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Features of photoconductivity and luminescence of CdS thin films and $Cd_{1-x}Zn_xS$ solid solutions under laser excitation

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The features of photoconductivity and luminescence of CdS thin films and $Cd_{1-x}Zn_xS$ solid solutions obtained by chemical pulverization with subsequent pyrolysis under laser excitation have been studied experimentally. Pulsed liquid (473−547 nm) and nitrogen (337 nm) lasers were used as a radiation source. An experimental study was made of the photoconductivity and photoluminescence spectra of $Cd_{1-x}Zn_xS$ thin films depending on the composition x at different excitation intensities and the relaxation curves of nonequilibrium photoconductivity. It is shown that the observed features in the photoconductivity and photoluminescence spectra of $Cd_{1-x}Zn_xS$ thin films are due to direct band-to-band transitions. Amplification of light is observed at high intensities of optical excitation in thin CdS films.

Keywords: Thin films CdS, $Cd_{1-x}Zn_xS$, laser, photoconductivity spectra, photoluminescence

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Introduction

Semiconductor compounds A^2B^6 and their solid solutions due to their optical, photoluminescent and photosensitive properties are promising materials for science and technology. Compounds of the A^2B^6 group are widely used in optoelectronic technology as luminescent screens, scintillation sensors, photodetectors, and laser structural elements. These direct-band-gap semiconductors, having a high radiation efficiency, cover the entire spectrum range from the ultraviolet to the IR region. Cadmium sulfide (CdS) is distinguished from all compounds along with zinc sulfide by the scale of application. It is widely used in combination with other semiconductors to create various heterojunction devices, in particular quantum cascade lasers, solar cells, and photodetector On the basis of CdS single crystals, devices for detecting elementary particles and gamma radiation have been created. Cadmium sulfide is widely used in nanoelectronics [1–5].

Of special interest are studies of the optical, photoelectric, and luminescent properties of CdS and solid solutions based on them ($Cd_{1-x}Zn_xS$) at high levels of optical excitation. This is due, on the one hand, to the enormous possibilities offered by the use of these materials for the purposes of nonlinear optics, and, on the other hand, the possibility of realizing in them completely new phenomena of great fundamental importance, which were previously practically inaccessible for experimental research [6–8].

In this work, one experimentally study the photoconductivity and luminescence of thin CdS films and $Cd_{1-x}Zn_xS$ solid solutions obtained by chemical pulverization followed by pyrolysis under laser excitation.

Experiment procedure

Thin CdS films and $Cd_{1-x}Zn_xS$ solid solutions were obtained by chemical spray-on process followed by pyrolysis. This method ensures the deposition at moderate temperatures of sufficiently perfect films over large areas, which have stronger adhesion and high mechanical strength compared to films obtained by other methods. In this case, an aqueous solution of cadmium chloride $CdCl_2$, thiocarbamide $(NH_2)_2CS$, and zinc chloride $ZnCl_2$ were used. The concentration of cadmium chloride and thiocarbamide was 0.5 mol/l in the proportion 1 : 1, and the concentration of $ZnCl_2$ varied depending on the zinc content in the $Cd_{1-x}Zns\mathit{olidsolution}_xS$. CdS and $Cd_{1-x}Zn_xS$ films were formed by pyrolytic decomposition of sputtered particles on the substrate surface according to the following reactions:

$$CdCl_2 + (NH_2)_2CS + 2H_2O \rightarrow CdS + 2NH_4Cl + CO_2, \quad (1)$$

$$(1-x)CdCl_2 + xZnCl_2 + (NH_2)_2CS + 2H_2O \rightarrow Cd_{1-x}Zn_xS + 2NH_4Cl + CO_2. \quad (2)$$

The substrate temperature (chemically cleaned glass substrates) was $\sim 400^\circ C$ and was measured using a chromel-alumel thermocouple fixed on the substrate surface. The spray-on rate of the solution was maintained at $\sim 5\,\mu m/min$, which provided the film growth rate at ~ 50 nm/min. The thickness of the $Cd_{1-x}Zn_xS$ films was measured using an MII-4 interference microscope and was $\sim 10\,\mu m$. The area of the studied films was 0.5 cm^2.

The CdS and $Cd_{1-x}Zn_xS$ films were irradiated with pulses from a dye laser pumped by a nitrogen laser. The pulse power was 120 kW with a duration of 3 ns, and the

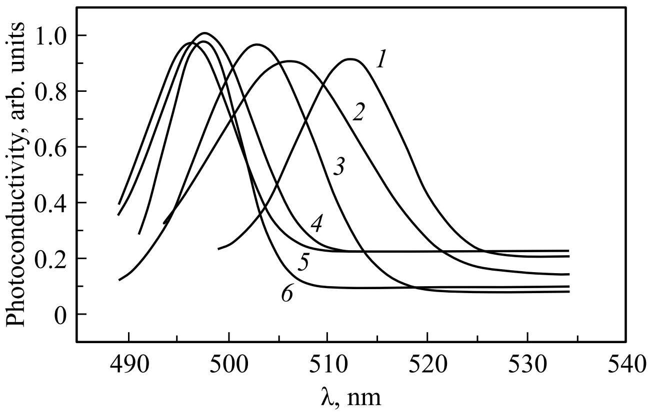

Figure 1. Photoconductivity spectra of thin CdS films and $Cd_{1-x}Zn_xS$ solid solutions exposed to laser radiation at different values x: *1* — 0, *2* — 0.05, *3* — 0.10, *4* — 0.15, *5* — 0.25, *6* — 0.30. $T = 300\,K$.

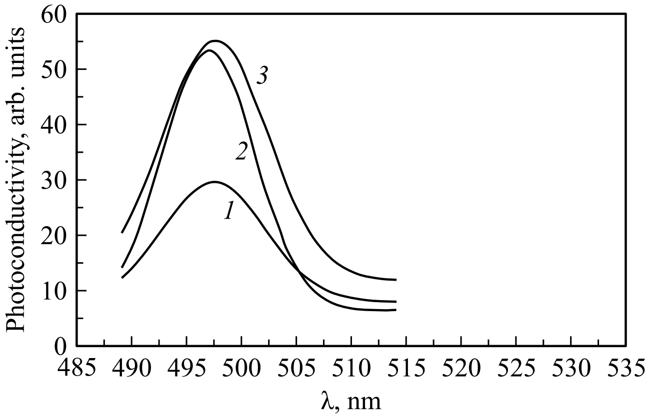

Figure 2. Photoconductivity spectra of $Cd_{1-0.75}Zn_{0.25}S$ for samples with different electrical resistances, ρ (Om·cm): *1* — 1.85×10^6, *2* — 6.4×10^5, *3* — $3.74 \cdot 10^5$.

repetition frequency was 20 Hz. The laser intensity was varied by rated neutral density filters. Photoluminescence was excited by radiation from a nitrogen (N_2) laser ($\lambda = 337\,nm$) with a pulse duration of ~ 1 ns and a peak power of 2 MW. The laser beam was directed at a small angle (~ 20°) to the film surface, and the luminescence was recorded from the side of the sample surface illuminated by the laser.

The luminescence spectra were analyzed using the monochromator (JOBIN-YVON) with a diffraction grating with dispersion of 2.4 nm/mm. The photoconductivity of thin CdS films and $Cd_{1-x}Zn_xS$ solid solutions was measured when they were excited by a dye laser. The laser reconfiguration range covered wavelengths in the range 473–547 nm. As ohmic contacts for photoelectric measurements, indium contacts were used, which were deposited on the surface of the samples by vacuum deposition. The photocurrent recording system was represented by a transient digitizer system , which included a storage oscilloscope (Le Croy 9400) and a computer system (board Master 800 AB I 8).

Experimental results and discussion

Fig. 1 shows the photoconductivity spectra of thin CdS films and $Cd_{1-x}Zn_xS$ solid solutions exposed to laser radiation at $T = 300\,K$. As can be seen from the figure, the photosensitivity spectra of thin $Cd_{1-x}Zn_xS$ ($x = 0-0.30$) films cover the wavelength range 490–520 nm.

The maximum of photoconductivity for thin CdS films corresponds to the wavelength $\lambda = 511\,nm$. As x-increases, the photoconductivity maxima of $Cd_{1-x}Zn_xS$ solid solutions shift towards short wavelengths from 511 nm ($x = 0$) to

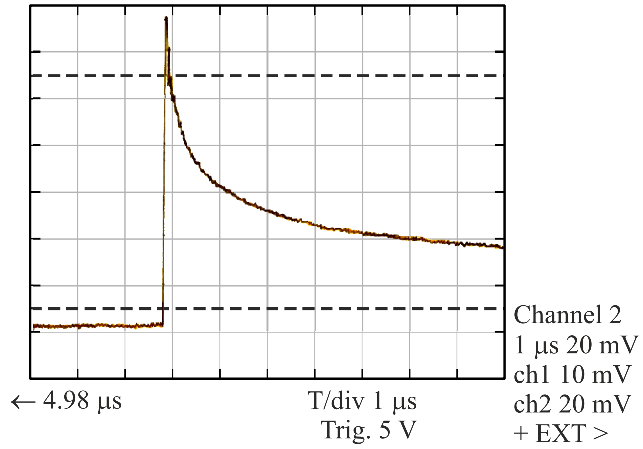

Figure 3. Oscillogram of the photoconductivity of a thin CdS film.

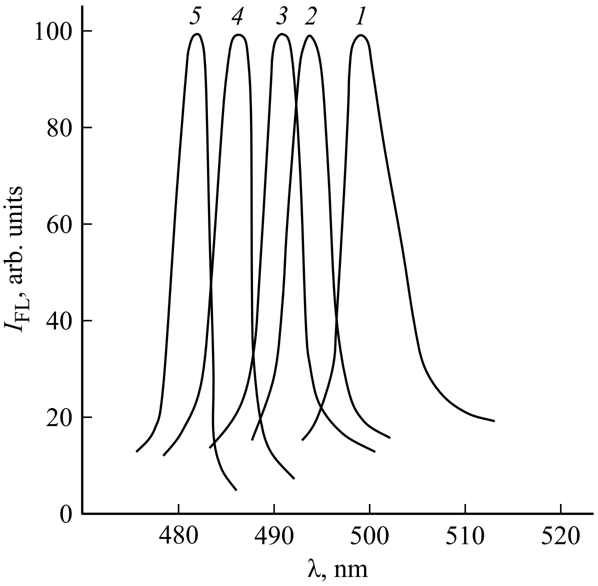

Figure 4. Photoluminescence spectra of thin CdS films and $Cd_{1-x}Zn_xS$ solid solutions exposed to laser radiation at different values x: *1* — 0, *2* — 0.05, *3* — 0.15, *4* — 0.25, *5* — 0.30. $T = 300\,K$.

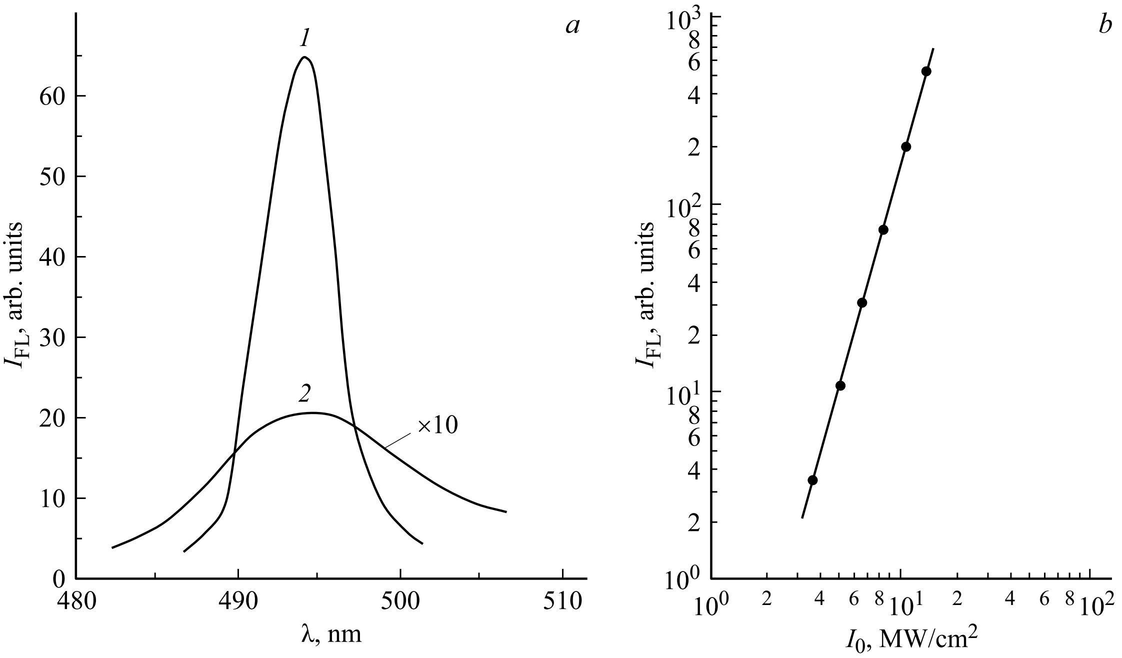

Figure 5. (*a*) Photoluminescence spectra of thin CdS films at two intensities of exciting laser radiation, $I_{\mathrm{las.}}$ (MVt/cm^2): *1* — 8, *2* — 12. (*b*) Dependence of the photoluminescence intensity (I_{lum}) of thin CdS films at the wavelength maximum ($\lambda = 499\,\mathrm{nm}$) on the laser radiation intensity I_{las}.

495 nm ($x = 0.30$). As an example, Fig. 2 shows the photoconductivity spectra of $\mathrm{Cd_{0.75}Zn_{0.25}S}$ for samples with different resistivities.

As can be seen from the figure, changing the resistivity ~ 10 times (from $1.85 \cdot 10^6 - 3.74 \cdot 10^5\,\Omega \cdot \mathrm{cm}$) does not affect the position and shape of the photoconductivity spectra, but only affects their magnitude. Similar characteristic properties are also observed for other $\mathrm{Cd_{1-x}Zn_xS}$ compositions. The dependence of photoconductivity on the pumping intensity for all compositions of $\mathrm{Cd_{1-x}Zn_xS}$ thin films varies linearly. Photoconductivity relaxation curves for thin CdS films and $\mathrm{Cd_{1-x}Zn_xS}$ solid solutions usually consist of two components, a fast one (with a decay time of $\sim 1\,\mu\mathrm{s}$) and a slow one, extending up to $7\,\mu\mathrm{s}$ and more (Fig. 3).

Fig. 4 shows the photoconductivity spectra of thin CdS films and $\mathrm{Cd_{1-x}Zn_xS}$ solid solutions exposed to laser radiation at $T = 80\,\mathrm{K}$. As in the case of photoconductivity spectra, with an increase in the Zn content in $\mathrm{Cd_{1-x}Zn_xS}$, the photoluminescence spectra also shift towards shorter wavelengths, but (in contrast to the photoconductivity spectra) they cover more shortwave region of the spectrum. The maximum of photoluminescence for thin CdS films at $T = 80\,\mathrm{K}$ corresponds to the wavelength $\lambda = 499\,\mathrm{nm}$. In addition, the half-width of the CdS emission line is 2 times smaller with respect to the photoconductivity line and amounts to $\sim 20\,\mathrm{meV}$.

Of particular interest are studies of the photoluminescence spectra of thin CdS films at various excitation intensities (Fig. 5, *a*). As can be seen from the figure,the increase in the pump power from 8 to 12 MW/cm^2 leads to significant increase in the photoluminescence intensity. Figure 5, *b* shows the dependence of the photoluminescence intensity (I_{FL}) of thin CdS films at the maximum wavelength ($\lambda = 499\,\mathrm{nm}$) on the intensity laser radiation I_{las}. It can be seen that this dependence is sublinear, $I_{\mathrm{FL}} \sim E_{las}^{3.5}$. This indicates that, at high levels of optical excitation in thin CdS films, light amplification [9] occurs.

Comparison of the photoconductivity spectra of thin CdS films and $\mathrm{Cd_{1-x}Zn_xS}$ solid solutions with their absorption spectra shows that the photoconductivity spectra observed upon laser excitation are due to direct band-band transitions [10]. This is also evidenced by the coincidence of the maximum photoconductivity of CdS with their band gap, which at 300 K equals 2.42 eV [11,12]. The shift of the photoconductivity spectra to the short-wave region with a change in the composition x finds its explanation on the basis of a change in the dependence E_g on x. Indeed, as the zinc content in the $\mathrm{Cd_{1-x}Zn_xS}$ solid solution increases, E_g increases, which leads to a shift of the absorption band edge towards short wavelengths. The characteristic properties of the observed photoconductivity spectra of $\mathrm{Cd_{1-x}Zn_xS}$ depending on the resistivity of the studied samples show that the photoconductivity is due to interband absorption, and not to the influence of impurities. This is also evidenced by the presence of a fast recombination channel in the photoconductivity relaxation curves. The linear dependence of the photoconductivity on pumping indicates the linear character of recombination processes [13,14].

The photoluminescence spectra of thin CdS films and $Cd_{1-x}Zn_xS$ solid solutions at 80 K, compared with the photoconductivity spectra measured at 300 K, are located in the short-wave region of the spectrum. This difference is apparently due to the change in the energy gap width with temperature, $\frac{dE_g}{dT} = 5.2 \cdot 10^{-4}\,\text{eV}\cdot\text{K}$. It is known that thin films of cadmium sulfide, like other A^2B^6 compounds, are direct-band-gap semiconductors [15,16]. The observed power-law dependence $(I_{\text{FL}} \sim I_{las}^{3.5})$ of the radiation intensity on the pumping power suggests that laser radiation can be obtained based on thin CdS films.

Conclusion

Thin CdS films and $Cd_{1-x}Zn_xS$ solid solutions were obtained by chemical spray on followed by pyrolysis. The photoconductivity and luminescence spectra of $Cd_{1-x}Zn_xS$ at 300 and 80 K were experimentally studied. It is shown that when $Cd_{1-x}Zn_xS$ is excited by laser radiation, interband optical optical absorption takes place. As x increases, the photoconductivity and luminescence spectra of $Cd_{1-x}Zn_xS$ shift towards short wavelengths from 511 ($x = 0$) to 495 nm ($x = 0.30$). The linear dependence of the photoconductivity on pumping indicates the linear character of the recombination processes. At high levels of optical excitation, enhancement is observed in CdS, which suggests that on their basis it is possible to create a semiconductor laser.

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