Comparison of the Optical Properties of $CuInS_2$ Crystals Grown by Different Methods

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ABSTRACT: In this work we present a comparative analysis of excitonic features in the photoluminescence (PL) spectra measured at 4.2, 78 and 300 K in $CuInS_2$, grown by the traveling heater (THM) and the chemical vapor transport (CVT) methods. The A free exciton in the crystals grown by the THM method, reveals a doublet, corresponding to the lower (A_{LPB}) and upper (A_{UPB}) polariton branches, and a number of bound excitonic lines whereas the PL spectra of the crystals grown by CVT method exhibit a single line of the A exciton and only three bound exciton lines. Excited states of the free A excitons were observed in the PL spectra of the crystals grown by both methods. Binding energy of the A exciton of 18.5 meV and 19.7 meV have been estimated using the hydrogenic model for the THM and CVT grown crystals, respectively. The Bohr radii of the exciton, dielectric constants and the bandgaps in the two types of $CuInS_2$ are calculated.
Ketwords: $CuInS_2$, Photoluminescence, Defects

1 INTRODUCTION

The chalcopyrite semiconductor $CuInS_2$ is one of the most promising materials used in the absorber of high-efficiency, thin-film photovoltaic devices [1, 2]. The band gap $E_g \sim 1.55$ eV, high absorption coefficient $\alpha \sim 10^5$ cm^{-1}, good chemical and thermal stability make this compound very attractive for solar cells [3, 4]. However the 12% [3] conversion efficiency achieved to date is significantly lower than the theoretical maximum of 30% for a single-junction solar cell. Improvements in the performance can not be achieved without a better understanding of physics of this material and in particular its optical properties.

Excitonic features in optical spectra can give accurate information on the electronic band structure revealing fine structure that can deepen the understanding of the defect physics of this material and allow estimation of important physical parameters. One such parameters is the binding energy of free excitons E_{ex}, which can be accurately derived from the positions of excited states of these excitons, and used to calculate important parameters, such as the bandgap E_g, which is vital for a knowledge-based design of electronic devices. Variations of the binding energy would manifest themselves in fundamental changes in the material and in particular of the optical bandgap.

In this paper we report on a comparative analysis of excitonic features in the photoluminescence spectra (PL) measured from $CuInS_2$ single crystals, grown by two different techniques and reveal how the growth technique affects the binding energy and Bohr radius of the A free exciton, bandgap and dielectric constant.

2 EXPERIMENTAL DETAILS

High-quality $CuInS_2$ single crystals were grown by the two different techniques: the traveling heater method (THM), using indium as a solvent, or the chemical vapor transport (CVT) method, using iodine as the transporting agent. The chemical composition of the compounds determined by energy dispersive X-ray (EDX) analysis was Cu: 24.3, In: 25.8 and S: 49.9 % and Cu: 24.8, In: 25.2 and S: 50.0 % for the THM and CVT grown crystals, respectively. PL spectra were taken from as cleaved surfaces of two crystals grown by the THM technique (THM1 and THM2) and two crystals grown by the CVT technique (CVT1 and CVT2). PL was excited by the 514 nm line of an Ar^+ ion laser with power up to 200 mW. The PL spectra were detected by a photomultiplier tube (Hamamatsu R 7400U-20) and amplified using low-noise phase-sensitive lock-in-techniques. A 0.6 m single grating monochromator with 1200 grooves/mm grating was used.

3 RESULT AND DISCUSSION

Figures 1 and 2 show near-band-edge regions of the PL spectra taken in $CuInS_2$ single crystals grown by the CVT and THM methods, respectively.

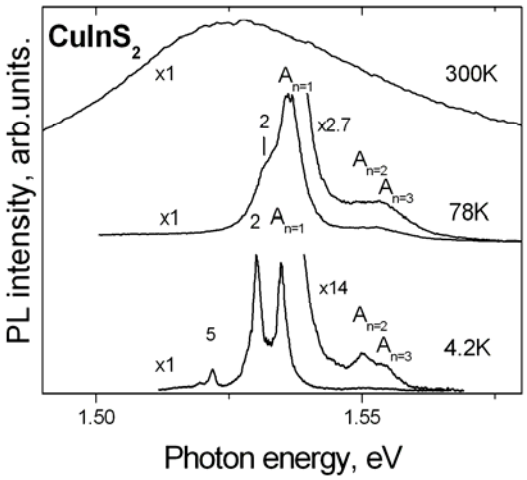

Figure 1: Near-band-edge region of the PL spectra of $CuInS_2$ single crystals grown by chemical vapor transport (CVT) taken at different temperatures.

Each Figure has PL spectra taken at the three different temperatures 4.2, 78 and 300 K. The spectral resolutions of these spectra are 0.2, 0.5 and 1.0 meV, respectively.

A broad band, with a maximum at ~1.525 eV and full width at half maximum (FWHM) of ~ 60 meV, can be seen in the PL spectra of both types of crystals taken at room temperature. This band has been assigned to the band-band optical transition [5, 6].

The A line, with the maximum at ~1.537 eV and FWHM of about 7 meV, dominates the PL spectra of both types of crystals at 78 K. This line has been assigned to the ground state (n = 1) of the A free exciton [5-7]. A partially-resolved peak 2 at 1.532 eV on the low-energy slope of the A exciton corresponds to a bound excitons. A low intensity peak at 1.552 eV, at the high-energy side of the A can be assigned to the first $A_{n=2}$ and second $A_{n=3}$ excited states of the A exciton, which are non-resolved at 78 K.

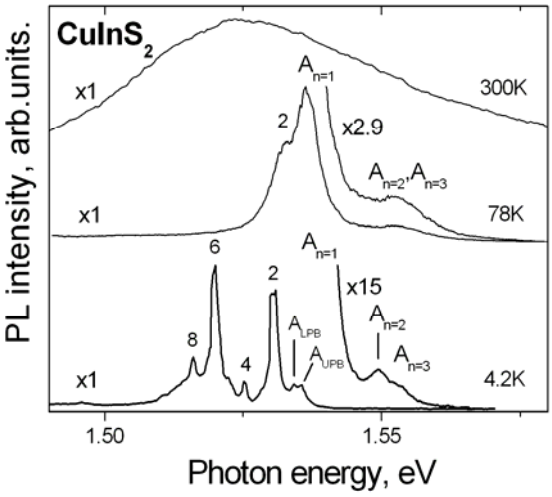

Figure 2: Near-band-edge region of PL spectra of $CuInS_2$ single crystals grown by traveling heater method (THM), using indium as a solvent, taken at different temperatures.

All the discussed peaks become sharper in the PL spectra taken at 4.2 K as shown in Figure 1and 2. The FWHM of the peaks for excited states of the A exciton also become smaller and the lines $A_{(n=2)}$ and $A_{(n=3)}$ can be seen resolved. At temperatures above 78 K these states merge into a broader line which should be assigned to the excited states of the A exciton rather than to the degenerated BC sub-band, of the valence band, split into A and BC sub-bands due to spin-orbital coupling, as suggested earlier [5-7]. Besides the free excitonic lines several lines 2, 4, 5, 6 and 8 appear in the spectra. The notations, where bound excitons are denoted by the numbers, were proposed in our previous report [6]. Some of the lines (2, 4, 5, 6 and 8) were reported earlier in Ref. [5,7-9] and assigned to excitons bound to shallow either donor- or acceptor-type defects.

It can be seen that all the observed excitonic lines in the PL spectra from the samples fabricated by both CVT and THM techniques shift to higher energies when the temperature increases from 4.2 to 78 K. The A free excitonic line shifts in this interval of temperatures by 1.8 – 2 meV for all the investigated HTM and CVT crystals.

At 4.2 K the PL spectra grown by the THM technique reveal a fine structure of the A free exciton with two lines corresponding to the lower (A_{LPB}) and upper (A_{UPB}) polariton branches [5,10].

After studying more than 20 samples of $CuInS_2$ grown by each technique we can discuss differences observed in the PL spectra corresponding to each technique. The near-band-edges of the PL spectra taken in the four samples discussed here (THM1, THM2, CVT1, CVT2) are compared in Figure 3. It can be seen that each growth technique results in its own pattern of excitons. These patterns significantly differ in the constituent lines as well as in their intensities suggesting that some defects are inherited from the growth technique whereas other defects are common for both the CVT and THM methods. For example lines 1, 4 and 8 are present only in the spectra of HTM grown samples. The presence of a particular line can be taken as an evidence of a considerable concentration of the particular defect and the intensity of this line is proportional to on the defect concentration.

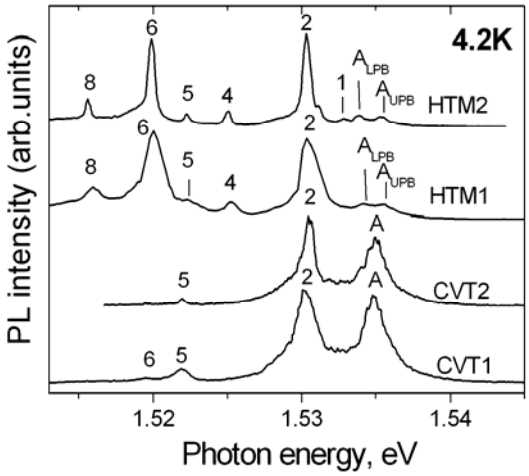

Figure 3: Near-band-edge region of PL spectra of four $CuInS_2$ single crystals grown by the two techniques, traveling heater method, HTM1 and HTM2, and chemical vapor transport, CVT1 and CVT2, taken at 4.2 K.

The PL intensity in the THM grown material was found to be higher than in the CVT grown ones by about one order of magnitude which suggests the presence of effective channels for non-radiative recombination in the CVT grown material. However the intensities of the A free excitons relative to the bound excitons are higher in the CVT grown samples. In all the studied CVT grown crystals we observed comparable intensities of the free and bound excitons whereas the PL spectra taken from the THM samples are dominated by bound exciton emission, in particular by lines 2 and 6. The intensity of line 6 is low in all CVT samples and the spectra are dominated by the A free and 2 bound excitonic lines as shown in Figure 1 and 3. For the THM samples the A exciton intensity was always low. However in the case of high intensity of line 2 the polariton doublet structure, the A_{LPB} and A_{UPB} lines, could be seen resolved [10]. The FWHM of the A free exciton peaks in the CVT and THM crystals was found to be close 1.6 - 1.8 meV at 4.2 K.

The FWHM of bound exciton peaks was found to be different in different crystals grown by the same method depending as well as in those from different growth techniques. The smallest FWHM is ~0.5 meV, measured at 4.2 K in the PL spectra of two THM samples, taken

from different sides of the same ingot. A PL spectrum, measured in one of these samples, THM2, is shown in Figure 3. For other THM grown samples, for example THM1, also shown in Figure 3, the FWHM of the bound exciton peaks varied from 1 to 1.5 meV. Similar differences were observed in the FWHM of the bound exciton peaks for CVT grown samples. In CVT1 the FWHM peaks was ~ 0.9 meV whereas in CVT2 it varied from 1 to 1.7 meV. The spectral position of the exciton peaks, measured at 4.2 K with an accuracy of 0.2 meV, also differed by 0.3-0.4 meV. In our opinion the observed differences in the width and spectral positions of the free and bound excitonic lines are determined by the internal stress in the crystalline lattices. This stress is induced by defects and depends on their type and concentration. These defects include intrinsic defects, which appeare due to deviations from the ideal stoichiometry. We can not rule out contaminants introduced during the growth such as iodine, oxygen, hydrogen and carbon present in unknown concentrations in the samples. Measurements of the FWHM of free and bound exciton peaks at helium temperatures can be a good method to estimate the quality of the material. Judging by the FWHM of excitonic lines the quality of the studied $CuInS_2$ single crystals is of the best reported to date.

The binding energy of the A exciton, calculated from the spectral distance of the ground $A_{(n = 1)}$= 1.5351 ± 0.0002 eV and the first excited state $A_{(n = 2)}$=1.5499 ± 0.0002 eV of the A exciton as $E_{ex} = 4/3[A_{(n = 2)} - A_{(n=1)}]$, was E_{ex} = 19.7 ± 0.5 meV for the CVT grown samples. For the THM grown ones this binding energy was found to be slightly smaller E_{ex} = 18.5 ± 0.5 meV [10]. Using the hydrogenic model and values for the effective masses of electron $m_e = 0.16m_o$ and hole $m_h = 1.3m_o$, from the literature [11], we can calculate physical parameters of $CuInS_2$ such as the dielectric constant, Bohr radius of the exciton and the bandgap in the material grown by the two different techniques. The values of these parameters are shown in Table I.

TABLE I: Variations of the binding energy (E_{ex}) and Bohr radius (a_B) of the A free exciton as well as the bandgap (E_g) and dielectric constant (ε) in $CuInS_2$ single crystals grown by the two different techniques: traveling heater (THM), using indium as a solvent, and chemical vapor transport (CVT).

Method of growth	E_{ex} (meV)	E_g (eV)	a_B (nm)	ε
THM	18.5	1.5536	3.8	10.2
CVT	19.7	1.5548	3.7	9.9

4 CONCLUSION

A comparative analysis of the PL spectra measured at 4.2, 78 and 300 K in $CuInS_2$, grown by the traveling heater (THM) and the chemical vapor transport (CVT) methods shows considerable differences in the excitonic features. The A free exciton in the crystals grown by the THM method, reveals a doublet, corresponding to the lower (A_{LPB}) and upper (A_{UPB}) polariton branches, and a number of bound excitonic lines whereas the PL spectra of the crystals grown by CVT method exhibit a singlet line of the A exciton and only three bound exciton lines. Excited states of the free A excitons were observed in the PL spectra of the crystals grown by both methods. The binding energy of the A exciton of 18.5 meV and 19.7 meV have been calculated using a hydrogenic model for the THM and CVT grown crystals, respectively. The Bohr radii of the exciton, the bandgaps and dielectric constants in the two types of $CuInS_2$ are also calculated.

5 ACKNOWLEDGEMENT

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6 REFERENCES

[1] R.Scheer, T.Walter, H.W.Schock, M.L.Fearheiley, H. J. Lewerenz, Appl. Phys. Lett. 63 (1993) 3294.
[2] K.Siemer, J.Klaer, I.Luck, J.Bruns, R.Klenk, D. Braunig, Sol. Energy Mater. Sol Cell. 67 (2001) 159.
[3] R.Klenk, J.Klaer, R.Scheer, M.Ch.Lux-Steiner, I. Luck, N.Meyer, U.Rühle, Thin Solid Films 480-481 (2005) 509.
[4] J.Klaer, J.Bruns, R.Henninger, K.Siemer, R.Klenk, K.Ellmer, J.Braunig. Semicond. Sci. Technol., 13 (1998) 1456.
[5] S. Shirakata, H.Miyake. J. Phys. Chem. Solids. 64 (2003) 2021.
[6] M.V.Yakushev, A.V.Mudryi, I.V.Victorov, J.Krustok, E.Mellikov, Appl. Phys. Lett. 88 (2006) 011922.
[7] J.M.Binsma, L.J.Giling, J.Bloem. J. Lumines. 27 (1982) 55.
[8] K.Wakita, G.Hu, N.Nakayama, D.Shoji. Jpn. J. Appl. Phys. 41 (2002) 3356.
[9] K.Yoshino, T.Ikari, S.Shirakata, H.Miyake, K.Hiramatsu. Appl. Phys. Lett., 78 (2001) 742.
[10] M.V.Yakushev, R.W.Martin, A.V.Mudryi, A.V.Ivaniukovich. Appl. Phys. Lett. 92 (2008) 111908.
[11] D.C.Look, T.C.Manthuruthil. J. Phys. Chem. Solids 37 (1976) 173.