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# PHOTOELECTRICAL PROPERTIES OF CdMnSe THIN FILMS

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**Abstract.** The studied semiconductor structure for photovoltaic cells is composed of $SnO_2$-coated glass and CdMnSe thin film. A study is made by examining the photoluminescence from the surface of the CdMnSe thin film with laser power and sample temperature for an as-grown, then an air-annealed thin film and undergone $CdCl_2$ treatment. Thin films of $Cd_{1-x}Mn_xSe$ ($x$=0.02) were grown on a glass substrate. The lifetime of charge carriers under pulsed illumination was determined from the kinetic decay of the photocurrent. The study of relaxation curves of nonequilibrium photoconductivity under the influence of laser radiation confirmed the presence of two recombination channels - intrinsic and impurity. Photocurrent relaxation occurs through fast and slow recombination channels. The fast relaxation time $\tau = 6$ μs associated with the intrinsic transition and the slow relaxation time is due to impurity excitation and $\tau = 22$ μs. The photoluminescence spectra of thin films of $Cd_{1-x}Mn_xSe$ ($x$=0.02) were studied. In the photoluminescence study, two maxima are observed due to donor-acceptor recombination and intracenter transition of Mn atom.

***Keywords:*** *Thin film, semimagnetic semiconductor, lifetime, recombination center, photoluminescense.*

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## 1. Introduction

CdSe compound based thin films attract the attention of researchers as a promising material (Luceño-Sánchez *et al*., 2019; Paranthaman *et al*., 2016) in photovoltaic.

In recent years, low dimension semiconductor structures have been the subject of researchers by many scientific centers around the world (Silva *et al*., 2012; Badera *et al*., 2008; Munde *et al*., 2018; Dargad & Deshmukh, 2009; Mali *et al*., 2021; Gonullu & Kose, 2017; Nwori *et al*., 2021; Scragg *et al*., 2012). In order to obtain high quality and inexpensive solar cells, it is important to have the following conditions: replacement of massive crystals with thin-films, proper selection and development of thin-film technology. By replacing massive crystals with thin-film structures, the total amount of

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material used for structures obtained on different substrates can be reduced by 100 or even 1000 times. On the other hand, the transition to thin films simplifies the requirements for the crystallographic quality and purity of the material, reducing the resistance, which is one of the main parameters of the solar cell. For this reason, the choice of the optimal value of the layer thickness is a key factor and this can be achieved by the molecular beam condensation method.

In recent years, new types of materials have been used for solar cells. For example, copper-indium-diselenide, GaAs, CdS, CdTe, CdSe, etc. thin-film photovoltaic elements based on them. These solar cells have been used for commercial purposes in recent years and their production technology is constantly evolving. Over the last decade, the efficiency of such thin-film structures has almost increased for 2 times.

The material for the absorbing layer of flexible solar cells can be thin films based on cadmium selenide (CdSe). The advantages of this material include an optimal band gap of ~1.71 eV, as well as a high absorption coefficient of solar radiation (~$5 \cdot 10^5$ $cm^{-1}$) (Gremenok *et al*., 2013).

Thin films of semimagnetic semiconductors based on Cd are of particular interest for the purpose of using these materials in photovoltaics (Nuriyev *et al*., 2017; Mehrabova *et al*., 2022; Mehrabova *et al*., 2019; Mehrabova *et al*., 2018; Scarpulla *et al*., 2023). Many physical properties of semiconductors are determined by the nature, state and location of local levels in the band gap. The study of current-voltage characteristics (CVC) and thermally stimulated current (TSC) spectra does not fully allow us to judge such important parameters as the capture center, depth, concentration and capture cross sections, as well as information about the nature of the distribution of local levels in the band gap of high-resistance materials.

Over the last few years, solar cells based on thin films of CdMnSe semimagnetic semiconductors (SMSC) are of great interest. These materials have unique properties: high photosensitivity at room temperature, the wide band gap and the ability to control a number of physical properties by changing the concentration of the transition metal element in the sample, etc.

The study of recombination processes is a necessary essential stage in the study of the physical properties of semiconductor materials and devices based on them. It is the mechanism of charge carrier recombination that determines the features of the occurrence of photoelectric, luminescent and injection phenomena that underlie most areas of practical use of semiconductors. In this work, the recombination processes of charge carriers in thin films of semimagnetic semiconductors $Cd_{1-x}Mn_xSe$ are investigated.

## 2. Experiments and discussions

In this work, solid solutions of $Cd_{1-x}Mn_xSe$ ($x$ = 0.02) were synthesized and thin films on their basis were grown on a glass substrate with a conduction $SnO_2$ layer at a source temperature $T_{sour}$ = 1100 K, substrate temperature $T_{sub}$ = 670 K using the molecular beam condensation (MBC) method in a vacuum installation УВН-71-Р3 in a vacuum of $10^{-4}$ Pa (Mehrabova & Mekhrabov, 2023; Nuriyev *et al*., 2019; Mehrabova *et al*., 2020; Antoszewski & Pecold, 1980; Dargad, 2015). Ni contacts were deposited on thin films. The type of conductivity was determined by the t.e.m.f, which showed that the obtained $Cd_{1-x}Mn_xSe$ thin films have p-type conductivity.

The crystal structure of the obtained thin films was studied by X-ray diffraction method on an XRD Broker, D8 ADVANGE, Germany. In the X-ray diffraction patterns of $Cd_{1-x}Mn_xSe$ thin films, all diffraction peaks confirm that the thin films have a sphalerite-type cubic structure with a lattice parameter of *a* = 6.05 Å (Figure 1).

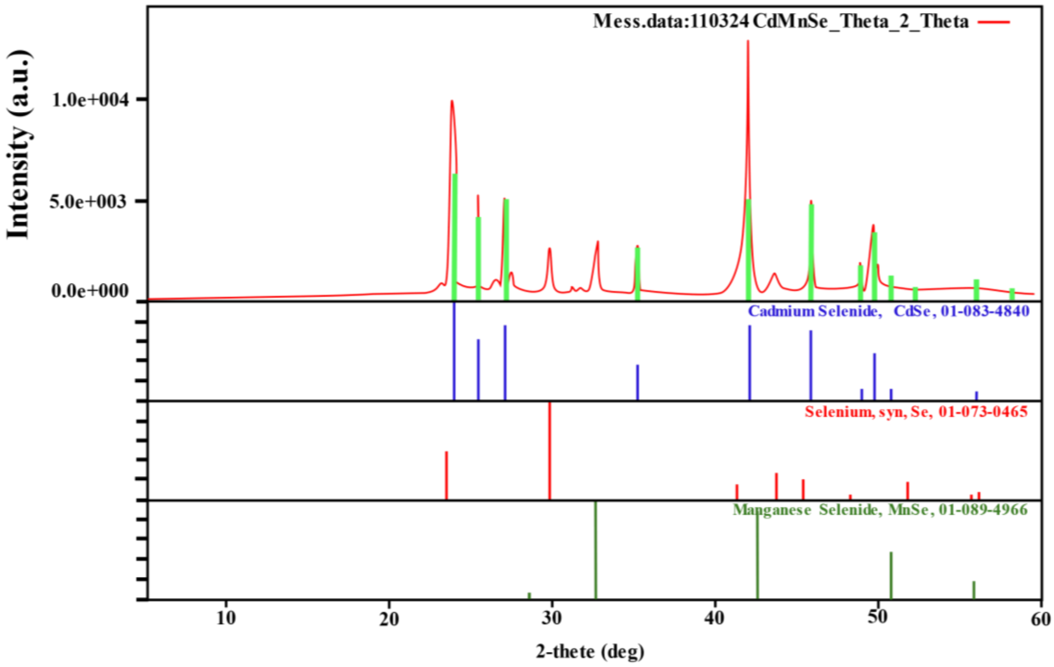



**Figure 1.** XRD spectrum of CdMnSe thin films

In order to determine the recombination mechanism, parameters of recombination centers and processes of electronic transitions in $Cd_{1-x}Mn_xSe$ ($x$=0.02) films, we used a complex of stationary and kinetic research methods. To obtain kinetic characteristics, semiconductors were illuminated with short pulses (t~$10^{-6}$s) of LEDs. The photoelectric signal, caused by a change in the potential of the semiconductor under the influence of pulsed illumination, after preliminary amplification by a broadband transistor amplifier, was fed to the input of the oscillograph and recorded by a computer (Figure 2). The time resolution of the selective circuit was no worse than $10^{-8}$ s, which made it possible to record the signal in a time interval of $10^{-8}$÷$10^{-2}$ s.

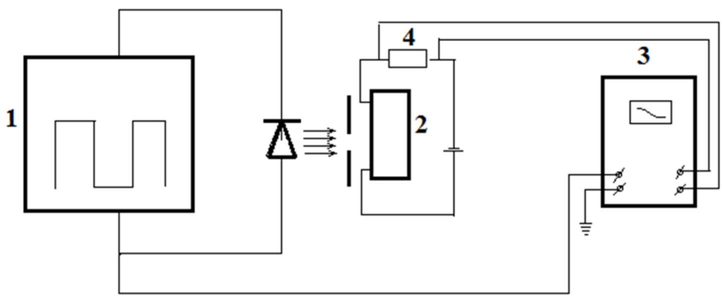



**Figure 2.** Block diagram of the installation for measuring the kinetics of the photoelectric effect:
1 – generator; 2 – cell; 3 – amplifier with polarization unit; 4 – oscillograph

In Figure 3 shows the photocurrent relaxation curve in $Cd_{1-x}Mn_xSe$ ($x$=0.02). The study of the relaxation curves of nonequilibrium photoconductivity under the influence of laser radiation also confirms the presence of two recombination channels in $Cd_{1-x}Mn_xSe$ ($x$=0.02) - intrinsic and impurity. Photocurrent relaxation occurs through fast and slow recombination channels. The fast relaxation time $\tau$, which is ~ 6 μs, is associated with the intrinsic transition and the slow relaxation time is due to impurity excitation and is $\tau$ ~6 μs.

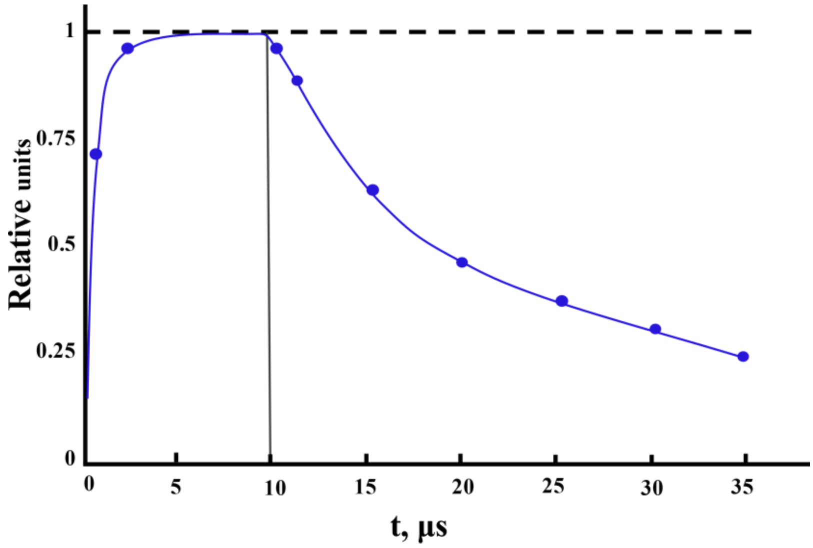



**Figure 3.** Kinetics of photocurrent changes for $Cd_{1-x}Mn_xSe$ ($x$=0.02) at room temperature

All these studies have clearly shown that for high-resistance CdMnSe crystals, the main role in recombination processes is played the various types of recombination centers: fast (s-) and slow (r-) – sensitive. Under pulsed illumination, the lifetime of charge carriers is determined from the kinetic decay of the photocurrent. The study showed that the decay of the photocurrent is not monoexponential, which indicates the presence of several types of recombination. Depending on the energy state of these centers, the effective lifetime was $10^{-6}$-$10^{-3}$s.

We have studied lifetime of nonequilibrium charge carriers in a defective surface layer. In the presence of several types of recombination, the effective carrier lifetime can be found from the expression

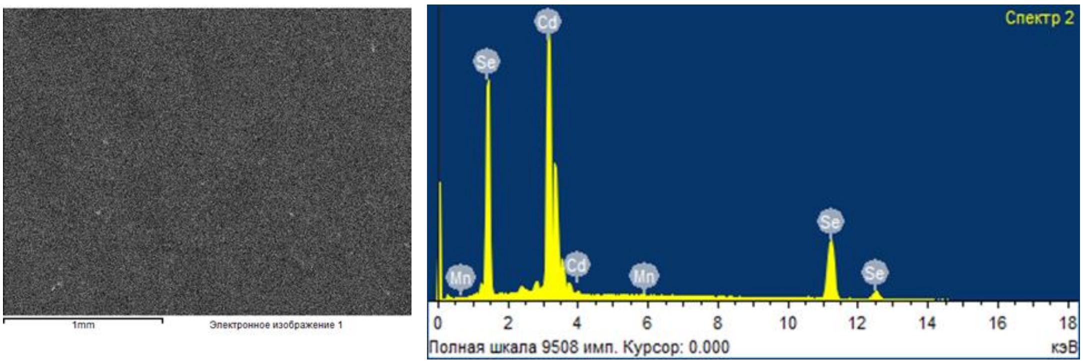
$$\frac{1}{\tau_{eff}} = \sum_i \tau_i.$$

For a thin film of $Cd_{1-x}Mn_xSe$ ($x$=0.02), taking into account the introduced structural defects and the influence of the surface, the effective lifetime can be determined as

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_l} + \frac{1}{\tau_s} \ ,$$

where $\frac{1}{\tau_s} = \frac{2s}{d}$; $\tau_l$ - taking into account the recombination of carriers on structural defects in the thin film, $\tau_s$ - surface lifetime; $s$ - surface recombination rate; $d$ - plate thickness. Analyzes have shown that the lifetime is $\tau$ =5÷22 μs and the surface recombination rate $s$ = 40$\frac{sm}{s}$ .

It was determined surface morphology and content of $Cd_{1-x}Mn_xSe$ ($x$=0.02) thin films by SEM method (Figure 4) on Jeol JSM-6610LV Series Scanning Electron Microscope.




a) b)

**Figure 4.** Surface morphology (a) and EDX analysis (b) of $Cd_{1-x}Mn_xSe$ ($x$=0.02) thin films

In our previous works the photoluminescence (PL) spectra of $Cd_{1-x}Mn_xSe$ ($x$=0.05) thin films were studied. In this work PL spectra of $Cd_{1-x}Mn_xSe$ ($x$=0.02) thin films were studied (Mehrabova *et al*., 2024). PL measurements were carried out using a PL/PLE/Raman spectrometer device manufactured in Japan. The emission of the samples was studied using lasers with different wavelengths: 325nm (HeCd), 532nm (Nd-YAG). Photoluminescence from the sample was scattered by a grating (100 g/mm − 1 ) monochromator MS 5207 I (SOL Instruments, Inc) and detected by a CCD multiplier DU 491A-1.7 (Figure 5).

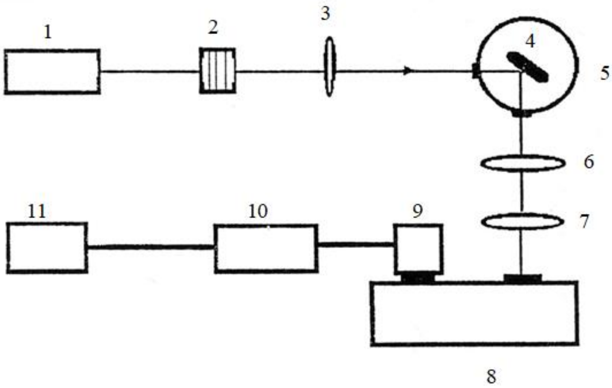



**Figure 5.** Scheme of the experimental setup for measuring photoluminescence of thin films of $Cd_{1-x}Mn_xSe$ (x=0.05) under the influence of laser radiation: 1- pulsed Nd:YAG laser, 2- light filters, 3, 6, 7 - lenses, 4 - sample, 5- cryostat, 8 - monochromator, 9 - photoelectric current amplifier, 10 - storage oscillograph, 11 - computer system

If we look at the current literature, we can see that in the last decade, works devoted to the magnetic properties of $A^{II}_{1-x}Mn_xB^{VI}$ type compounds (where $A^{II}$ = Zn, Cd, Hg and $B^{VI}$ = S, Se, Te) have been studied to some extent (Lee *et al*., 2019; Oladeji *et al*., 2000). However, although photoluminescence properties have been studied in this sulfur compound (Reddy *et al*., 2007), this study is not found in selenium compounds. Taking into account this facts, the photoluminescence property of $Cd_{1-x}Mn_xSe$ (x=0.02) thin film was investigated by us for the first time.

The research covered the wavelength range of 600-950 nm (Figure 6). Two maxima with emission maxima of 720 nm(1.72eV) and 871nm(1.42eV) were observed. In Wahab et al. (2012), the absorption spectrum of the $Cd_{1-0.5}Mn_{0.5}Se$ compound was investigated and the forbidden zone was determined to be 2.1 eV. Considering this, the peak at 720 nm can be associated with donor-acceptor recombination. In Antoszewski and Pecold (1980), the maximum at the wavelength of 871 nm is not coincidental in the CdSe photoluminescence study. This peak formed by the introduction of the additive into this compound can be associated with the internal center transition of Mn atom $^6A_1(^6S)$ $(^4T_1(^4G))^6 \rightarrow {}^6A_1(^6S)^6A_1(^6S)$.

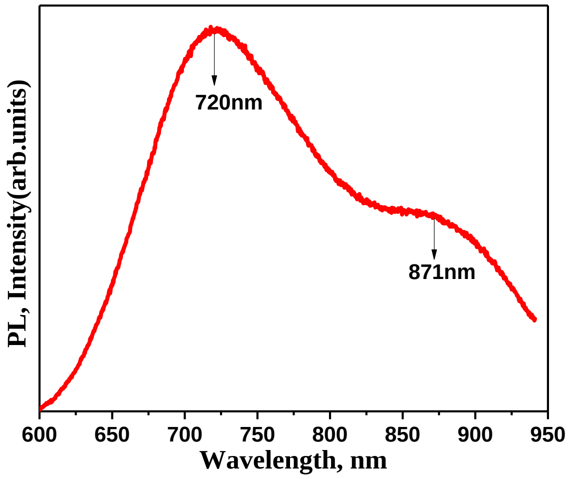



**Figure 6.** PL spectrum of $Cd_{1-x}Mn_xSe$ (x=0.02) thin films at room temperature

## 3. Conclusion

The studied semiconductors for photovoltaic cells is composed of $SnO_2$-coated glass and CdMnSe thin film. A study of the cells is made by examining the photoluminescence from the surface of the CdMnSe thin film with laser power and sample temperature for an as-grown cell, an air-annealed cell and a cell that has undergone $CdCl_2$ treatment.

$Cd_{1-x}Mn_xSe$ ($x$=0.02) thin films were grown on a glass substrate. The lifetime of charge carriers under pulsed illumination was determined from the kinetic decay of the photocurrent. The study of relaxation curves of nonequilibrium photoconductivity under the influence of laser radiation confirmed the presence of two recombination channels - intrinsic and impurity. Photocurrent relaxation occurs through fast and slow recombination channels. The fast relaxation time $\tau$ =6 μs associated with the intrinsic transition and the slow relaxation time $\tau$ = 22 μs is due to impurity excitation.

The photoluminescence spectra of thin films of $Cd_{1-x}Mn_xSe$ ($x$=0.02) were studied. In the photoluminescence study, two maxima are observed due to donor-acceptor recombination and intracenter transition of Mn atom.

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