Fluorescence of $Pb_{1-x}Cd_xSe$ nanocrystal films

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Abstract. The interest in lead chalcogenide structures is driven by the possibilities of using nanocrystal lead selenide films, for example $Pb_{1-x}Cd_xSe$, as fast and compact sources of infrared range with low energy consumption. Besides, PbSe films oxidised in the atmosphere of oxygen can serve as optical light receivers of infrared range in gas sensors.

Keywords: fluorescence, nanocrystalline films, semiconductor compounds, solid solutions, quantum dots, surface morphology, luminescence spectrum, band gap.

Introduction

The fluorescence of thin $Pb_{1-x}Cd_xSe$ films obtained by vacuum deposition is well-known (Yunovich, Averyushkin, Drozd, Ogneva 1979; Nepomnyaschij, Pashkevich, Shelekhin, Dijkov 1984). For instance, fluorescence may be observed during optical excitation of films heat-treated in the atmosphere of oxygen. The interest in $Pb_{1-x}Cd_xSe$ films fluorescence is driven by the possibility of using them in optics as a fast and compact light source with low energy consumption. For example, light sources based on $Pb_{1-x}Cd_xSe$ (Nepomnjashchij, Pogodina, Shelekhin, Maksjutenko 2003) are widely used in gas analyzers in the spectral range of 2–5 μm to address greenhouse gases (Gamarts, Moshnikov, Chesnokova 2006).

Besides, semiconducting compounds PbSe and CdSe form $Pb_{1-x}Cd_xSe$ solid solutions, where the width of the band gap increases as x rises. This makes it possible to move spectral characteristics of photoconductivity and photoluminescence to short-wave spectrum area compared to lead selenite.

Current LEDs based on inter-band transitions in narrow-band-gap semiconductors such as InAsSb have fundamental defects, such as challenging production technology, low light intensity, low radiation stability, etc.

Significant progress has been recently made in the study of fluorescent characteristics of $Pb_{1-x}Cd_xSe$ solid solutions due to the technological possibilities of building quantum dots in these materials. It is expected that in quantum dots, non-radiation dissipation of electron excitation energy may be significantly reduced due to the low electron-phonon interaction, which in turn will increase the emitting power of the infrared source.

Materials and methods

Fluorescence spectra of PbSe and $Pb_{1-x}Cd_xSe$ polycrystalline films have been investigated. X-ray phase analysis data showed the lead selenide precursor being stoichiometry; the x composition of $Pb_{1-x}Cd_xSe$ solid solution varied within x = (0.1 ÷ 0.2).

The films were obtained by thermal deposition on 20 × 20 mm² C-29 glass substrates. The thickness of PbSe and $Pb_{1-x}Cd_xSe$ films amounted to 2 ÷ 2,5 μm. As a source for film deposition, we used compressed tablets of corresponding precursors on the basis of binary compound of lead selenide and lead selenide solid solution—cadmium selenide pre-treated thermally in dynamic vacuum by the procedure described in (Henry 1993; Bestaev, Makhin, Moshnikov, Tomaev 2000). To augment the uniformity of film thickness during application, a template-rotating device was used. The distance between the vapour source and the templates and their design ensured the consistency of layer thickness; the dispersion was no more than 0.05 μm. The temperature of the template and the vapour source was monitored by chromel-alumel thermocouples. The condensation rate value was selected by trial and error and was estimated based on the evaporation time of the material. During the diffusion of precursor tablets the temperature of the heater varied from 700 to 730°C, and the templates' temperature varied from 250 to 280°C.

To obtain the needlelike structure, the surface of the glass templates was exposed to chemical etching in a weak hydrofluoric acid solution. The needles with an average size of 1–2 μm, which formed on the surface of the glass template, acted as film crystallization centres. Changes in the resistance of polycrystalline films and compressed tablets in the 298–498 K temperature range in dry and argon ambient have been investigated.

It has been shown that the characteristics of temperature resistance relationships in PbCdSe oxidised samples may be related to their micro-structure and the state of the environment. It has been found that at temperatures higher than room temperatures but lower than 100°C all samples that had been pre-oxidised in the air showed an anomalous change in resistance.

We used electronic microscopy, X-ray diffractometry and thermal conductivity study methods to analyze oxidation mechanisms of semiconductor structures with varying levels of structural perfection and differing geometric structures. The following results were obtained:

external shell of PbSe structures exists in room temperatures and upwards and relates to $PbSeO_3$ phase,

volume of $PbSeO_3$ oxide phase on the surface of PbCdSe increases with the temperature growth, in the structures investigated in the specified temperature range phases other than PbSe and $PbSeO_3$ were not detected.

The surfaces and chips of original (Fig. 1a) and oxidised films (Fig. 1b) were investigated by scanning electron microscopy.

Figs. 1a and 1b present micrographs of $Pb_{1-x}Cd_xSe$ films before and after heat treatment in the oxygen atmosphere. It is quite clear that the template morphology modifies the original unoxidised surface; on oxidised surface larger crystals are evident, resulting from thermal recrystallization of the original crystals and oxidation processes. The thickness of the film may vary from 500 nm to 2500 nm.

Spectral luminescence measurements were performed using fluorimeter SHIMADSU. An example of the resultant spectrum is shown in Fig. 2.
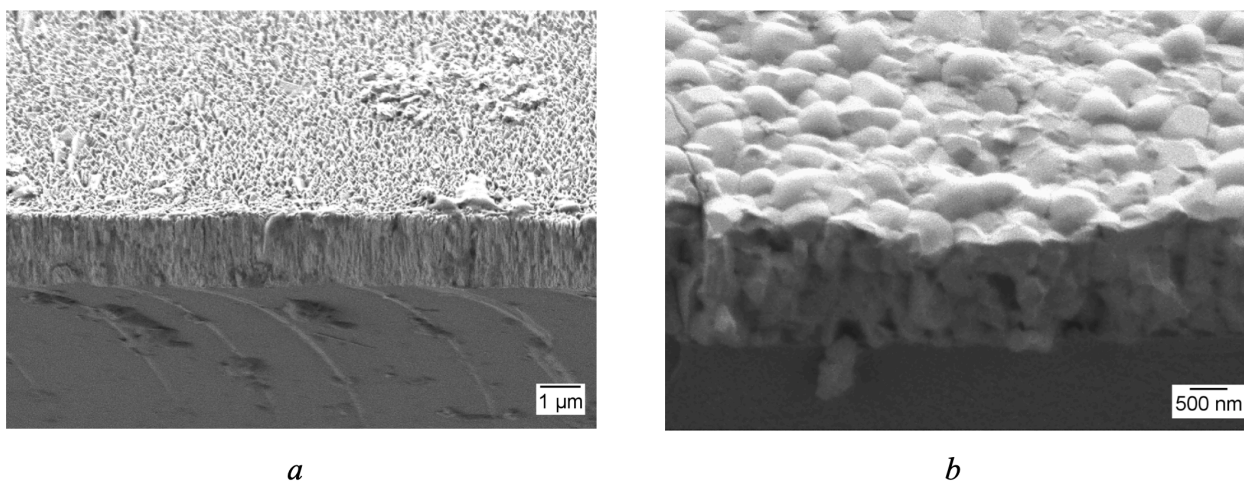

| a | b |

Fig. 1. Morphology of $Pb_{1-x}Cd_xSe$ film surface before (a) and after (b) temperature treatment

<div align="center">

Results and discussion

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Spectrum of luminescence of Pb$_{1-x}$Cd$_x$Se polycrystalline films generated by light with wavelength λ ≈ 900 nm is presented in Fig. 2. The resulting spectrum is well described by the formula of W. van Roosbroeck and W. Shockley (Tomaev 2009) for inter-band electron-hole recombination. Spectral dependency of radiative recombination speed $F(\omega)$ is related to dependency of absorption coefficient k_ω. With no degeneration or if ω ≈ *kT* this dependency can be recorded in a more convenient way:

$$F(\omega) = B^2(\omega)k_\omega \exp(-\frac{\hbar\omega - E_0}{kT}) \qquad (1)$$

where *B (ω)* is directly related to the band gap E_0 and to solid solution compounds used for film deposition. The position of the luminescence spectral maximum depends on the Cd concentration, and it moves to the short-wave area with increasing Cd concentration.

Fig. 3 presents spectra of luminescence registered for different Pb$_{1-x}$Cd$_x$Se polycrystalline films. Curves № 1, 2, 3, 4 correspond to four different samples of polycrystalline films made under similar conditions.

To reduce the reflection of each layer of film, an immersion layer is applied to it. In addition, the immersion layer provides better temperature stability of the spectrum of luminescence, because it works like a thermal insulator protecting the film from overheating.

To reduce losses from film-air surface, the immersion layer is formed from a material with a refraction coefficient between those of semiconductor film and air. Typically, AsSSe chalcogenide glass is used for this purpose. This increases the output intensity of luminescence by 15–20%. Spectra 1, 2, 3, 4 in Fig. 3 show that despite the unavoidable changes in film parameters which occur during the deposition process (influence of template surface structure, deposited film thickness errors, chemical composition of Pb$_{1-x}$Cd$_x$Se solid solution), basic spectral parameters of fluorescence, such as line width and maximum position, are easily reproducible. Deposition of several Pb$_{1-x}$Cd$_x$Se films with different thickness and chemical composition allows for controlling spectral width of luminescence. This is illustrated by curve 5 in Fig. 3.
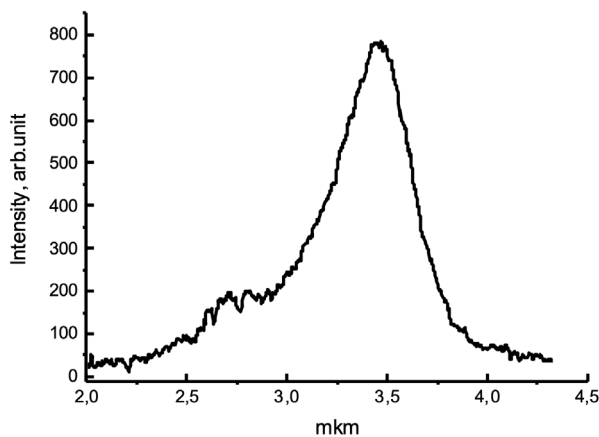
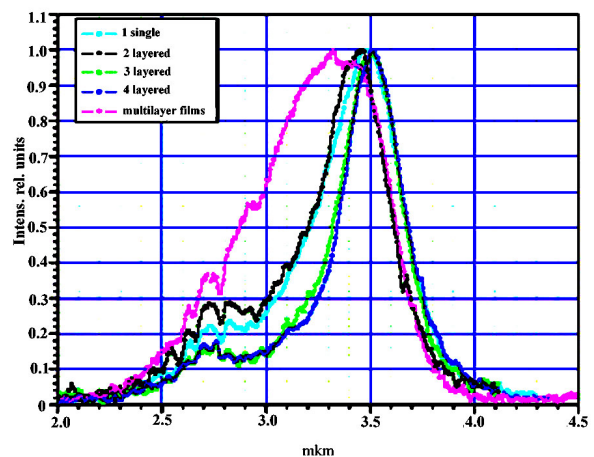Fig. 2. Pb$_{1-x}$Cd$_x$Se film luminescence spectrum (λ$_{ex}$ = 900 nm)

Fig. 3. PbCdSe film luminescence spectrum by number of layers

To reduce the absorption of light from low-lying films in multi-layer structures, the thickness of each subsequent layer shall be reduced by 20–25% compared to that of the previous layer. To reduce the mixing between Pb$_{1-x}$Cd$_x$Se layers, a 5 nm thick SiO$_2$ dielectric layer was applied, which was transparent to both excitation and infrared radiation of luminescence.

In the standard operational temperature range. i.e. between −20 and +40°C, maximum luminescent spectrum shift from temperature is linear with the slope coefficient 4,48 10^{-3} μm/^{0}K, which is obviously related to the temperature dependency of the band gap width of PbSe p-n-junction (Fig. 4).
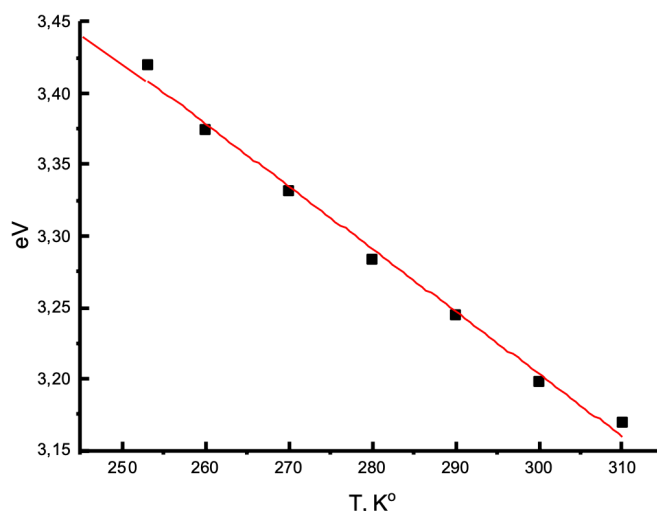
Fig. 4. Width of the band gap of PbSe p-n-junction by temperature

Findings

1. $Pb_{1-x}Cd_xSe$ polycrystalline film luminescence spectra are presented.
2. Luminescence efficiency for $Pb_{1-x}Cd_xSe$ film at λ_{ex} = 900 nm is about 1% of pumping power.

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