LUMINESCENCE AND PHOTOCONDUCTIVITY OF CdS UPON MULTIPHOTON EXCITATION

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The luminescence and kinetics of photocurrent relaxation in thin CdS films upon excitation by light from a Nd:YAG laser were studied experimentally. Comparison of the luminescence spectra under single-photon excitation with the spectra under two- and three-photon excitation showed that there is no free exciton line in the luminescence spectrum under bulk excitation. The effect of impurities on the luminescence spectra and photocurrent relaxation curves upon excitation by the 1st-3rd laser harmonics is studied.

Keywords: CdS, photocurrent relaxation, multiphoton absorption, luminescence.
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1. INTRODUCTION

The wide-gap semiconductor cadmium sulfide (CdS) has long been used in applications of optoelectronics, in particular, as the working medium of optoelectronic emitters, single-electron transistors, quantum dot displays, lasers, nanoelectronics, solar energy converters, etc. [1–8]. The evolution of photoinduced electrons and holes and, consequently, the luminescence and relaxation kinetics of nonequilibrium carriers strongly depend on the excitation parameters and characteristics of the sample. Thus, the concentration of carriers generated by laser radiation can vary over a wide range in the case of multiphoton excitation. In this work, we experimentally studied the luminescence and photoconductivity of thin CdS films under multiphoton excitation.

2. EXPERIMENTAL METHODS

The studies were carried out at 300 K in thin CdS films obtained by chemical pulverization followed by pyrolysis [9]. Both high-resistance ~ 10^6 Ω·cm and low-resistance samples with an impurity concentration of ~ 10^{18} Ω·cm were studied. The thickness of the CdS films was measured using an MII-4 interference microscope and was ~10 microns. The area of the studied films was 0.5 cm^2. For photoelectric measurements, indium contacts were used as ohmic contacts, which were deposited on the sample surface by vacuum deposition.

The radiation source was a pulsed Nd:YAG laser with built-in generators of the 2-nd and 3-rd harmonics, designed to generate radiation with a wavelength of 1064, 532, and 335 nm. The laser pulse duration was 10 ns with a maximum power of ~12 MW/cm^2. The radiation intensity was varied using calibrated neutral light filters. Using a lens, the incident laser beam was focused onto the sample surface with a spot diameter of ~2.0 mm. The photoluminescence spectra of CdS were studied using an automatic double dispersion monochromator M833 (spectral resolution ~0.024 nm at a wavelength of 600 nm), with computer control and a detector that records radiation in the wavelength range of 350–2000 nm. Registration of photocurrent pulses was carried out according to a technique that allows one to record single nanosecond pulses on the screen of a storage oscilloscope ((Le Croy).

3. EXPERIMENTAL RESULTS AND DISCUSSION

On fig. 1 shows the luminescence spectra of thin CdS films upon single-photon excitation by laser radiation with a wavelength of $\lambda = 355$ nm. As can be seen from the figure, two narrow emission lines are observed in the luminescence spectrum, a short-wavelength one with a maximum of $\lambda = 485$ nm (a) and a long-wavelength one (b) with a maximum of $\lambda = 853$ nm. The half-widths of the emission lines are 50 A^0 and 15 A^0, respectively.

Under two- and three-photon excitation by the 2nd ($\lambda = 532$ nm) and 1st harmonic ($\lambda = 1060$ nm) Nd:YAG laser, the luminescence spectrum of thin CdS films lacks a short-wavelength emission line with a maximum of $\lambda = 485$ nm, but a long-wavelength emission line with a maximum of $\lambda = 853$ nm is observed which takes place under single-photon excitation (Fig. 1b).

In low-resistance samples with two-photon excitation, a wide band (half-width ~ 160 A^0) of radiation at the same wavelength $\lambda = 853$ nm is observed (Fig. 2).

Simultaneously with the study of luminescence, the kinetics of photoconductivity was studied on these samples. On fig. 3 shows the relaxation kinetics of the photocurrent of the nonequilibrium photoconductivity of thin CdS films upon single-photon excitation by the 3rd harmonic of a Nd:YAG laser ($\lambda = 355$ nm).

As can be seen from the figure, the photocurrent kinetics consists of two components, a straight line and a relaxation curve with a half-width of ~12 μs (a).

An analysis of the ultrashort component in the nanosecond interval showed that the straight line is an oscillogram with a relaxation time of ~25 nanoseconds (b). As shown by the experimental results for two and three-photon excitation, there is no ultrashort relaxation of the photocurrent.

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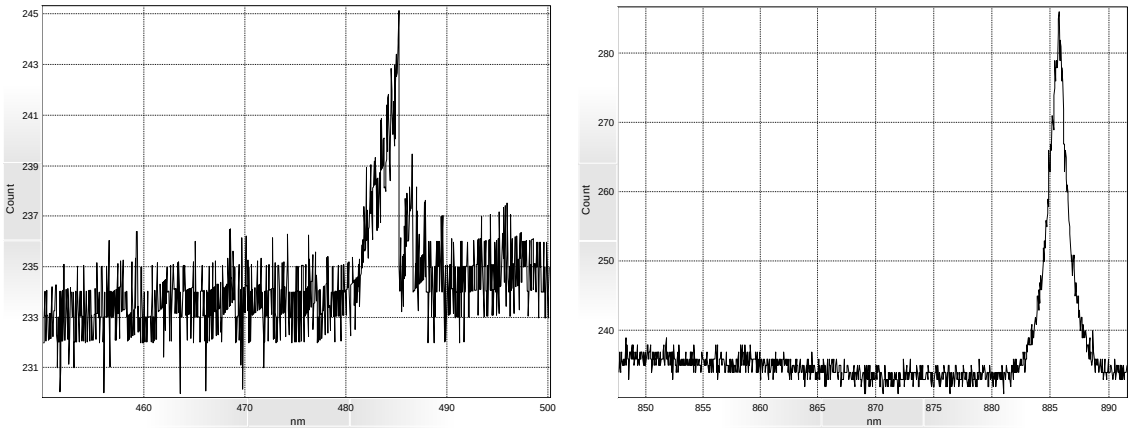

a *b*

Fig.1. Emission spectrum of thin CdS films upon single-photon excitation by the 3rd harmonic of a Nd:YAG laser ($\lambda = 355$ nm).

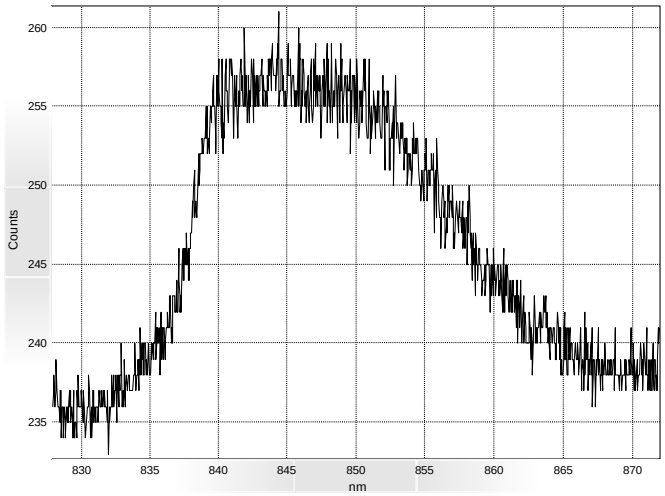

Fig. 2. Emission spectrum of low-resistance thin CdS films upon single-photon excitation by the 3rd harmonic of a Nd:YAG laser ($\lambda = 355$ nm).

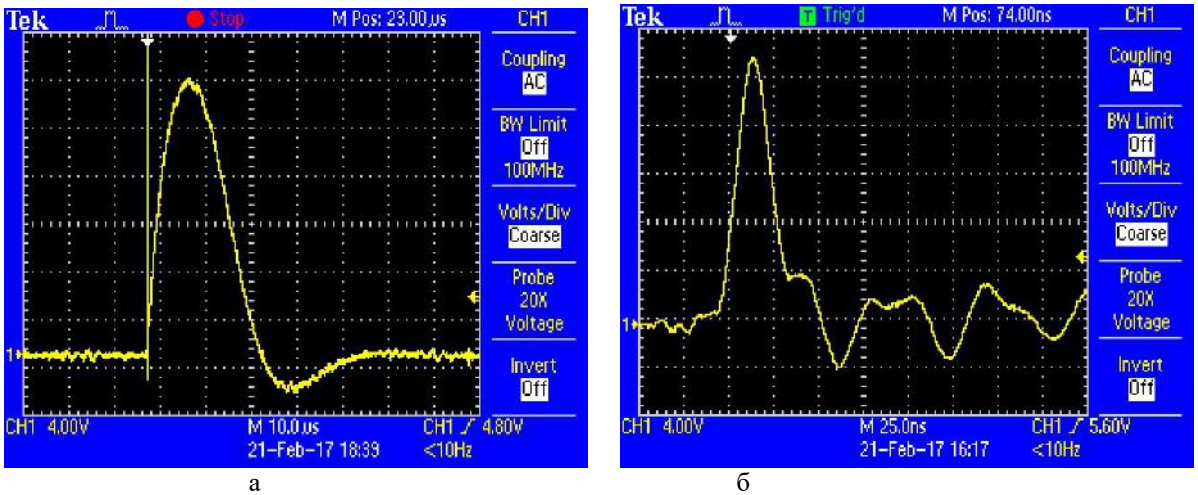

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Fig. 3. Photocurrent kinetics upon excitation of thin CdS films under single-photon excitation by the 3rd harmonic of the Nd:YAG laser ($\lambda = 355$ nm).

In our opinion, the short-wavelength $\lambda = 485$ nm emission line observed upon single-photon excitation in thin CdS films is due to the emission of free excitons.

The presence of a blue emission band associated with the luminescence of free excitons in CdS crystals under the action of ordinary light sources was previously indicated in numerous works [6, 10, and 11]. This is also evidenced by the observation of an ultrashort component in the photocurrent relaxation curves. As a rule, the lifetime of excitons in semiconductors is several nanoseconds [12–15].

The long-wavelength emission line $\lambda = 853$ nm is apparently due to the radiative recombination of free electrons with holes trapped in impurity levels.

When comparing the luminescence spectra of CdS induced by two and three photon excitation with the spectra of single photon excitation, the absence of the free exciton line $\lambda = 485$ nm in the luminescence spectra of two and three photon excitation attracts attention. Similar features are also observed in the kinetics of photoconductivity relaxation. In contrast to single-photon excitation, there is no ultrashort section associated with free excitons in the photocurrent relaxation curves for two- and three-photon excitation.

In our opinion, the absence of a free exciton line under two and three-photon volume excitation may be due to the fact that the probability of multiphoton processes rapidly decreases as the multiplicity of the process increases (at a given radiation intensity). The ratio of the probability of an n-photon stimulated process to the probability (n-1) of a photon process is equal in order of magnitude to (E/Ea)2, where E is the field strength of the initial light wave, Ea is the strength of intraatomic fields. In semiconductors with single-photon absorption, the fundamental absorption coefficient at the edge of the absorption band is ~ $\alpha^{(1)}$ 10^4-10^5 cm^{-1}, while with two-photon absorption ~ $\alpha^{(2)}$ 10^{-2} cm^{-1}, and with three-photon excitation ~ 10^{-8} cm^{-1}, which makes it difficult to observe at room temperature, exciton luminescence and photoconductivity under two and three-photon excitation. In addition, it is known that the radiative decay of a free exciton is an unlikely process, since there are relatively few excitons with a wave vector equal to the wave vector of the emitted photon. Interaction with the surface and defects can facilitate the decay process. Thus, this line is generated predominantly in the surface region, which is small compared to the entire volume of the sample, from where the exciton radiation originates. In addition, the exciton line experiences strong reabsorption, and under such conditions, the observation of the exciton line becomes difficult. If in high-resistance samples with two and three-photon excitation there is no free exciton line, then in heavily doped samples (see Fig. 2) no luminescence is observed at all in the blue region, which indicates the absence of excitons. The latter is apparently due to the presence in these samples of the effect of screening of the Coulomb interaction of nonequilibrium electron-hole pairs by equilibrium current carriers.

4. CONCLUSION

An experimental study was made of the luminescence of thin CdS films upon excitation by a Nd:YAG laser. It is shown that the short-wavelength emission line with a maximum of $\lambda = 485$ nm, observed upon single-photon excitation, is due to the radiative recombination of free excitons. With two and three-photon excitation, this emission line is absent. Similar features are also observed in the kinetics of photoconductivity relaxation. In our opinion, the absence of a free exciton emission line during two and three-photon volume excitation can be associated with a decrease in the probability of multiphoton processes with an increase in the multiplicity of the process and reabsorption of the exciton line due to the generation of this line in the surface region of the sample. The absence of exciton absorption in heavily doped CdS samples is due to the screening effect in these samples of the Coulomb interaction of nonequilibrium electron-hole pairs by equilibrium current carriers. As experimental results show, in thin CdS films, the lifetime of excitons is three orders of magnitude shorter than the lifetime on impurity transitions and amounts to ~15 nanoseconds.

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