Nanoscope D3000 atomic force microscope (AFM) (Digital Instruments). The crystal structure of films was studied by X-ray diffraction analysis with a ДРОН-3М diffractometer (CuK_α radiation). The photoluminescence (PL) was excited by a nitrogen laser ($\lambda = 337$ nm).

3. Results and discussion

Thermal analysis of initial materials dtc_2Zn and dtc_2Cd has shown that they have similar stages of material transformation under the action temperature. However, dtc2Zn all critical temperature points (melting, decomposition and crystallization of decomposition products) are 20 to 30°C higher than those for dtc_2Cd.

It was established that the polymeric substances are formed for dtc_2Cd of yellow colour or colorless for dtc_2Zn after heating at temperature 300°C (exceeding temperature of decomposition). Polycrystalline powder is formed at temperatures above 400…500°C. It consists mainly of ZnS or CdS as X-ray analysis showned. It is evidence of temperature decomposition of dtc_2Zn or dtc_2Cd jointly with a formation of particles ZnS or CdS in a polymeric matrix. Such process availability allows obtaining the composite material as a film.

To decrease the formation temperature of particles ZnS or CdS in a polymeric matrix, the polar solvent (PS) was inserted into initial solution. The PS presence should promote destruction of chemical bonds in dtc_2Cd or dtc_2Zn molecules at lower temperatures.

The quality of films was investigated versus a relationship of PS volume to the volume of ethanol solution of dtc_2Zn or dtc_2Cd in a wide range: from 0.005 up to 1.000. It was established that the films formed were of a good quality at the relationship about 0.01 only. Films were continuous, homogeneous and with a minimal roughness. There was it at temperature in the range 40…120°C, instead of ~300°C temperature in the absence of PS.

Thus, it is possible to believe that PS influencing on initial substance plays a paramount role on the film formation at so low temperatures.

Apparently, the chemical bond of metal atom with MOC elements except sulfur decreases at the introduction of PS into solution containing dtc_2Zn or dtc_2Cd. It allows to considerably reduce the molecule decomposition temperatures. It is the most probable process that the smallest ZnS or CdS particles are formated due to destruction of complex MOC molecules, since the metal and sulfur in a molecule are tightly bound by the direct and strong chemical bond. Other process of a matrix formation has place from the rests of a dtc_2Zn or dtc_2Cd molecules simultaneously.

The X-ray analysis of composite film structures prepared from dtc_2Cd at temperatures within the range 40…60°C has shown that researched films contain crystalline structures with sizes 1…5 nm. It confirms the results of morphology surface investigations.

The complex structure of the prepared films was revealed using AFM. The morphology of dtc2Cd film surface is illustrated in Fig. 1. The films were prepared at the temperature 60°C. It is seen in Fig. 1 that against a background basic of fine-grained film surface the embedded grains are observed (sizes along the vertical direction are purposely 8-fold increased in comparison with the horizontal one). The horizontal sizes of these separate large grains change from 25 nm up to 1000 nm depending on conditions of solution preparation and a substrate temperature. The size of grains in the fine-grained area of a surface amounts to 5 nm. The microrelief investigation of film grown at the various substrate temperatures show that films with small sizes of grains have grown at the substrate temperature of 40…60°C and with large grain sizes – at 100…120°C. The similar behaviour is observed also for a composite structures obtained from dtc_2Zn.

The investigation of luminescence spectra has shown that obtained composite structure containing ZnS and CdS nanoparticles have rather bright luminescence. The spectral location of luminescence maximum is connected with conditions of preparing this material and, first of all, with the temperature substrate.

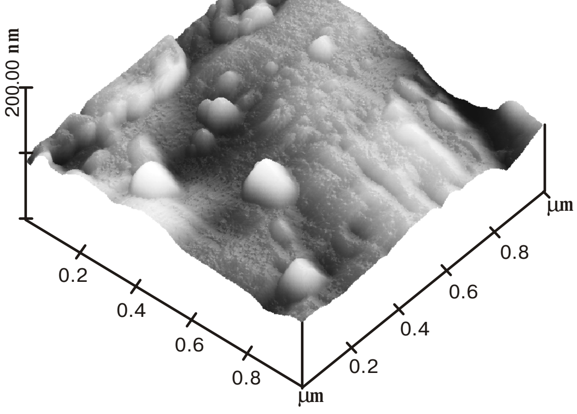

Fig. 1. The surface morphology of a nanocomposite layer prepared using CdS.

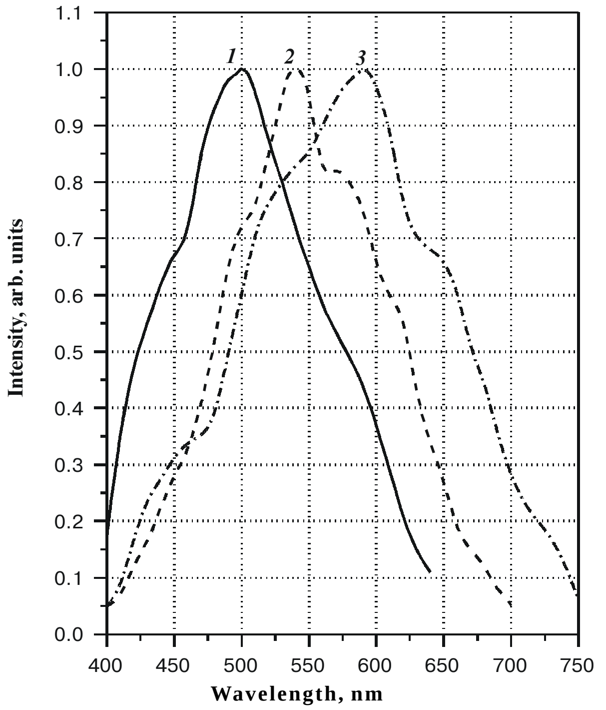

Fig. 2. The photoluminescence spectra of nanocomposite layers based on ZnS and obtained at various substrate temperatures: *1* – 50, *2* – 90, and *3* – 120°C.

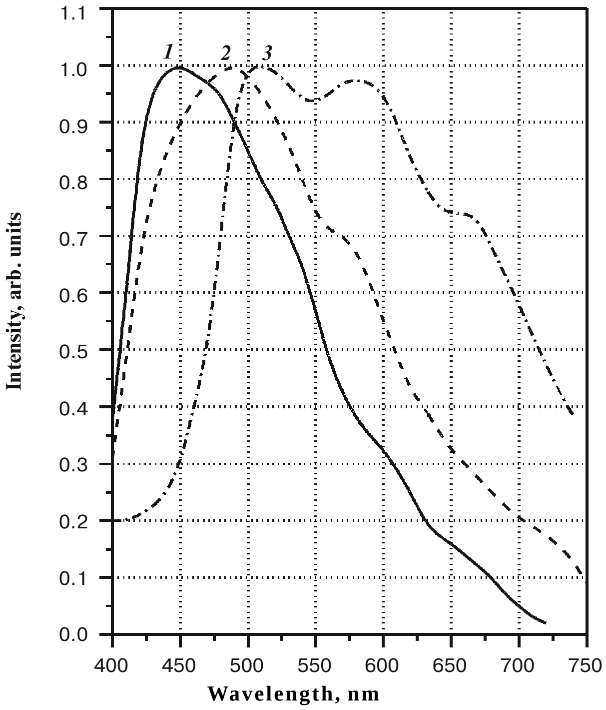

Fig. 3. The photoluminescence spectra of nanocomposite layers based on CdS and obtained at various substrate temperatures: *1* – 40, *2* – 60, and *3* – 100°C.

The photoluminescence spectra of the composite polymeric structures including ZnS and CdS particles are submitted in Figs 2 and 3. The wide band in the range of 400 to 700 nm peaking at 590 nm was observed in spectra of the composite structure based on ZnS grown on the substrate at temperatures of 100...120°C (Fig. 2, curve 1). The luminescence band contains “shoulders” at 650, 520 and 450 nm. It testifies that this band is complex and contains, at least, three bands in red, green and dark blue areas of the spectrum. Such spectral structure causes yellow colour of luminescence. The decrease of the substrate temperature results in the change of a luminescence colour from yellow to blue. Such change of a luminescence colour is caused by the change of the contribution of various emitting bands into common intensity. The contribution of more high-energy emitting bands is increased when the substrate temperature is decreased from 120 down to 50°C. At the substrate temperature 50°C, the luminescence peak is located at 500 nm. In this case, the structure has the blue colour of luminescence, because the dark blue emission band peaking at 450 nm gives a main contribution to luminescence. The half-width of the photoluminescence band is decreased.

The effect of “blue” displacement is expressed even more sharply (Fig. 3) for composite layers based on CdS. In this case, the luminescent spectrum of the layer deposited on the substrate at 100°C has a wide band with a maximum at 500 nm and two less intense bands in orange (580 nm) and red (650 nm) spectral regions. It is necessary to note that green emission in monocrystals and polycrystalline CdS films, as a rule is observed only at low temperature (~ 77 K) [12]. The decrease of a substrate temperature at the precipitation of polymeric composite layer results in sharp reduction of intensity of long-wave bands and growth of the short-wave emission intensity. Simultaneously, the displacement of a short-wave emission peak from 500 nm down to 450 nm is observed. In this case, the halfwidth of the photoluminescence band is nearly halved.

The presence of the green band in the photoluminescence spectrum of layers based on CdS even at the room temperature, apparently, due to using high-energy excitation (N_2 - laser, $\lambda = 337$ nm) and presence of a sufficient set of grains with a rather perfect crystal structure. The 50 nm shift of the green emission band into the short-wave spectral region correlates with an increase of the contribution of very small grains (~5 nm) into the total luminescent intensity and can be explained by the presence of the quantum size effect [4] in CdS nanocrystals. Apparently, it testifies that the composite layers formed at low temperatures contain CdS (ZnS) crystals with very small sizes, which provide a more short-wave emission in comparison with monocrystals and polycrystalline films.

4. Conclusions

Thus, the new composite structures containing ZnS and CdS nanoparticles were prepared. These structures possess bright blue luminescence.

The change of a luminescence colour from yellow to green and dark blue is achieved by the change of a substrate temperature at the constant component composition. To shift the luminescence into the short-wave region, it is not necessary to increase, as usual, but decrease the substrate temperature from 120 down to 40…60°C. This execution satisfies to more nonequilibrium rate of a crystals growth and reduces their sizes.

This method for preparation of light-emitting structures is very cheap because allows to use glasses of simple marks and flexible substrates.

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