EFFECTS OF 6 MeV ELECTRON IRRADIATION ON PHOTOLUMINESCENCE OF HIGH-QUALITY $CuInSe_2$ SINGLE CRYSTALS

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ABSTRACT: High-quality single crystals of $CuInSe_2$ with near-stoichiometric elemental compositions, grown by the Bridgman method, were irradiated by 6 MeV electrons with doses from $5\cdot10^{15}$ to 10^{18} cm^{-2}. The crystals were studied before and after irradiation using photoluminescence (PL) at a temperature of 4.2 K. The PL spectra, measured before the irradiation, reveal a number of sharp and well resolved lines associated with free- and bound-excitons. The lower energy region of the spectra also reveals broader peaks related to band-impurity, donor-acceptor pair recombination and their phonon replicas. The irradiation resulted in a reduction of the intensity of the free- and bound-excitons observed in the non-implanted material. Such a reduction is observed for quite low doses of $5\cdot10^{15}$ cm^{-2}. Irradiation also induces new sharp PL lines W_1 at 1.03, W_2 at 1.01 eV and W_3 eV at 0.99 eV below the free-exciton emission. Two deeper broad bands, associated earlier with the acceptor-type defects, interstitial selenium (Se_i) and copper on indium site (Cu_{In}), have become more intense suggesting an increase in the concentration of these defects due to irradiation.
Keywords: $CuInSe_2$, Radiation Damage, Photoluminescence

1 INTRODUCTION

$CuInSe_2$ attracts great interest because of its application in the absorber layer of thin-film solar cells. Currently $CuInSe_2$-based solar cells with the structure $ZnO/CdS/Cu(InGa)Se_2/Mo$ hold the world record efficiency for solar energy conversion (about 20%) by a thin film device [1]. Several internationally based companies have started the manufacture of $CuInSe_2$-based solar power modules. One of the very promising fields of their application is spacecraft power generators. In the harsh environment of outer-space solar cells are intensely bombarded with high-energy electrons and protons in the solar wind as well as heavier ions in cosmic rays. Currently only single crystalline solar cells are in use for this purpose due to their high efficiency but in the near future the $CuInSe_2$-based technologies may offer a better solution because of their superiority in cost, weight, stability and radiation hardness. Measurements of solar cells parameters after high-energy electron radiation demonstrated almost total insensitivity of the $CuInSe_2$-based cells to high-energy electrons [2].

The radiation hardness issue is linked with a general understanding of the defect physics in $CuInSe_2$. The number of studies concerned with the radiation hardness problem in $CuInSe_2$ is significantly lower than that for Si - or binary compound-based solar cells resulting in the low level of understanding of $CuInSe_2$ physics in general and of damage creation/repair mechanisms in particular. This level does not match the importance of the material.

High-energy electrons are convenient particles to study the nature of radiation-induced defects because electrons do not dope semiconductors. Also they generate spatially uniform populations of defects without gradients which helps to clarify the defect nature.

Optical spectroscopy methods have been used successfully to identify defects in semiconductors by analysing excitonic features in spectra from the highest quality samples. Excitons can provide accurate information on the defect nature. However very few reports revealing resolved excitonic features can be found in the literature on $CuInSe_2$ [3, 4, 5] because of the difficulty of growth of high-quality material.

In this paper we report effects of high-energy electron irradiation on PL spectra in particular on free- and bound-excitons as well as free-to-bound bands in high-quality $CuInSe_2$ single crystals, and discuss the nature of the defects generated by such irradiation.

2 EXPERIMENTAL DETAILS

High-quality $CuInSe_2$ single crystals with EDX measured elemental composition of Cu:25.2; In:24.7; Se:50.1 at. % (Cu/In = 1.02) were grown using the vertical Bridgman method. These samples were irradiated by 6 MeV electrons, with doses from $5\cdot10^{15}$ to 10^{18} cm^{-2} on a linear electron accelerator in Minsk, Belarus, with an electron current density set at about $2\cdot10^{12}$ $cm^{-2}s^{-1}$ and a temperature held below 50°C using a water-cooled stage.

The samples were analysed using photoluminescence (PL) at 4.2 K before and after irradiation. The measurements were carried out employing liquid helium-bath cryostats with optical windows. More experimental details can be found elsewhere [4,5]. The 514 nm line of a 100 mW Ar^+ laser was used for excitation. Neutral density filters were used for attenuation of the excitation intensity. A lock-in-amplifier with mechanical chopping at a frequency of about 35Hz was used for signal recovery.

3 RESULTS AND DISCUSSION

The PL spectrum, taken before irradiation, is shown in Figure 1(a). In the near-band region it exhibits a number of high-energy sharp lines, assigned earlier to excitons [3, 4, 5]. The full width at half maximum (FWHM) of the excitonic lines is about 1meV for bound- and 1.5 meV for free-excitons. At such width excitonic features can be used as very sensitive tools for studying changes in the defect balance of the materials under modifications of this material and in particular changes after high-energy electron irradiation.

At lower energies the spectrum shown in Figure 1(a) exhibits broader bands, zero-phonon P (at ~0.972 eV) and K (at ~0.902 eV) bands, associated with free-to-bound recombination mechanisms, and their longitudinal phonon (LO ~ 29 meV) replicas P_{1LO} (at ~0.943 eV), K_{1LO}(at ~0.873 eV), K_{2LO}(at ~0.844 eV), K_{3LO}(at ~0.815 eV) [5]. The P band was associated with free-to-bound recombination of electrons from the conduction band to an acceptor level (e, A) assigned to the acceptor-type anti-site defect copper on indium site (Cu_{In}) [5]. Such a defect generates an intr-gap level at about 77 meV from the valence band. The K line was also associated with free-to-bound recombination of electrons from the conduction band to an acceptor level (e, A) with an ionisation energy of about 147 meV. In this case the acceptor has been assigned to interstitial selenium (Se_i) [5]. These assignments are rather speculative and further studies should be carried out to establish the nature of these defects.

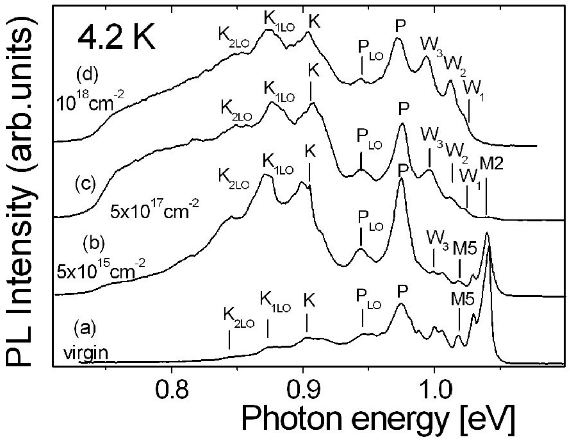

Figure 1: The evolution of the PL spectrum, measured in a $CuInSe_2$ single crystal before irradiation (a), and after the doses of $5{\cdot}10^{15}$ (b), $5{\cdot}10^{17}$ (c) and 10^{18} (d) cm^{-2} of 6 MeV electron radiation.

Figure 2 shows the near-band-edge region of the PL spectra above 0.98 eV. Several very sharp lines can be seen in the spectrum taken before the irradiation. The A and B lines, at about 1.0416 eV and 1.0447 eV, were assigned [3, 4] to the A and B free excitons. The M1 at 1.0386 eV, M2 at 1.0353 eV, M3 at 1.0341 eV, M4 at 1.0324 eV and M5 at 1.0278 eV lines were assigned to recombination of excitons bound to shallow donors and acceptors [3, 5].

Considerable changes in the lower energy region of the PL spectrum can be seen in Figure 1(b) after irradiation with the lowest dose of $5{\cdot}10^{15}$ cm^{-2}. The P and especially K bands intensities increase significantly. After higher doses of electrons the low energy background emission from 0.75 to 1 eV in this region increased whereas the intensities of both the K and P bands are gradually becoming lower. Assuming the assignment of the P band to the acceptor, copper on indium site (Cu_{In}), and the K band to another acceptor, interstitial selenium (Se_i), [5] we can interpret the increased intensities of these bands after irradiation as an increase in the population of Cu_{In} and Se_i. The acceptor nature of the defects is in a good agreement with the n- to p-conductivity type conversion of n-conductivity type $CuInSe_2$ after ion-bombardment as observed after bombardment by Ar^+, Xe^+, O^+ and a number of other ions [6, 7, 8, 9].

In the near-band-edge region of PL spectra the irradiation reduces the intensity of the A and B free- and M1 – M5 bound-excitons. Their peaks become broader and shift to the lower energies, as can be seen in Figure 2. Such a reduction has started from quite a low dose of $5{\cdot}10^{15}$ cm^{-2} suggesting that high-quality material with low concentrations of intrinsic defects is not radiation hard.

Also the three new sharp lines W_1 at ~1.0215 eV, W_2 at ~1.0102 eV and W_3 at ~0.9909 eV appear in the spectra and become more prominent with the dose increase. These lines have not been observed in the PL spectra of any non-irradiated $CuInSe_2$ samples studied by the authors. After higher doses of electrons these lines become broader and gradually shift towards lower energies. These lines are probably associated with optically active intrinsic defects generated by the radiation or/and their complexes, formed shortly after the irradiation carried out at room temperature. The origin of these lines is not clear and requires further investigation.

The increases in the irradiation dose result in a redistribution of the PL emission between the lower and higher energy regions. Radiative recombination through deeper bands and non-radiative recombination mechanisms both become more probable. Low-energy red shifts by up to 2 meV have been observed for the excitonic lines A, B and M-lines as well as for free-to-band P and K peaks after irradiation with higher doses, from $5{\cdot}10^{15}$ cm^{-2} to 10^{18} cm^{-2}.

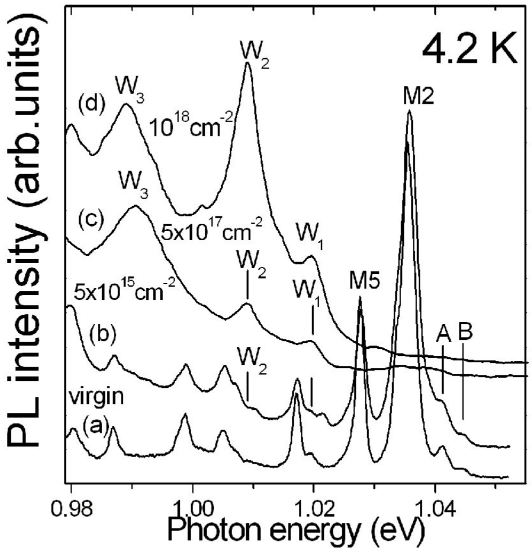

Figure 2: The evolution of the near-band-edge region of the PL spectrum measured in a $CuInSe_2$ single crystal before irradiation (a), after the doses $5{\cdot}10^{15}$ (b), $5{\cdot}10^{17}$ (c) and 10^{18} (d) cm^{-2} of 6 MeV electron radiation.

This shift and the broadening can be explained by an increase of the internal stress induced by high concentrations of radiation generated defects. Similar effects of broadening of the A and B free-excitonic lines as well as their shifts to lower energy have been observed earlier in high-quality $CuInSe_2$ single crystals with small deviations from the ideal stoichiometry [10]. Deviations of the In/Cu ratio from unity induce redshifts of the spectral position and an increase of the width of the A and B free excitons excitons in PL and reflectivity spectra. These effects were also associated with internal stress induced by high populations of intrinsic defects.

High-energy electrons displace atoms of the crystalline lattice generating primary defects, vacancies and interstitials. At room temperature these vacancies and especially interstitial atoms become mobile. They recombine during or shortly after the irradiation creating antisite defects. Pairing antisite defects with vacancies and interstitials results in the formation of defect-complexes. Theoretical calculations [11] demonstrated that in $CuInSe_2$ the formation energies of such complexes are low and sometimes can be negative. The generation of complexes merging several vacancies ca also be expected. According to experimental measurements of diffusion coefficients the mobility of interstitial atoms of Cu, In and Se is different. Indium- (In_i) and especially copper-interstitials (Cu_i) are known to be significantly more mobile than selenium (Se_i) atoms which are more likely to diffuse as neutral monoatomic species via interstitial sites [12]. This conclusion agrees with our observation of a significant increase in the K band intensity, as show in Figure 1, associated with Se_i, after the irradiation.

The presence of cation-cation antisite defects, or copper on indium site Cu_{In} and indium on copper site In_{Cu} make the lattice more sphalerite type. A sphalerite to chalcopyrite phase transition has been reported for $CuInSe_2$ at 810° C [13], requiring a very slow decrease in the temperature during the solidification [14] to reduce concentrations of these defects in the material. However quite a high intensity of the P band associated with Cu_{In}, can be seen in the PL spectra, Figure 1, taken from our high-quality material before the irradiation. Ion bombardment and subsequent annealing introduce a disorder on the Cu-In sublattice changing the two-fold symmetry of the (112) plane, corresponding to chalcopyrite, in the electron diffraction patterns for three-fold one, corresponding to sphalerite [15, 16]. Therefore we can expect significant concentrations of Cu_{In} and In_{Cu} to be present after the electron irradiation. Due to the mixed covalent and ionic type of bonding in $CuInSe_2$ the formation of cation-anion type of antisite defects can also not be ruled out.

$CuInSe_2$ single crystals with a copper-excess elemental composition, irradiated with 10^{18} cm^{-2} dose of 2 MeV electrons at 4 K with subsequent annealing at temperatures up to 450 K, have been studied by positron lifetime spectroscopy [17]. It was concluded that annealing of the irradiated samples at about room temperatures results in the formation of defect complexes without vacancies or defect complexes containing positively charged vacancies, undetectable by positron lifetime spectroscopy. This conclusion rules out the possibility of the presence of copper (V_{Cu}^-) and indium vacancies (V_{In}^-) as well as two copper vacancies + indium on copper site ($2V_{Cu}^- + In_{Cu}^{2+}$) complexes suggesting rather the generation of copper on indium site Cu_{In} antisites and the defect complexes, copper on the indium site + two interstitial copper atoms (Cu_{In} + $2Cu_i$), as more probable candidates. This conclusion is in a good agreement with our observation of an increase in the intensity of the P band associated with Cu_{In} after the electron irradiation which can be seen in Figure 1. According to Ref. [18] selenium vacancies V_{Se} can be charged positively, but the formation of donors contradicts the trend of acceptor-type nature of radiation induced defects in $CuInSe_2$ [7, 8, 9]. According to [11] defects formation energies in $CuInSe_2$ depend on the Fermi level in the material and so in our copper excess p-type $CuInSe_2$ we can probably expect the following order for the formation energies: $Cu_{In}<V_{Cu}<V_{In}<Cu_i<In_{Cu}$ (excluding Se-related defects). Ruling out the vacancies we have Cu_{In}, Cu_i, In_{Cu} and their complex $Cu_{In} + 2Cu_i$ as the main candidates for the radiation induced defects.

Considering the list of the defects, which can be expected in this material, we should also take in account possible contaminating species like Fe, found in $CuInSe_2$ single crystals [14] (grown using the same technique) in the 10^{17}-10^{18} cm^{-3} concentration range, oxygen, hydrogen and carbon, which might be present in the material at concentrations exceeding the initial concentrations of intrinsic defects. These contaminants significantly complicate the analysis of the nature of the irradiation induced lines W_1, W_2 and W_3. Further investigation is required for understanding their nature.

4 CONCLUSION

The irradiation of $CuInSe_2$ single crystals by 6 MeV electrons with doses from $5\cdot10^{15}$ to 10^{18} cm^{-2} resulted in a reduction of the PL intensity of both the free- and bound-excitonic lines observed in the virgin material. Such a reduction has started from quite a low dose of $5\cdot10^{15}$ cm^{-2} suggesting that high-quality material with low concentrations of intrinsic defects is not quite radiation hard. The irradiation also induced new sharp PL lines W_1 at 1.03, W_2 at 1.01 and W_3 at 0.99 eV below the free-exciton emission. Two deeper broad bands, associated with the acceptor-type defects, interstitial selenium (Se_i) and copper on indium site (Cu_{In}), have become more intensive suggesting an increase in the concentration of these defects due to irradiation.

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