OPTICAL AND PHOTOELECTRICAL CHARACTERISTICS OF GaSe (Cu)/OXIDE SEMICONDUCTOR HETEROJUNCTION

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1. Introduction

The $A^{III}B^{VI}$ layered semiconductors are perspective materials for photoelectrical and luminescent device fabrication, for use in visible and near IR spectral region [1, 2]. GaSe and InSe semiconductors, having the bandgap equal to 2.0 eV and 1.2 eV respectively, are most often used for device fabrication [3, 4].

The applicability of GaSe crystals as a heterojunction component is limited by their low electrical conductivity (the hole concentration is ~ 10^{13} cm^{-3} at 293 K) [5]. Cu (0.10 at %) doping of GaSe crystals causes the hole conductivity increase by more than 5 orders of magnitude and its value is ~ $(8\div9)\cdot10^{-2}$ $\Omega^{-1}cm^{-1}$ [6]. Cu impurity atoms form two acceptor levels in GaSe positioned at 0.12 eV and 0.038 eV [1], which enlarge the applicability domain for these materials.

The SnO_2, In_2O_3 (SnO_2), ZnO and others [7, 8] are used as optically transparent semiconductors in the visible and near IR spectral region and as an element of heterojunction based optoelectronic devices.

This paper presents the investigation of the photoelectrical properties of GaSe (0.10 at % Cu)/ ZnO, In_2O_3, SnO_2, Bi_2O_3, and Cu_2O oxide semiconductor heterojunction.

2. Experimental details

The p-GaSe single crystals have been grown by Bridgman method. Doping with 0.10 at % Cu was carried out during compound synthesis. The acceptor concentration has been measured in the 100÷300 K temperature range. The intensity of the magnetic field was 1 T and it has been applied perpendicular to C_6 axis. Thermally evaporated ($3\cdot10^{-5}$ Pa vacuum), In thin films have been used as contacts.

Heterojunction manufacturing: as-cleaved surface of p-GaSe and p-GaSe (Cu) monocrystalline films (5÷15 μm thick) have been covered by a thin (100÷180 nm) metal layer (Zn, In, Sn, Bi, and Cu) by vacuum ($3\cdot10^{-5}$ Pa) thermal evaporation. Similar layers have been deposited onto glass substrates. The oxidation of the metal layer has been done in air at 700÷710 K for 8÷10 min. The oxidation level and optical transmittance has been studied by use of He-Ne laser radiation (λ=0.6328 μm).

The I-V dependences have been measured in DC current regime by commonly used, two-electrode method. The photocurrent spectral distributions have been measured with a diffraction grating-based monochromator (600 mm^{-1}). The modulated light beam method has been used. It generates nonequilibrium charge carriers in GaSe (Cu) layer at the heterojunction interface, and the illumination was through transparent metal-oxide layer. The modulation frequency was 37 Hz. The photocurrent measurements have been carried out at 78 K and 293 K.

3. Experimental results

The majority charge carriers temperature dependence for undoped (curve 1) and 0.1 at % Cu doped p-GaSe (curve 2) is given in Fig. 1. As one can see, an acceptor level is present in undoped p-GaSe; its activation energy ΔE_a is given by

$$p(T) = p_0 e^{-\frac{\Delta E_a}{2KT}}, \qquad (1)$$

where K ia the Boltzmann constant, p_0 is the holes concentration at 0 K, ΔE_a= 0.4 eV.

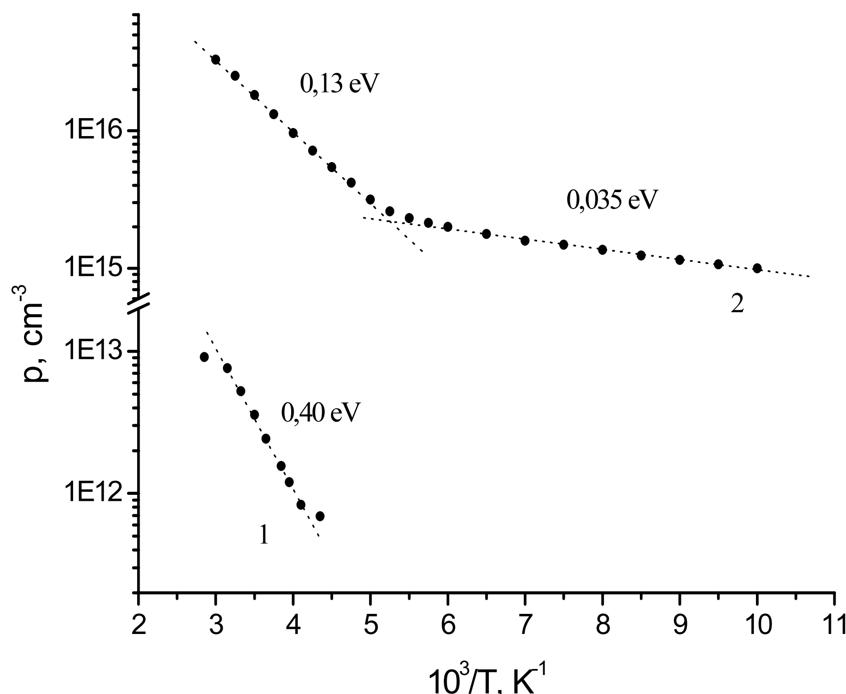

Figure 1. The majority charge carriers temperature dependence for undoped (curve 1) and 0.1 at % Cu doped p-GaSe (curve 2).

The 0.1 at % Cu doping of p-GaSe results in formation of two acceptor levels positioned at ΔE_{a1} = 0.130 eV and ΔE_{a2} = 0.035 eV. As it follows from curve 2 (Fig. 1), the acceptor concentration has been determined as N_{a1} and N_{a2} being equal to $2.2\cdot10^{16}$ cm^{-3} and $4\cdot10^{15}$ cm^{-3}, respectively, at 293 K. The presence of a shallow level ΔE_{a2} (ΔE_{a2} = 0.035 eV) determines the high electrical conductivity at 293 K ($0.75\cdot10^{-1}$ Ω^{-1}cm^{-1}).

The results of the investigation of the I-V (current-voltage) dependences for (In_2O_3+0.2%SnO_2)/p-GaSe (0.10 at % Cu), In_2O_3/p-GaSe (0.10 at % Cu), SnO_2/p-GaSe (0.10 at % Cu), and Cu_2O/p-GaSe (0.10 at % Cu) structures at 293 K are given in Fig. 2. At forward biases (U≤0.3 V) curves I-V can be fitted by [9]

$$I = I_0 \exp\left(\frac{eU}{nKT} - 1\right), \qquad (2)$$

where I_0 is the saturation current density, e is the electron charge, K is the Boltzmann constant. The diode quality factor n varies from 1.23 for (In_2O_3+0.2%SnO_2)/p-GaSe (0.10 at % Cu) heterojunction up to 2.5 for Cu_2O/p-GaSe (0.10 at % Cu) heterojunction.

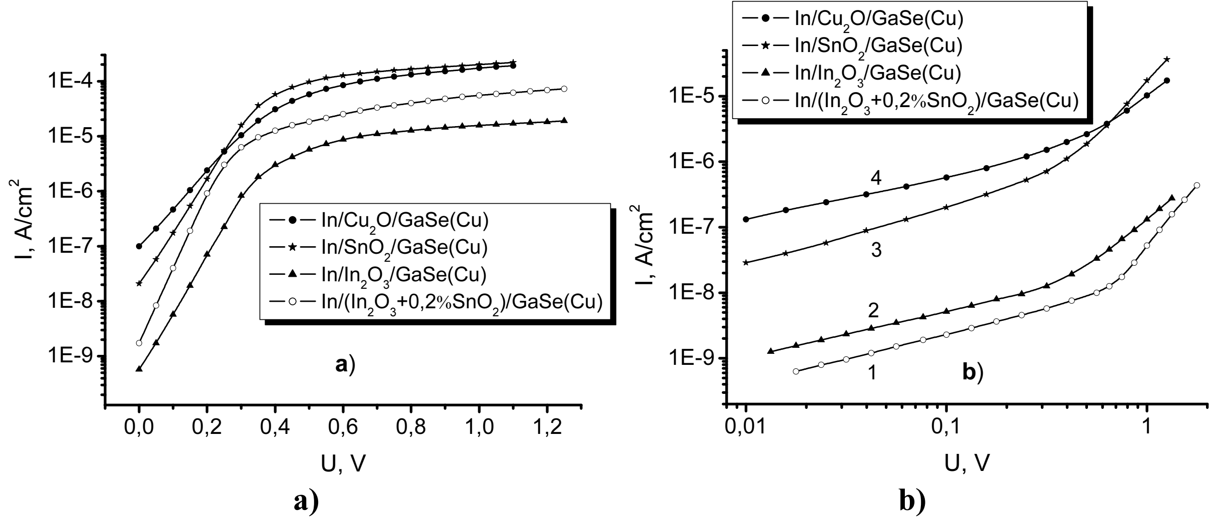

Figure 2. The current voltage dependences for (In_2O_3+0.2%SnO_2)/p-GaSe (0.10 at % Cu), In_2O_3/p-GaSe (0.10 at % Cu), SnO_2/p-GaSe (0.10 at % Cu), and Cu_2O/p-GaSe (0.10 at % Cu) structures at 293 K at forward biases (a) and reverse biases (b).

The diode quality factor is larger than unity if along with the diffusion current I_d given by

$$I_d = \left(\frac{eD_p p_{n0}}{L_p} + \frac{eD_n n_{p0}}{L_n} \right) \exp\left(\frac{eU}{KT} - 1 \right), \tag{3}$$

a considerable influence on the total current value belongs to recombination current [10] given by

$$I_r = A \exp\left(\frac{eU}{2KT} - 1 \right), \tag{4}$$

where A is the temperature independent parameter.

The heterojunction total current can be written as [11]

$$I = I_d + I_r . \tag{5}$$

The charge carrier recombination takes place through low lifetime interface states in the space charge region [9].

As it follows from the analysis of the results presented in Fig. 2, the density of recombination states is lower for ITO based heterojunction, for which n=1.23. The defects along with heterojunction recombination states are influencing the ideality factor n value (leakage current). These two mechanisms predominate in Cu_2O/p-GaSe (Cu). So, we can admit that during the thermal oxidation process a Cu enriched GaSe defect layer is formed at the interface of heterojunction. Cu atoms at exterior surface of Se-Ga-Ga-Se stratified packing form new valence bonds. Thus, a considerable density of surface (interface) states is formed.

Dependences I-V at reverse bases of ITO/p-GaSe (Cu) (curve 1), In_2O_3/p-GaSe (Cu) (curve 2), SnO_2/p-GaSe (Cu) (curve 3), and Cu_2O/p-GaSe (Cu) (curve 4) are given in Fig. 2b. As it follows from the analysis of curves 1-4 (Fig. 2b), the reverse current depends on voltage as a power function

$$I = CU^m \tag{6}$$

for the entire voltage range, where C is voltage independent constant.

Such a I-V dependence is due to space charge-limited current. For U<0.5 V the m factor varies from 0.65 for Cu_2O/p-GaSe (Cu) heterojunction to 0.8 for In_2O_3/p-GaSe (Cu) and

ITO/p-GaSe (Cu). For voltage U>0.7 V the power factor is bigger than unity (2.2 for Cu_2O/p-GaSe (Cu) and 3.3 for ITO/p-GaSe (Cu)). To be mentioned that the current flow through the space charge region considers m=2 as well as m=3 [12].

The typical dependence of the short-circuit current I_{sc} and open circuit voltage U_{oc} on the illumination F of the sample for ZnO/GaSe(Cu) structures is presented in Fig. 3, curves 1 and 2, respectively. As one can see from this figure, the current I_{sc} depends linearly on F for a wide range of illumination value (more than 3 orders of magnitude). The open circuit voltage depends on illumination F as

$$U_{oc} \sim \ln F \,. \tag{7}$$

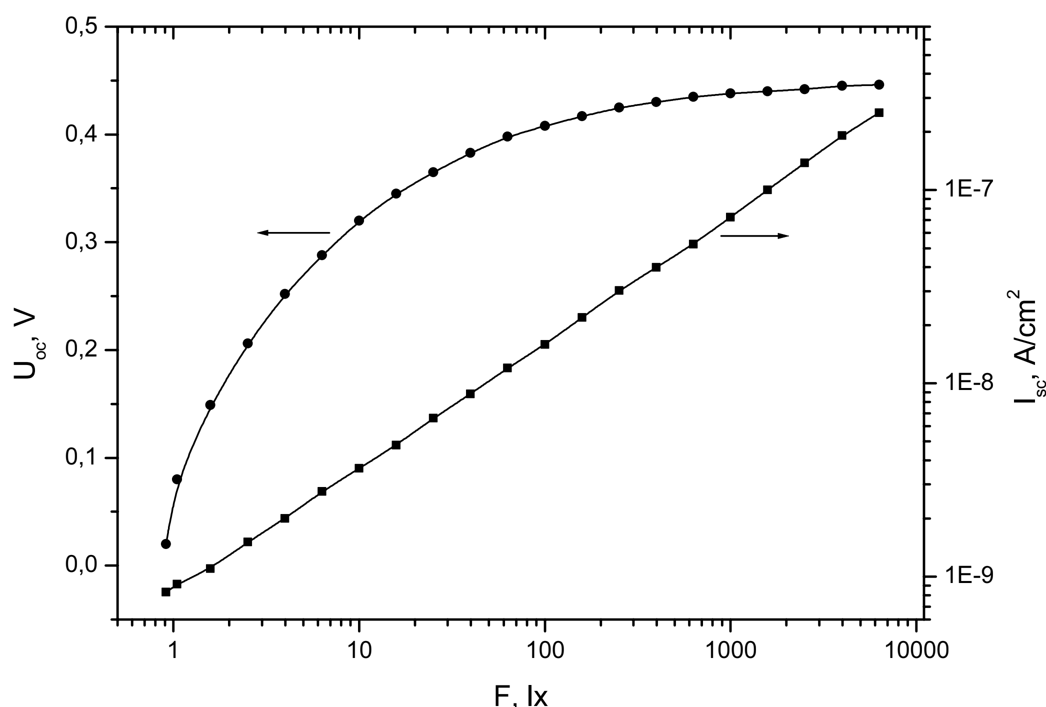

Figure 3. Typical dependence of the short circuit current I_{sc} and open circuit voltage U_{oc} on the sample illumination F for ZnO/GaSe(Cu) structures.

The oxide semiconductor (ITO, ZnO, Bi_2O_3, SnO_2, and Cu_2O)/p-GaSe (Cu) are photo-sensitive in the visible spectral region. The current to incident beam energy ratio is presented in Fig. 4a for ITO/GaSe (Cu) heterojunction at 293 K. A continuos current increase is observed in the 2.0÷3.2 eV energy interval. It points at a relatively low surface (interface) state concentration in the GaSe layer next to the heterojunction interface. In this spectral interval the absorption coefficient increases from 10^3 cm^{-1} to ~ 10^5 cm^{-1} [13]. The average GaSe thickness, in which the nonequilibrium charge carriers are generated, is about 0.1÷10 μm. The density of low lifetime states is considered to be low for above mentioned thickness range. Along with band to band transitions in the center of Brillouin zone, the transitions from the second valence subband to the conduction band are taking place for photon energies $\hbar\omega$>3.2 eV. These electronic transitions are determined by absorption coefficients $\alpha \gg 10^5$ cm^{-1} and occur in a GaSe layer having thickness d<<0.1 μm. Considering that the photocurrent through the heterojunction decreases sharply with photon energy increase, one can assume that low lifetime states are formed at the interface of the heterojunction for the above stated GaSe (Cu) layer thickness.

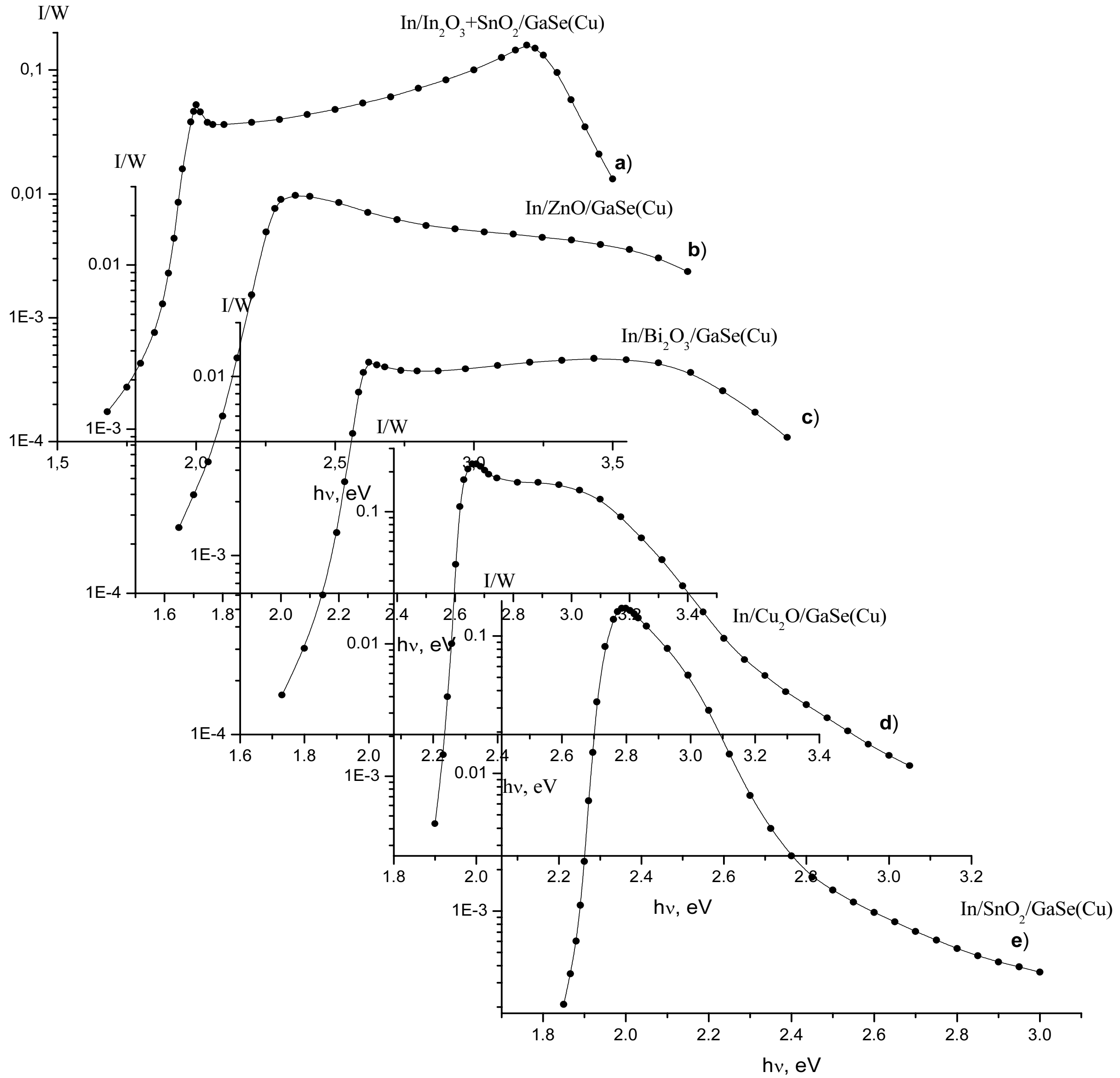

Figure 4. The photocurrent to incident beam energy ratio spectral distribution for (ITO, ZnO, Bi_2O_3, SnO_2 and Cu_2O)/p-GaSe (Cu) heterojunctions at 293K.

As one can see in Fig. 4a, the photosensitivity edge of ITO/GaSe(Cu) heterojunctions is localized in the impurity photoconductivity (ħω~1,65 eV) domain. In the 1.65÷1.8 eV spectral region, the absorption band determined by Cu acceptor atoms is localized [13]. An exponential increase of the quantum efficiency up to ~ 2.0 eV is determined by the absorption coefficient increase. The shape of the I/W=f(ħω) dependence demonstrates the high quality of the ITO/p-GaSe (Cu) heterojunction and, in particular, indicates a lowered concentration of the interface states.

A sharp increase of the quantum efficiency in the impurity absorption region is found for ZnO/p-GaSe (Cu) (Fig. 4b) and Bi_2O_3/p-GaSe (Cu) (Fig. 4c). Analogous to the ITO/p-GaSe (Cu), this increase results in a maximum at about 2.0 eV corresponding to the direct optical transition in the center of Brillouin zone (Γ point). The monotonic decrease of the quantum efficiency with energy increase can serve an indicator that a gradient of surface

states exists in the Bi_2O_3/p-GaSe (Cu) and ZnO/p-GaSe (Cu) heterojunction interface. Their concentration decreases in the GaSe crystal volume. This heterojunction has a wide photosensitivity range and covers the visible and near UV spectral range. The high recombination rate states density is larger in the GaSe layer at the Cu_2O/p-GaSe (Cu) heterojunction and especially in SnO_2/p-GaSe (Cu) (Fig. 4d and Fig. 4e). The nonequilibrium charge carrier photogeneration in the impurity absorption is missing.

So, to conclude, as a result of high temperature Cu_2O and SnO_2 layer deposition, the Cu and Sn atom diffusion takes place in GaSe substrate. As a result, localized states are formed in the GaSe, at the interface. These states along with attenuation of the photogeneration of nonequilibrium charge carriers create low lifetime surface states, which cause a high recombination rate of the charge carriers diffused to the junction.

4. Conclusions

– The Cu impurity atoms create two acceptor levels in GaSe, positioned energetically at 0.038 eV and 0.130 eV.
– The current through the oxide semiconductor (ZnO, SnO_2, ITO, Cu_2O)/p-GaSe (0.10 at % Cu) heterojunction is determined by the diffusion current of the minority charge carriers and by the interface states recombination processes.
– The density of the low lifetime surface states is low in ITO/p-GaSe(Cu) heterojunctions and it increases in the following order of oxide semiconductors ZnO, SnO_2, Bi_2O_3, and Cu_2O.

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