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CdMnSe THIN FILMS FOR SOLAR ENERGY CONVERTERS

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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=0.05) 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 τ = 13 µs associated with the intrinsic transition, and the slow relaxation time is due to impurity excitation and τ = 20 µs. The photoluminescence spectra of thin films of $Cd_{1-x}Mn_xSe$ (x=0.05) were studied. The observed emission lines can be divided into three parts. Emission lines with maxima λ_1 = 868 nm, λ_2 = 888 nm and λ_3 = 933 nm, which are caused, respectively, by an optical transition in the region of the edge of the absorption band, an acceptor level located in the band gap and an optical zone-band transition or annihilation of free excitons.

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

Introduction.

One of the current trends in the development of alternative energy is building photovoltaics, which involves the integration of solar panels with residential buildings or industrial facilities. As a rule, such devices are assembled on a rigid basis, but assembling panels on a flexible basis would significantly reduce their specific weight and also facilitate installation.

In recent years, the market demand for solar modules has increased significantly. Strong competition among manufacturers in the world market requires continuous improvement of the technical parameters of solar cells and reduction of their prices.

The vast majority of solar cells currently produced for commercial purposes are made of silicon (Si). Photoelements made of Si solids are widely used, as their absorption, spectral characteristics correspond to the spectral characteristics of solar radiation and the theoretically calculated maximum efficiency under standard conditions is 30%. 91% of the energy of light flux falling through silicon, i.e. the part of the solar spectrum with a wavelength of 1.1 µm and shorter, can be converted into electricity. Their main drawback is the high cost of silicon ingots due to the expensive operation of the cutting technology [1].

GaAs and CdTe compounds attract the attention of many researchers as a very promising material. Because of their use, it was possible to obtain a very large efficiency. Although GaAs have a number of advantages over silicon, they also have some disadvantages, such as brittleness and high density. At large values of the band qap E_g, its ability to convert long-wavelength rays is limited (it absorbs rays with a wavelength less than 0.9 μm). CdTe-based solar cells are more durable and strong [1,2].

In recent years, low dimension semiconductor structures have been the subject of researchers by many scientific centers around the world [3-10]. 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 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 ($\sim 5 \cdot 10^5$ cm^{-1}) [11].

Thin films of semimagnetic semiconductors based on Cd are of particular interest for the purpose of using these materials in photovoltaics [12,13]. 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.

Experiments and discussions.

In this work, solid solutions of $Cd_{1-x}Mn_xSe$ (x = 0.05) 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 [14,15]. 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. (Fig. 1).

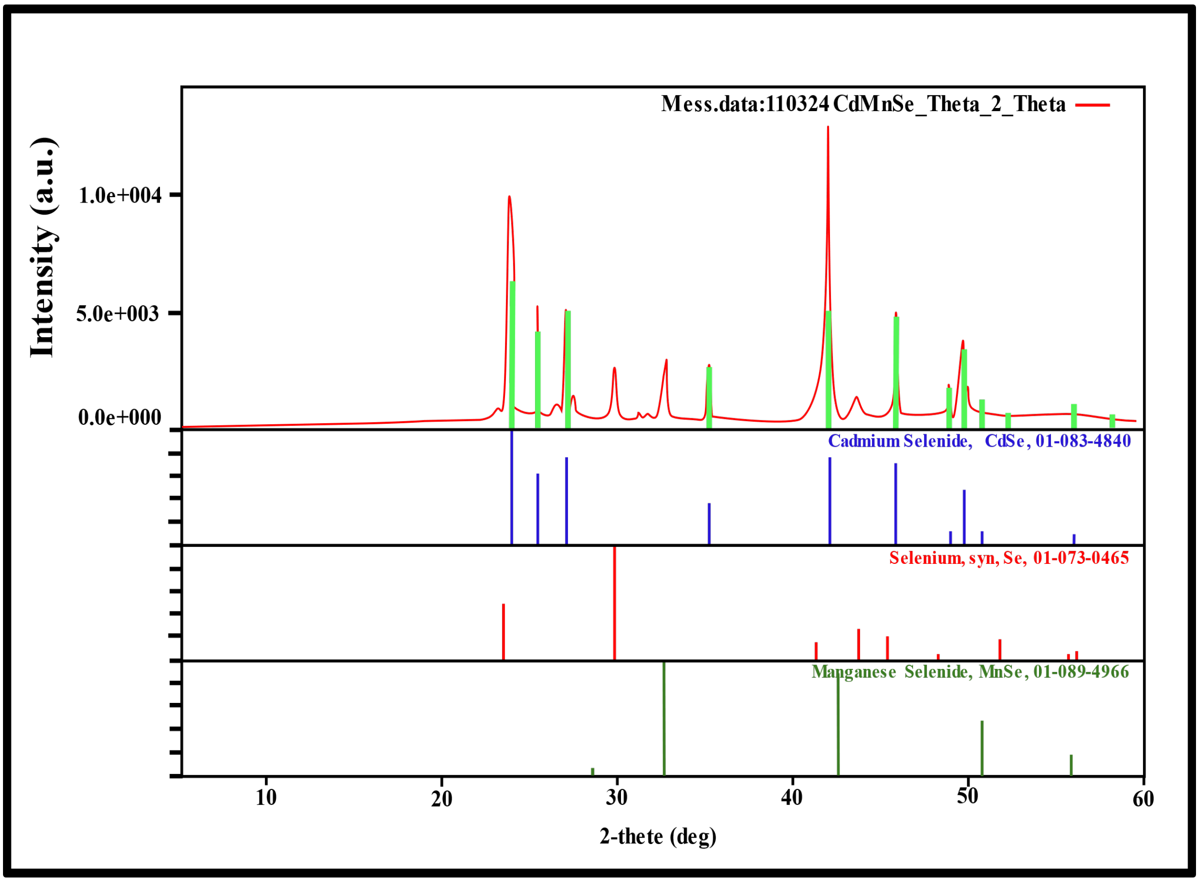

Figure 1. XRD spectrum of CdMnSe thin films

In order to determine the recombination mechanism, parameters of recombination centers and processes of electronic transitions in $Cd_{1-x}Mn_xSe$ (x=0.05) films, we used a complex of stationary and kinetic research methods. To obtain kinetic characteristics, semiconductors were illuminated with short pulses ($t \sim 10^{-6}$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 oscilloscope and recorded by a computer (Fig. 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 $10^{-8} \div 10^{-2}$ s.

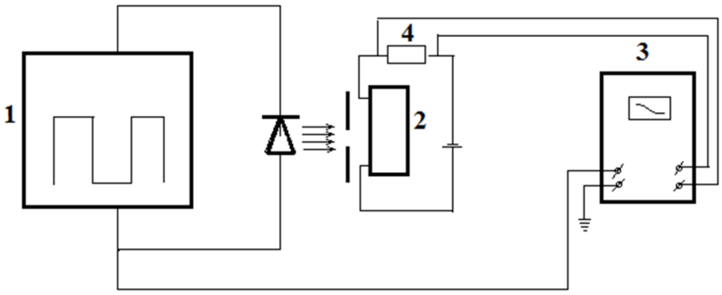

Figure2. Block diagram of the installation for measuring the kinetics of the photoelectric effect: 1 –generator; 2 – cell; 3 – amplifier with polarization unit; 4 – oscilloscope

In Fig. 3 shows the photocurrent relaxation curve in $Cd_{1-x}Mn_xSe$ (x=0.05). 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=0.05) - intrinsic and impurity. Photocurrent relaxation occurs through fast and slow recombination channels. The fast relaxation time τ, which is ~13 µs, is associated with the intrinsic transition, and the slow relaxation time is due to impurity excitation and is τ ~20 µs.

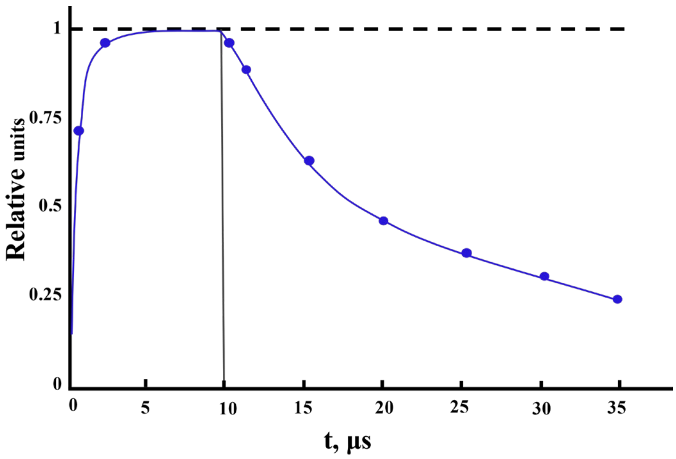

Figure 3. Kinetics of photocurrent changes for $Cd_{1-x}Mn_xSe$ (x=0.05) at room temperature.

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.

It was considered possibility of estimating the lifetime of nonequilibrium charge carriers in a surface layer with defects. 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=0.05), 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 $\frac{1}{\tau_s} = \frac{2s}{d}$; τ_l - taking into account the recombination of carriers on structural defects in the thin film, τ_s - surface lifetime; s - surface recombination rate; d - plate thickness. Analyzes have shown that the lifetime is τ =13-20 µs, and the surface recombination rate s = $40\frac{sm}{s}$.

To measure photoluminescence, a pulsed Nd:YAG laser with built-in 2nd and 3rd harmonic generators designed to generate radiation with wavelengths of 1064, 532 and 335 nm was used as a radiation source. 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 surface of the sample with a spot diameter of ~2.0 mm. The luminescence spectra of thin films of $Cd_{1-x}Mn_xSe$ (x=0.05) were studied using an M833 automatic monochromator with dual dispersion (spectral resolution ~0.024 nm at a wavelength of 600 nm), with computer control and a detector that records radiation in the wavelength range 350 – 2000 nm (Fig. 4).

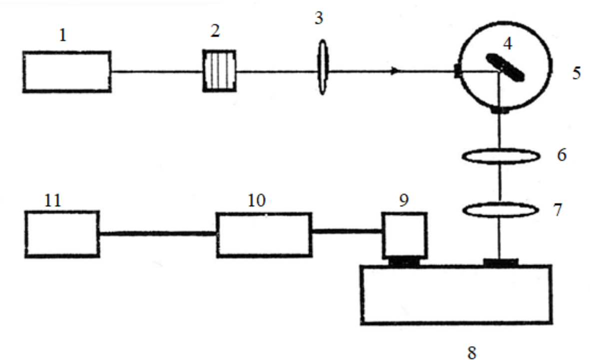

Figure 4. Scheme of the experimental setup for measuring photoluminescence of thin films of $Cd_{1-x}Mn_xSe$ (x=0.05) under the influence of laser radiation: 1- pulsed Nd:YAG laser, 2- light filters, 3, 6, 7 - lenses, 4- sample, 5- cryostat, 8-monochromator, 9-photoelectric current *amplifier*, *10-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

The observed emission lines can be divided into three parts. Short-wave emission lines with maxima λ_1 = 868 nm (with a half-width of 3A°) and λ_2 = 888 nm refer to radiation associated with $Cd_{1-x}Mn_xSe$ (x = 0.05) and long-wave emission lines λ_3 = 933 nm (with a half-width of 4A°) (Fig.5).

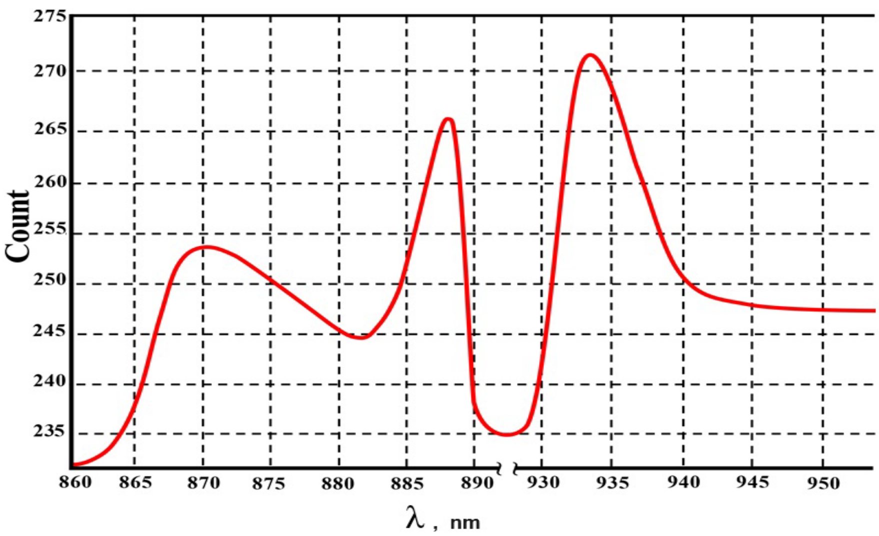

Figure 5. Luminescence spectra under the action of laser radiation in $Cd_{1-x}Mn_xSe$ (x=0.05) thin films at room temperature

In our opinion, the short-wavelength emission line corresponds to an optical transition in the region of the absorption band edge, since the band gap of $Cd_{1-x}Mn_xSe$ (x=0.05) is 1.7 eV [16-18]. Emission with a maximum λ_2 can be caused by an acceptor level located in the band gap of $Cd_{1-x}Mn_xSe$ (x=0.05) with activation energy E_a = 0.42 eV, or by a vacancy. As for the long-wavelength emission line, this is a fairly well-known line associated with the optical band-band transition and the annihilation of free excitons with a binding energy of - 15 meV.

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=0.05) 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 τ = 13 μs associated with the intrinsic transition, and the slow relaxation time τ = 20 μs is due to impurity excitation.

The photoluminescence spectra of $Cd_{1-x}Mn_xSe$ (x=0.05) thin films were studied. The observed emission lines can be divided into three parts. Emission lines with maxima λ_1 = 868 nm, λ_2 = 888 nm and λ_3 = 933 nm, which are caused, respectively, by an optical transition in the region of the edge of the absorption band, an acceptor level located in the band gap and an optical zone-band transition and annihilation of free excitons.

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