

Absorption spectra and extrinsic photoconductivity of Cu and Cd doped GaSe single – crystal films

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GaSe single crystal films were doped during growth process with Cu or Cd atoms with concentration ranged between 0.05 and 0.50 at. %. Single crystal films (with thickness about 0.5 μm) were obtained by mechanical splitting of bulk single crystals. Impurity concentration was determined using atomic emission spectroscopy. Spectral dependences of absorption coefficient and photoconductivity were studied in the range 1.50 eV – 3.70 eV. It was experimentally established that the absorption spectra have an additional absorption band and its corresponding energy depends on the nature (Cu or Cd) and concentration of the doping atoms. Also, independently on the presence of the dopant, other two absorption bands in the IR region are present.

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1. Introduction

Stratified crystals (GaSe, GaS etc.) are strongly anisotropic semiconductors [1–5]. These compounds are characterized by a hexagonal symmetry within each layer and extremely weak bonding between layers [2]. These specific bonding structures (consisting in chalcogen/metal/metal/chalcogen packages) cause the easy cleavage perpendicular to c-axis for these compounds and is a convenient characteristics from the point of view of sample preparations (particularly for reflectivity and absorption measurements) and also for various modern technologies (optoelectronic devices, tandem solar cells structures, interferometric devices, etc.) [2–4].

Gallium selenide (GaSe) has been regarded as material with many attractive properties such large absorption coefficient, remarkable photoconductivity in vicinity of fundamental absorption edge, large band-gap, etc. Consequently, this compound offers an important number of applications in above mentioned domains [2, 6, 7].

In this paper, some optical and photoelectrical properties of Cu and Cd doped GaSe single-crystal films ($d = 0.5 \mu\text{m}$) are investigated. The obtained results are correlated with structural characteristics of the samples.

2. Experimental

Cu and Cd doped GaSe single-crystals were grown by Bridgmann method. Dopant concentration (ranged between 0.01 at. % and 0.50 at.%) has been determined using spectral emission analysis [6, 7]. The following spectral lines were used as analytical lines: $\lambda_1 = 3247.5 \text{ \AA}$ and $\lambda_2 = 3273.9 \text{ \AA}$ for Cu atoms, and $\lambda_1 = 3261.06 \text{ \AA}$ and $\lambda_2 = 3467.6 \text{ \AA}$ for Cd atoms.

The absorption and photoconductivity spectra were recorded using a spectrophotometric arrangement based on a monochromator equipped with diffraction gratings

(1200 mm^{-1} and 600 mm^{-1}) in the spectral range from 1.50 eV to 3.70 eV, the energy resolution of respective arrangement being about 2 meV [6–8].

The parallelepiped samples of ($0.05 \times 3 \times 6 \text{ mm}^3$) were used for photoconductivity measurements. Indium films ($d = 1.20 - 1.80 \mu\text{m}$), deposited by thermal evaporation under vacuum, were used as electrodes (ohmic contacts).

The absorption coefficient, α , was calculated from the following expression [8]:

$$T_\lambda = \frac{(1 - R_\lambda)^2 e^{-\alpha d}}{1 - R_\lambda^2 e^{-2\alpha d}}$$

where d represents the film thickness and R_λ and T_λ are the reflection and transmission coefficient at wavelength λ .

The experimental procedure has been described in details in our previous papers [6-8].

3. Results and discussion

The study on the spectral dependence of the reflection coefficient (for photons with energy $\hbar\omega \geq E_g$, where E_g is the band-gap energy) may provide useful information on the optical transitions between extremities of the valence and conduction bands in the different points [9-11].

It is known that the metallic atoms impurity of I, II and IV groups introduced in GaSe crystals determine a decrease of metallic vacancies and the excess of the respective atoms are localized between chalcogen layers of the stratified crystalline structure [5]. Because the cleavage planes contain the chalcogen atoms, the doping elements little influence the shape of the reflection spectra for photon energy $\hbar\omega \geq E_g$.

Fig. 1 illustrates typical reflection spectra for three studied sample: non-doped GaSe (curve 1) and doped with 0.50 at.% Cu (curve 2) and 0.50 at.% Cd (curve 3). It can be observed that Cu and Cd atoms do not modify the energy values in characteristic (critical) points (located at 3.35 eV and 4.90 eV, respectively), but the small details (E, F and especially B) are strongly reduced. The decrease of C and D bands in reflection spectra of Cu and Cd doped GaSe single-crystals films is probably due to the presence of the new chemical bonding of impurity atoms in the reorganized lattice structure.

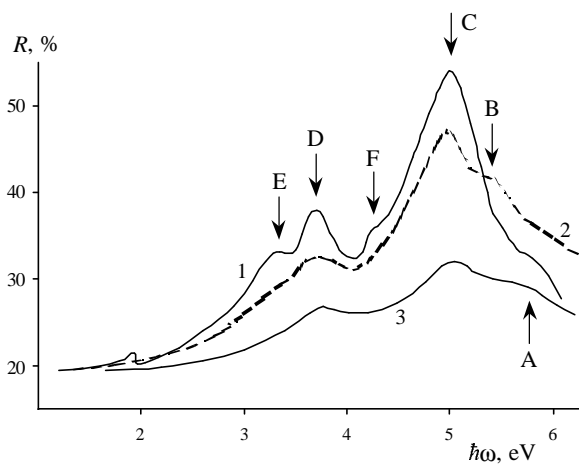


Fig. 1. Reflection spectra for GaSe single crystals: (1) – non-doped; (2) – at. 0.50 % Cu-doped; (3) – 0.50 at. % Cd-doped.

Fig. 2 shows the absorption spectra of Cu doped GaSe single crystal films (dopant concentration, C, ranged between 0.01 at. % and 0.50 at. %). It can be easily observed that the fundamental absorption edge for pure GaSe films and for the films doped with 0.01 at. % in practice coincide (Fig. 2a). For doping element concentration greater than 0.01 at. %, the slope of $\lg \alpha = f(\hbar\omega)$ curves decreases (Fig. 2b).

The spectral dependence of the absorption spectra for photon energy $\hbar\omega > 2$ eV, is influenced by formation of impurity acceptor levels (in forbidden band) situated near the top of valence band [6, 7, 12].

It is known that binding energy of excitons in GaSe crystals is about 25 meV [7, 12] (this value weakly differs from the thermal energy corresponding to room temperature) therefore, it can be supposed that fundamental absorption edge determined by photon absorption is associated with emission and absorption of the phonons (Fig. 2c).

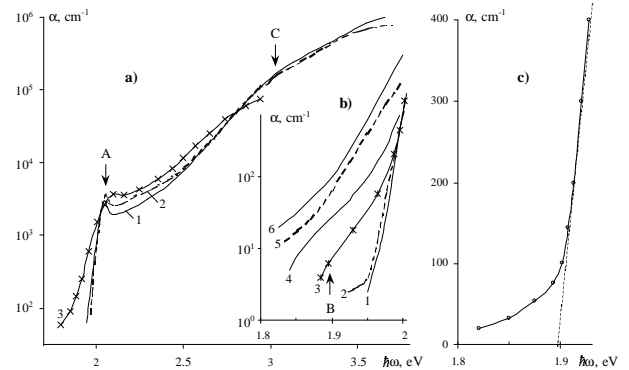


Fig. 2. a), b) Absorption spectra of Cu-doped GaSe crystals: 1 – 0.00 at. %; 2 – 0.01 at. %; 3 – 0.05 at. %; 4 – 0.10 at. %; 5 – 0.20 at. %; 6 – 0.50 at. % c) Spectral dependence of the absorption coefficient in the intrinsic domain for 0.50 at. % Cu-doped GaSe crystals.

It was experimentally established that spectral dependencies $\alpha = f(\hbar\omega)$, for non-doped GaSe and Cu doped (with C \cong 0.01 at. %) and Cd doped (with C < 0.10 at. %) may be described by an exponential law (Fig. 2.b and Fig. 3.b, respectively). At greater dopant concentrations, this behavior is not observed. The B shoulder located at 1.95 eV for GaSe crystals doped with 0.05 at. % Cd, permits to determine the position of the acceptor levels. They are positioned at 0.09 eV in respect of the top of valence band.

Fig. 2c illustrates the spectral dependence for Cu doped (0.50 at. %) GaSe crystals in the spectral range from 1.80 eV to 1.95 eV. By extrapolating the linear portion of the $\alpha = f(\hbar\omega)$ to $\alpha \rightarrow 0$, the energy corresponding to optical transitions between impurity levels and the bottom of the conduction band can be estimated. This energy value is equal with 1.89 eV. By taking into account that at room temperature ($T = 293$ K) the energy band-gap of GaSe crystals is 2.035 eV, the Cu impurity levels will be located at 0.14 eV above the top of the valence band.

The energy levels introduced in the forbidden band by Cu atoms determine an increase of the film photosensitivity. In the range $\hbar\omega \geq E_g$, the absorption coefficient slowly depends on the concentration of Cu atoms (Fig. 2). But in this spectral range, the photosensitivity of the films strongly decreases with increasing photon energy [12]. Consequently, the doping process weakly influences the generation-recombination processes of the excess carriers.

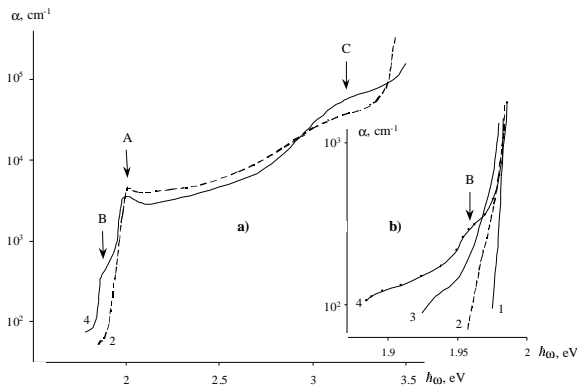


Fig. 3. a) Absorption spectra for Cd-doped GaSe samples; b) Absorption spectra in the extrinsic domain: 1 – 0.05 at. %; 2 – 0.10 at. %; 3 – 0.20 at. %; 4 – 0.50 at. %.

Fig. 4 shows the dependence of the photoconductivity, Σ/Σ_0 , of the GaSe films (Σ is the photoconductivity of the doped films and Σ_0 represents the photo-conductivity of the non-doped films) as a function of Cu dopant concentrations. The dependence was plotted for photon energy $\hbar\omega = 2.5$ eV (for this value of the photon energy, the spectral distribution of solar radiation has a maximum). It can be observed from Fig. 4 that an increase with 0.10 at. % of Cu concentration determines an increasing of 100 times of the photosensitivity.

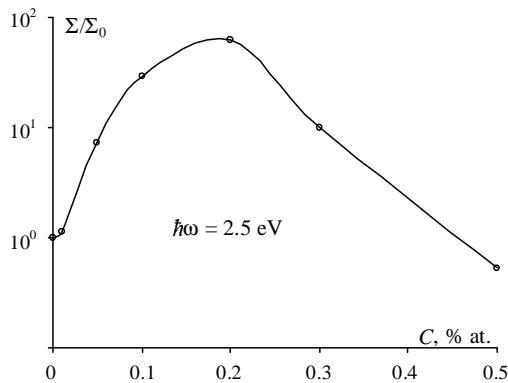


Fig. 4. Dependence of the relative photosensitivity of GaSe crystals as function of Cu concentration.

According to [1,12,13], the Cu atoms (with $C < 0.20$ at. %) introduced in GaSe crystals lead to a decrease of the structural defects concentration. Consequently, the concentration of levels with small recombination time also decreases. For greater values of Cu concentration (over 0.20 at. %), the excess atoms introduce in forbidden band new localized levels with small recombination time.

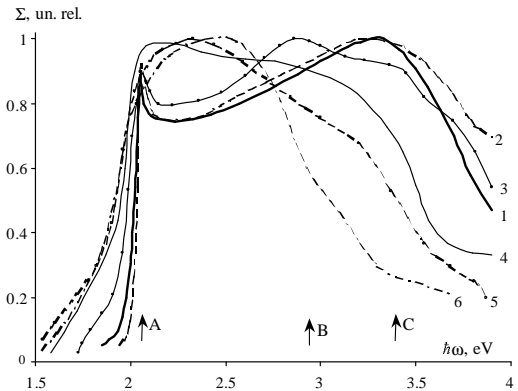


Fig. 5. Spectral distribution of the photosensitivity of Cu-doped GaSe crystal: 1 – 0.00 at. %; 2 – 0.01 at. %; 3 – 0.05 at. %; 4 – 0.10 at. %; 5 – 0.20 at. %; 6 – 0.50 at. %.

The spectral distributions of photo-sensitivity (photocurrent divided by number of incident photons) for Cu and Cd doped GaSe films are illustrated in Figs. 5 and 6. As it can be seen from these dependences, Cu doped GaSe films have larger domain of photo-sensitivity (from 1.90 eV to 4.00 eV), but in the case of Cd doping this domain is more limited (from 1.70 eV to 3.20 eV).

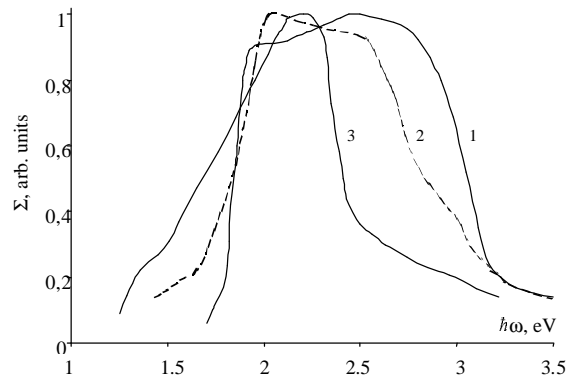


Fig. 6. a) Spectral distribution of the photosensitivity of Cd-doped GaSe crystals: 1 – 0.05 at. %; 2 – 0.10 at. %; 3 – 0.50 at. %. b) Dependence of the relative photosensitivity for 0.50 at. % Cd-doped GaSe crystals.

The peak localized at 2.06 eV, for Cu doped crystals ($C < 0.05$ at. %), is attributed to excitonic effects (Fig. 5). For Cd doped GaSe crystals the excitonic peaks in photoconductivity spectra are not observed.

4. Conclusions

Absorption and photoconductivity (in the spectral range from 1.50 eV to 3.70 eV) for Cu and Cd doped GaSe single crystals films have been investigated. It was established that the doping improve photosensitivity efficiency of studied films. This behavior is important for applications of respective films in semiconductor device technology (hetero-junction solar cells, photo-detectors, etc.).

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