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RADIATION HARDNESS OF $CuInSe_2$

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$CuInSe_2$ single crystalline specimen was grown from a near stoichiometric mixture of pure elements and then was ion implanted with $3 \cdot 10^{14}$, 10^{15}, $3 \cdot 10^{15}$, and 10^{16} cm^{-2} fluences of 5 keV H^+ at room temperature. The exceptionally high tolerance to radiation was observed. It was explained by the process of effective converting of radiative defects, generating during implantation, into charged defect complexes, which were present in material before implantation.

INTRODUCTION

$CuInSe_2$ is a semiconductor compound, which attracts great interest because of its application in the absorber layer of solar cells currently leading in terms of the conversion efficiency (19%) and stability amongst thin-film devices. One of the strong features of the material and $CuInSe_2$ – based photovoltaic devices is the exceptionally high tolerance to any radiation. Measurements of the solar cells parameters after irradiation demonstrate very low sensitivity to high-energy electron and proton irradiation [1]. Raman studies of $CuInSe_2$ single crystals irradiated at room by various ions showed a very high tolerance of the lattice for radiation damage and explained it by the presence of an efficient healing mechanism allowing the majority of the Frenkel-pairs to recombine during or shortly after the implantation [2].

Photoluminescence (PL) studies of $CuInSe_2$ single crystals with a broad and asymmetric peak in the PL spectrum measured before the irradiation and after ion implantation did not reveal any new band within the spectral range from 800 to 1700 nm [3]. A reduction in the peak intensity observed after irradiation was attributed to an increase in the concentration of non-radiative traps. No regorous analysis revealing physical mechanisms of influence of the radiation damage accumulation on the electronic properties of $CuInSe_2$, as will as of the changes in the PL spectra due to ion implantation has been reported yet.

The elemental composition of the $CuInSe_2$-based absorber layer, used in high-performance solar cells, is shifted towards indium excess. Such a shift dramatically increases the concentration of intrinsic defects in the semiconductor making it highly dopped and compensated. In this paper we present an attempt of detailed analysis of the changes in the PL spectra, in $CuInSe_2$ single crystals due to implantation of hydrogen using a theory developed by Levanyuk A.P. and Osipov A.L. for highly dopped and compensated semiconductors [4].

EXPERIMENTAL DETAILS

$CuInSe_2$ single crystalline ingot was grown from a near stoichiometric mixture of pure elements using the vertical Bridgman technique. Polished, etched and annealed samples were ion implanted to $3 \cdot 10^{14}$, 10^{15}, $3 \cdot 10^{15}$ and 10^{16} cm^{-2} fluences of 5 keV H^+ at room temperature. Then the sample was studied by photoluminescence at temperatures from 20K to 140K achieved by cooling the sample by a closed cycle refrigerator. The 514 nm line of a 100 mW Ar^+ laser was used for excitation. The emission was dispersed using a 1 m single-grating monochromator with 17 Å/mm dispersion and detected with a liquid-nitrogen cooled Ge pin diode.

RESULTS AND DISCUSSION

Two asymmetric bands at about 0.93 eV (BI-band) and 0.96 eV (BT-band) governed the obtained PL spectra (Fig. 1). In order to identify the origin of these bands, temperature and excitation intensity dependencies were measured. Analysis of these dependencies suggested that the dominant band at 0.96 eV originates from a band-to-tail recombination mechanism and the low-energy band from band to impurity recombination mechanism. Spatial potential fluctuations, generated by a large number of randomly distributed charged defects, create the band tails. In p-type semiconductors at low temperature, holes are captured at deep states in the valence band tail, which act like acceptor levels. Because of potential fluctuations, we cannot talk about single acceptor level but about the distribution of acceptor states. The amplitude of potential fluctuations strongly depends on the level of doping and compensation determining the spectral position of the bands in the PL spectra and the j-shift magnitude, high-energy shift of the PL peak at increase of the excitation intensity J by a factor of 10. The higher the potential fluctuation amplitude the greater the j-shift.

According to the theory of heavily doped semiconductors with spatially varying potential fluctuations, the radiative recombination can arise from three different

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channels. Firstly, it can comprise a free electron and a hole that is localised in the valence band tail (BT-band). Secondly, it can involve a free electron and a free hole (BB-band). Thirdly, it can occur through the acceptor state (BI-band) that is deep enough not to overlap with the valence band tail. The behaviour of our bands is in good compliance with proposed model and we believe that our bands originate from BT and BI recombination mechanisms. This theory is described in more detail in [4] and [5]. The BI-band can be observed if $\gamma < I_a$, where γ is the mean-square fluctuation of the potential energy of a hole and I_a is the ionisation energy of the acceptor state. The theoretical PL spectrum of this band is defined by the following expression:

$$I(h\nu) = h\nu \iint W(E_e, E_h)\rho_c(E_e)f_e(E_e) \times \times \rho_a(E_h)q_a(E_h)\delta(E_e - E_h - h\nu)dE_e dE_h, \quad (1)$$

where $W(E_e, E_h)$ is the recombination probability of a free electron and a localised hole with energies E_e and E_h, respectively, ρ_c is the electron density of states in the conduction band, f_e is the Fermi function, ρ_a is the hole density of states, and q_a is the filling probability of the hole states. The theoretical PL spectrum of BT-band is defined by the following expression:

$$I_{BT}(h\nu) \propto \iint W_{BT}(E_e, E_h)\rho_c(E_e)f_e(E_e) \times \times \rho_v(E_h)q_h(E_h)\delta(E_e - E_h - h\nu)dE_e dE_h, \quad (2)$$

where ρ_υ – density of states function for the localised holes and q_h is distribution function for the localised holes. The final shape of the PL band depends crucially on the actual shape of the density of states function for the localised holes. Therefore it is difficult to find any analytical function for the BT- and BI-band shapes. The low-energy side of BT-band $I_{LE}(h\nu) \propto \exp[-(E_g - h\nu)/\gamma]$ is defined by the ρ_υ function $\rho_\upsilon(\varepsilon) = \rho_0\exp(-\varepsilon/\gamma)$ while the high-energy side has much more complex nature. The shape of the low-energy side of the BT-band does not depend on temperature and excitation intensity. The intensity on the high-energy side I_{HE} of the BT-band has several common properties for all types of the density of states function for localised holes. At low temperatures ($kT < \gamma$) the curvature of $I_{HE}(h\nu)$ does not depend on temperature but at higher temperatures ($kT > \gamma$) its slope decreases linearly with temperature and the BT-band becomes more symmetrical. The easiest way to identify the BT-band is to find its maximum energy $h\nu_{max}$ and study its temperature and excitation intensity dependencies. The $h\nu_{max}$ for BT- band at low temperatures may be expressed as:

$$h\nu_{max} = h\nu^0_{max} - kT\ln N_V/(p + \theta n), \quad (3)$$

N_V – effective density of states in the valence band, n, p – concentration of free electrons and holes, respectively, θ is the ratio of electron and hole capture probabilities by localised state. Thus, the BT-band can be treated as a recombination of a free electron from Fermi level F_n with a hole, captured by the localised state with depth ε_1. As it can be seen from Eq. (3) the $h\nu_{max}$ shifts towards higher energies with increasing n and p, i. e. with excitation intensity. At higher temperatures, when $kT > kT_1 = \gamma[\ln N_\upsilon/(p + n\theta)]^{-1/2}$ $h\nu_{max}$ shifts towards higher energies until above some characteristic temperature T_2 it will follow the temperature dependence of the energy gap.

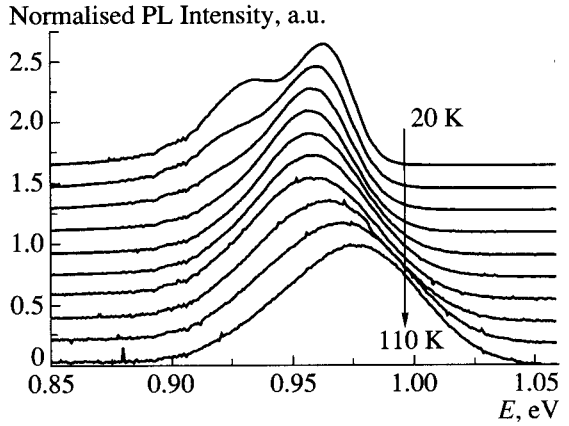

Fig. 1. Normalised PL spectra of implanted (implantation dose 10^{15} cm^{-2}) $CuInSe_2$ crystal at various temperatures. (Laser power 15 mW).

A typical shape of the PL spectrum in heavily doped crystal is asymmetric Fig.1. It has a steeper decline at high-energy side and a nearly temperature independent shape at the low-energy side. All the experimental spectra were fitted with the empirical asymmetric double sigmoidal function

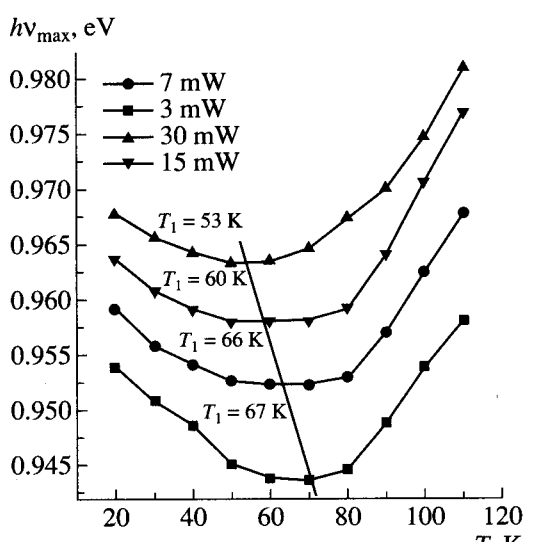

Fig. 2. Temperature dependence of BT peak position in implanted (dose 10^{15} cm^{-2}) $CuInSe_2$ crystal measured for various excitation intensities.

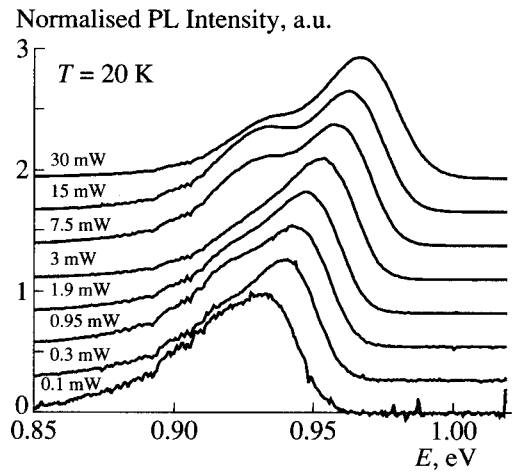

Fig. 3. Normalised PL spectra of implanted (dose 10^{15} cm^{-2}) $CuInSe_2$ at various exitation poweres.

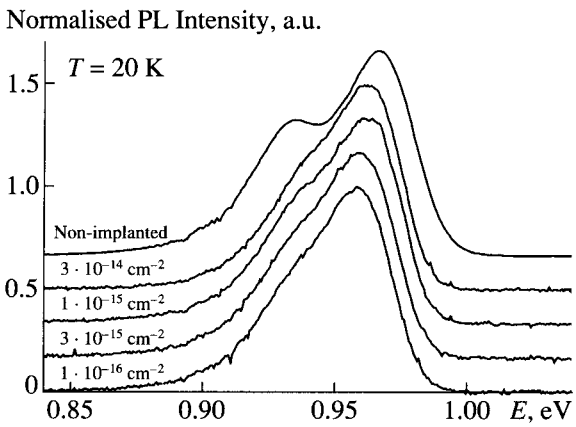

Fig. 4. The dependence of the spectra on implantation dose. (Laser power 30 mW).

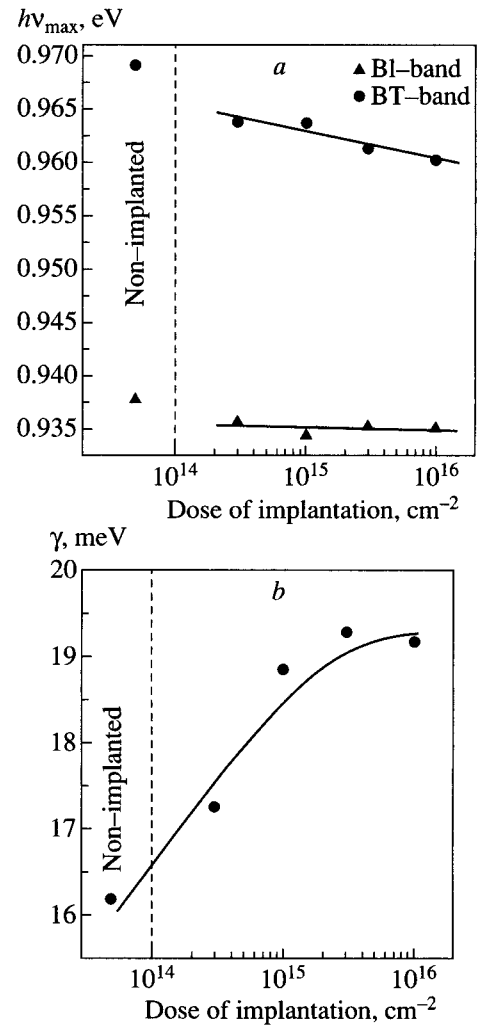

Fig. 5. (*a*) The dependence of peak position of BI- and BT-bands on implantation dose. (*b*) The dependence of average amplitude of the potential fluctuations on implantation dose.

$$I(h\nu) = A(1/(1 + \exp[-(h\nu - E_1)/W_1])) \times$$
$$\times (1 - 1/(1 + \exp[-(h\nu - E_1)/W_2])).$$

Here A, E_1, E_2, W_1, and W_2 are the experimental parameters. Parameters E_1 and W_1 represent the shape of the low-energy side of the PL bands while E_2 and W_2 belong to the high-energy side. This fitting function is purely empirical and was chosen from several candidates because it always seemed to give the best result. According to the theory, the nearly exponential low-energy side of the BT-band indicates that the hole distribution function in the forbidden gap $\rho_v(E_h)$ has also an exponential shape.

The temperature dependence of the spectrum follows theoretical predictions (Fig. 1). At low temperatures, the peak position energies of the spectrum decrease with increasing temperature, at some temperature T_1, the BT-band shifts towards higher energy again. The BI-band vanishes before reaching to the peak position energy minimum. The depth of the vale and its position depend on the carriers' concentrations, i.e. on the excitation power. Smaller carrier concentrations correspond to steeper declines (Fig. 2).

The behaviour of $h\nu_{max}$ can be explained as follows: the transition BT has a maximum probability at temperature T_1 after which the thermal activation process starts to dominate and thermalise localised holes to valence band. Accordingly, the PL band maximum shifts towards higher energies. PL spectra were also taken with various excitation intensities and both bands show a blue shift (j-shift) with increase in the excitation intensity (Fig. 3). This shift was generated by altering the laser power and was 7 meV per decade for BI-band and 16 meV per decade for BT-band. Due to its visible blue shift with excitation intensity, the BT-band is often thought to be a donor-acceptor pair (DAP) band. But the magnitude of the observed *j*-shift exceeds the typical energy shift for DAP band. The *j*-shift of the BT-band, according to Eq.(3), is determined by increasing the denominator (p +

$+ n\theta$), by excitation intensity J. The red shift of the position of both peak with implantation dose is shown in Fig. 4. As can be seen, the observed shift is larger for BT-band. This shift is associated with an increase in the mean-square amplitude of the spatial potential fluctuations γ induced by the implantation. The dependence of γ on the implantation dose is shown in Fig. 5*b*. The curve reveals a linear increse at lower doses and a saturation behaviour at higher doses. This saturation can be associated with an increase in the healing rate due to high concentration of defect in the lattice or/and with passivation effect of hydrogen accumulated in the near surface layer.

CONCLUSIONS

The fact that no new PL have been observed in the PL spectra after proton implantation from 0.8 to 1.6 μm suggests that the radiative defects, generated during the implantation, were efficiently converted into charged defect complexes, which were already present in the material before the implantation. Accumulation of such defect complexes was shown to gradually increase the mean-square amplitude of potential fluctuations.

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