INFLUENCE OF EuF$_3$ IMPURITY ON LUMINESCENCE AND PHOTOCONDUCTIVITY SPECTRA OF Se-As CHALCOGENIDE GLASS-LIKE SEMICONDUCTOR SYSTEM

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It was established that influence of the EuF$_3$ impurity on a luminescence and photoconductivity spectra of the Se-As chalcogenide glass-like semiconductor system have been explained within of the charged intrinsic D$^-$ and D$^+$ defects model. By investigation of the luminescence spectra and the photocurrent spectral distribution of the Se$_{95}$As$_5$ and Se$_{95}$As$_5$ (EuF$_3$) x (x = 0.01-1 at. %) film samples have been shown that the EuF$_3$ impurity changes the concentration of charged states nonmonotonically. It was shown that the participation of EuF$_3$ in Se$_{95}$As$_5$ leads to an increase in the transparency of the material as a result of a shift in the absorption edge toward shorter wavelengths and photo enlightenment of the material was observed and large number of the impurity result in radiative recombination. The positions of E$_d$ and E$_a$ recombination levels with respect to the edge of the valence band, also the activation energy of dark conductivity and some parameters of the charged defects model, the effective correlation energy U$_{eff}$ (0.6 eV), the polaron relaxation energy W$^+$ (0.4 eV), W$^-$ (0.45 eV) have been estimated.

1. Introduction

Investigation results of the optical and electrical properties of chalcogenide glass-like semiconductors (CGS) make it possible to control the concentration of intrinsic charged defects by doping with an impurity capable of forming charged states [1, 2]. It was proved that during the luminescence of the CGS, the states associated with these defects participate. Based on the results of the study, the recombination centers are due not to impurities, but to free bonds. The luminescence intensity increases significantly when As and Te added to Se, which lead to an increase in the number of free bonds: As branches, and Te shortens the chains of Se [3]. In the case of very thin samples (< 15 μm), the maximum of the excitation spectra and the high-energy region shift with a change in the thickness of the samples, and according to Bishop and Mitchell [4], the process of surface recombination is responsible for the decay of the excitation spectrum in the high-energy region. Another explanation for the recession in the excitation spectrum in the high-energy region according to Street [5] is not due to surface recombination, but to the dependence of the quantum yield on the excitation energy.

The use of EuF$_3$ in the Se-As chalcogenide glass-like semiconductor system as an impurity is due to the fact that the impurity creates additional levels associated with 4f states, which allows controlling the concentration of intrinsic charged defects [6, 7]. Investigations of recording medium based on chalcogenide glass-like semiconductor materials show that under the influence of electromagnetic radiation (laser beam, electron beam, incoherent radiation from ordinary light sources), as a result of complex physicochemical processes occurring in the material, the medium changes its basic optical properties: the position of the optical absorption edge, transmittance,

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reflection, refraction. Usually, the edge of the absorption band in such irradiated materials as As-S, As-Se and Ge-As-Te shifts toward long waves, photodarkening occurs [8, 9].

2. Experimental and sample preparation

The synthesis of the Se-As system with the EuF_3 impurity was performed by alloying corresponding amounts of ultra-pure-grade chemical elements in evacuated quartz cells at temperatures above 1173 K in a rotating furnace followed by cooling under turned-off-furnace conditions. The impurity was introduced during the synthesis, its concentration was within 0.001 – 1 at. %. Film samples were fabricated by thermal evaporation in a vacuum chamber with a residual pressure of 10^{-5} Torr. onto glass substrates in the VUP-2 installation. The thickness of the investigated films is 3 μm. Al or ITO was used as a conductive surface for measuring the photocurrent. Samples for measuring photoconductivity were a ''sandwich'' structures. The luminescence spectra of film samples of the Se-As system with an EuF_3 impurity are recorded on a Cary Eclipse spectrofluorimeter. As a source of electromagnetic radiation, a xenon lamp (A = 1000 nm) have been used. To measure the electrical conductivity and photocurrent, the Keithley 6487 automated installation was used as the current amplifier. All measurements were taken at room temperature.

3. Results and discussion

Fig. 1 shows the luminescence spectra of film samples of the $Se_{95}As_5$ and $Se_{95}As_5(EuF_3)_x$ (x = 0.25-1 at.%) compositions. The film of the Se-As glass upon irradiation with a xenon lamp becomes transparent due to a shift in the absorption edge towards shorter wavelengths. As can be seen from the figure, the participation of EuF_3 in $Se_{95}As_5$ results in photo enlightenment of the investigated material. The direction of the shift of the absorption edge depends on the parameters of the radiation source and the structural state of the glassy material. Influencing the concentration of charged centers, EuF_3 at high doses promotes radiative recombination.
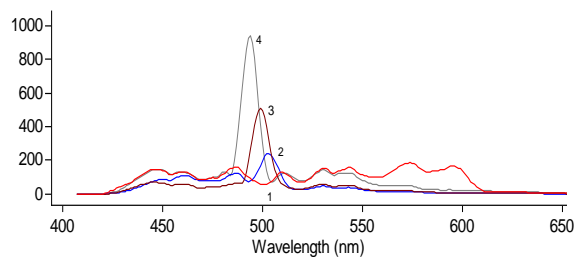

Fig.1. The luminescence spectra of a Se-As film with an EuF_3 impurity (λ_{ex}=255 nm, T=300K): 1-$Se_{95}As_5$, 2- $Se_{95}As_5(EuF_3)_{0.5}$, 3- $Se_{95}As_5(EuF_3)_{0.25}$, 4- $Se_{95}As_5(EuF_3)_1$

From the spectral distribution of the steady-state photocurrent (Fig. 2), we can see how the impurity weakens the features near the energies 1.6 and 1.8 eV at low concentrations, which indicates a decrease in the concentration of charged centers. At high impurity concentrations, there is a noticeable enhancement near 1.8 eV, contributing to an increase in D^- and a decrease in D^+ centers.
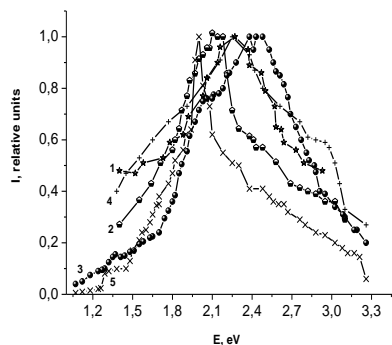
Fig. 2. The spectral distribution of the steady-state photocurrent of the composition
$Se_{95}As_5$ with the EuF_3 impurity (T = 300K): 1 - $Se_{95}As_5$, 2 - $Se_{95}As_5(EuF_3)_{0.01}$, 3 -
$Se_{95}As_5(EuF_3)_{0.05}$, 4 - $Se_{95}As_5(EuF_3)_{0.50}$, 5 - $Se_{95}As_5(EuF_3)_{1.00}$

The impurity EuF_3 strongly influences the value of dark conductivity (DC), photoconductivity (PC), and the spectral distribution of the photocurrent, as well as the concentration of intrinsic charged defects. Small concentrations of EuF_3 lead to a strong increase in both DC and PC (Fig. 3), which is explained by a decrease in the concentration of local states trapping free carriers, which is also associated with charged defects.
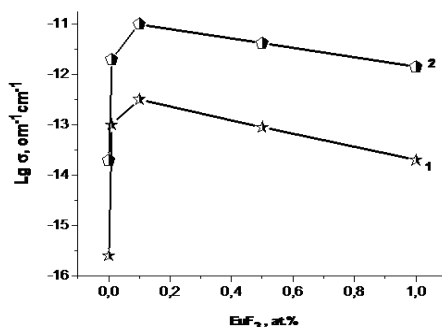

Fig. 3. Dependence of dark conductivity (curve 1) and photoconductivity (curve 2) of
$Se_{95}As_5$ on concentration of EuF_3 impurity: 1- in the dark, 2-under illumination

From the data on the photoconductivity, some parameters of the charged defects model were calculated, in particular, the value of the effective correlation energy U_{ef}, which is 0.6 eV and the energy of the polaron relaxation W^+ and W^-, 0.4 and 0.45 eV, respectively. From the data on the temperature dependence of the dark conductivity and photoconductivity, we have estimated the positions of the recombination levels E_d and E_a with respect to the edge of the valence band, and also the activation energy of the dark conductivity, i.e. position of the Fermi level (E_f) relative to the edge of the valence band (E_v), the results of which are presented in the table 1 below.

Table 1. Energy position of acceptor - and donor - like centers in $Se_{95}As_5$ with EuF_3 impurities

EuF_3, ат.%	E_A-E_V, eV	E_σ, eV	E_D-E_V, eV
0	0.6	0.98	1.18
0.01	0.62	0.96	1.2
0.05	0.62	0.96	1.2
0.1	0.64	0.95	1.2
0.5	0.64	0.96	1.2
1	0.66	0.97	1.22

4. Conclusions

Thin films production of Se-As system with EuF_3 impurity follows the creation of a new class of active medium - optoelectronic devices operating in the infrared region of the spectra. Investigations of the chalcogenide glasses structural features with an impurity of rare-earth elements trace the relationship between the materials composition and the centers nature responsible for radiative recombination and the luminescence quantum yield. The participation of the EuF_3 impurity in Se-As chalcogenide glass-like semiconductor system creates additional levels associated with the 4f states, which allows control of the intrinsic charged defects concentration. The luminescence spectra show that the films $Se_{95}As_5$ and $Se_{95}As_5(EuF_3)_x$ become transparent under the influence of electromagnetic radiation, and this is explained by the shift of the absorption edge toward shorter wavelengths. The impurity of EuF_3 in $Se_{95}As_5$ leads to photo enlightenment of the test material, and large amount of EuF_3 contribute to radiative recombination.

A similar phenomenon can also be observed in the spectral distribution of a steady-state photocurrent. The effect of the EuF_3 impurity in large amount occurs within the framework of the charged defects model. Investigation of the luminescence spectrum and the photocurrent spectral distribution of the of $Se_{95}As_5$ and $Se_{95}As_5(EuF_3)_x$ (x = 0.01-1 at.%) film samples shows that the EuF_3 impurity changes the concentration of charged states nonmonotonically. The impurity here is mainly manifested in the form of Eu^{3+} ions, as a result of which the concentration of D^- - centers increases, and the D^+ - centers decrease. From the data on photoconductivity, the parameters of the charged defects model, such as the value of the effective correlation energy U_{eff} (0.6 eV) and the energy of the polaron relaxation W^+ (0.4 eV), W^- (0.45 eV) are calculated.

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