

Optical Characterization of Deep Levels in Single Crystals of CuGaS₂ Grown by Chemical Vapor Transport

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Optical absorption spectra were measured in undoped and Fe- or Ni-doped single crystals of CuGaS₂ grown by the chemical vapor transport technique. Chemical analysis of Fe concentration by absorption spectrophotometry and optical characterization by absorption and photoluminescence (PL) spectroscopy in these materials revealed that the main trace impurities which darken undoped crystals are Ni and Fe. The excitation spectrum of the infrared PL due to Fe³⁺ was also measured. From this, the 1.8 eV peak of the strong absorption band introduced by trace Fe impurities was interpreted in terms of the transition from the valence band to the dangling bond state hybridized with 3d orbitals.

KEYWORDS: single crystals of CuGaS₂, iron and nickel impurities, coloration of crystals, absorption spectrum, photoluminescence spectrum, spectrophotometry of iron impurity, dangling bond hybrid state, ligand-field spectrum

§1. Introduction

I-III-VI₂ semiconductors are attracting much interest as new optoelectronic materials. These compounds with the chalcopyrite structure have direct band gaps, among which CuGaS₂ has a band gap at 2.5 eV in the green region and p-type conductivity. The band-edge emission of this material is promising for new light emitting devices. However, the crystallinity and the purity in these materials are far behind compared with those in III-V or II-VI compounds. In order to use this material for application, it is essential to control the species of impurities and defects which may reduce the efficiency of the band-edge emission, and yet there exist only a few reports on these intrinsic and extrinsic defects. The authors have been studying deep levels in I-III-VI₂ semiconductors with particular reference to optical properties of transition atom impurities in these materials. Doping of transition metals into this material causes unique optical phenomena, such as intense absorption bands^{1,2)} and luminescent centers³⁾ below optical band edges.

In this research, we carried out various optical studies on this material to determine how to control the crystallinity and the optical properties introduced by transition atoms. In addition, controversy^{4,5)} exists as to whether the dark green color in crystals grown by the iodine chemical vapor transport (CVT) technique is caused by native defects or foreign defects of Fe for example. In particular, Fe is easily substituted into the group III site, since the solution limit of Fe in I-III-VI₂ is 100%. In order to determine this, undoped and Fe- or Ni-doped single crystals of CuGaS₂ were grown by this technique, and polarized absorption spectra as well as photoluminescence and excitation spectra were measured.

§2. Experimental

Single crystals of undoped and Fe- or Ni-doped CuGaS₂, used for the present experiments, were grown by the iodine CVT method. The starting materials were polycrystalline powder of Cu₂S, Ga₂S₃, FeS and NiS sintered in vacuo using elements of Cu(5N), Ga(6N), S(6N), Fe(4N), and Ni(4N). Mixtures of the polycrystalline materials (about 5 g) with the appropriate molar ratio were sealed in vacuo of about 3×10^{-5} Torr together with iodine (12 mg/cc) and placed into fused silica ampules with an inner diameter of 13 mm. The sealed ampules were placed in a furnace with a source temperature of 900°C and a growth temperature of 750°C for 10 days. Obtained crystals were undoped CuGaS₂ and those doped with Fe (nominally 0.01, 0.3 and 1.0 mol%) and doped with Ni (nominally 0.1 mol%). The shapes of these crystals were platelets, columns and needles and the typical size of all of the crystals was not more than 1 cm in a side. Both Fe-doped and undoped crystals were colored dark green and became darker with an increase in the Fe content. The dominant crystal planes were determined as {112} by X-ray techniques.

Polarized absorption spectra of these compounds were measured between 0.5 eV and 2.5 eV. The typical size of the crystals used for these measurements was about $8 \times 3 \times 1$ mm². The rough sides were mirror-polished using the lapping films (3 μm, 1 μm and 0.3 μm). Polarized absorption spectra were measured at room temperature on the {112} plane for lights polarized parallel ($E \parallel C$) and perpendicular ($E \perp C$) to the C-axis. It should be noted that the notation $E \parallel C$ is nominal and only 2/3 of the intensity lies along the C axis since the {112} plane does not include the C axis. Hereafter, we use $E \parallel C'$ to describe this situation.

Light from a 150 W halogen tungsten lamp was dispersed with a JASCO CT25-C monochromator, chopped by a rotating sector and polarized by a Gran-prism

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polarizer. The transmitted light was detected by a photomultiplier (GaAs type), a silicon photocell and a liquid-nitrogen-cooled InSb photocell.

The excitation light source for the measurement of the photoluminescence (PL) spectrum was an Ar⁺ ion laser with suitable band-pass filters to select an appropriate wavelength; 514 nm for the measurement of infrared luminescence and 488 nm for band-edge luminescence. The temperature of the samples was maintained at 20 K with a He refrigerator. The emitted light was chopped, then dispersed by a JASCO CT25-A monochromator with gratings brazed at 1.6 μm (infrared region) or at 0.75 μm (visible region). The exit light was detected by either a cooled InSb photocell (infrared region) or a photomultiplier with a GaAs-photocathode (visible region).

For the measurement of the PL-excitation spectrum, the light from a halogen tungsten lamp dispersed by a CT25-C monochromator was employed. The emitted light from the sample was chopped and again dispersed by a Nikon P250 monochromator, the wavelength of which was fixed to the peak of the PL spectrum, and then detected by the cooled InSb photocell. The obtained spectrum was corrected for the spectral dependence of the excitation light measured by a thermopile.

Quantitative analysis of Fe in the crystals was carried out by means of absorption spectrophotometry as follows.⁶⁾ A weighed portion of the crystals was dissolved in concentrated, hot nitric acid. After the solution was cooled to room temperature, large amounts of copper were removed using electrolysis with a platinum electrode. Then, ethylenediamine-tetraacetic acid (EDTA) was added to mask the copper and nonferrous metal impurities, such as Ni(II), remaining in the solution. Spectrophotometric determination was carried out on a Shimadzu UV-150-02 double-beam spectrophotometer. The content of Fe was determined at 508 nm, using 1,10-phenanthroline as a coloring agent.

§3. Experimental Results

Figure 1 shows a concentration dependence of the absorption spectra in CuGaS₂ doped with Fe. Below the absorption edge of the host crystal, there exists an intense broad absorption band with two peaks, A and B, which gains intensity with an increase of the Fe content. Figure 2 shows magnified spectra in undoped samples. As shown in this figure, a broad absorption band similar to that in the Fe-doped samples exists even in undoped samples. The intense absorption band seen in Fe-doped samples has been assigned to the photoionization transition⁷⁾ from the valence band to the Fe-related levels reducing Fe³⁺ into Fe²⁺. Therefore, our experiment clearly suggests that undoped crystals contain Fe impurities.

Table I shows the result of quantitative chemical analysis of Fe impurity determined by the spectrophotometry. Absorption cross sections per Fe atom deduced from the absorption spectra shown in Fig. 1 using the content of Fe determined by the chemical analysis are shown in Fig. 3. The cross section of the undoped samples is larger than that of the intentionally Fe-doped samples, indicating that undoped crystals contain some

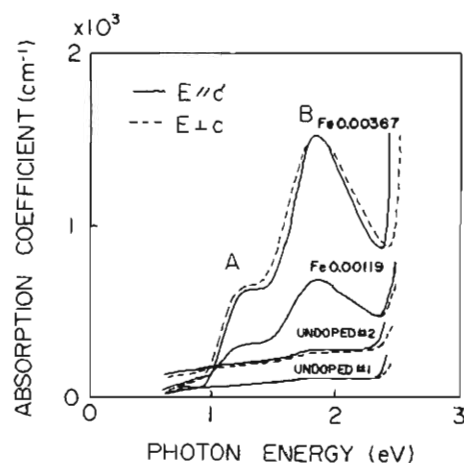


Fig. 1. Polarized absorption spectra of in single crystals of undoped (#1 and #2) and Fe-doped (0.119, 0.367 mol%) CuGa₂S₂ measured at room temperature.

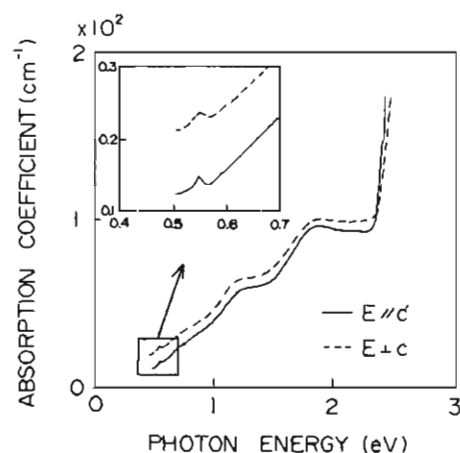


Fig. 2. Magnified polarized absorption spectra of undoped CuGa₂S₂ (#1) measured at room temperature. The inset shows a peak at 0.54 eV.

Table I. Results of the quantitative chemical analysis of Fe in single crystals of CuGaS₂ and CuGa_{1-x}Fe_xS₂.

Sample name	Fe concentration X	
	nominal	analyzed
Fe 0.01	0.01	0.0102
Fe 0.003	0.003	0.00367
Fe 0.0001	0.0001	0.00119
Undoped #1	0	0.00011
Undoped #2	0	0.00034

other impurities in addition to Fe.

In the absorption spectra of undoped and Fe-doped samples, we also found a peak at 0.54 eV, which may be associated with the ligand-field transition (²T₂ → ²E) of Ni²⁺ in CuGaS₂ reported by Kaufmann.⁸⁾ This result suggests that undoped crystals also contain Ni. We then measured a polarized absorption spectrum in Ni²⁺-doped CuGaS₂. As shown in Fig. 4, a broad intense absorption band similar to that in the Fe-doped sample was observed.

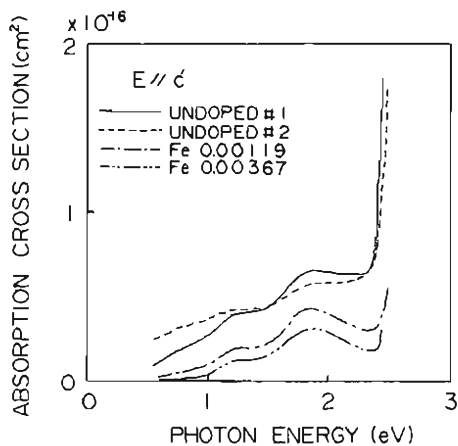


Fig. 3. Absorption cross sections in one Fe atom in undoped and Fe-doped crystals of CuGaS_2 deduced from the spectra shown in Fig. 1 using the value shown in Table I.

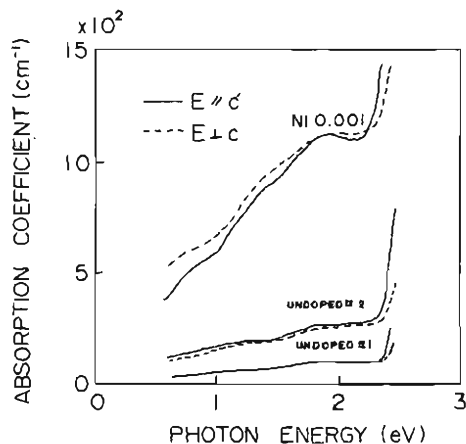


Fig. 4. Polarized absorption spectra in single crystals of undoped (#1 and #2) and Ni-doped (nominally 0.1 mol%) CuGaS_2 measured at room temperature.

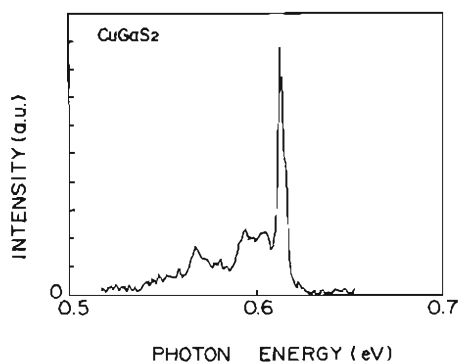


Fig. 5. Photoluminescence spectrum of undoped CuGaS_2 (#1) at 20 K. Excitation source is a 514 nm line of Ar^+ ion laser.

A sharp PL line ascribed to the crystal-field transition⁹⁾ (${}^6T_1 \rightarrow {}^6A_1$) of Fe^{3+} was observed in undoped CuGaS_2 at 20 K, irradiated by the Ar^+ ion laser (514 nm), as shown in Fig. 5. This fact also indicates that undoped samples contain some trace iron impurities.

An excitation spectrum for this emission measured at 20 K is given by the solid curve in Fig. 6. The absorption

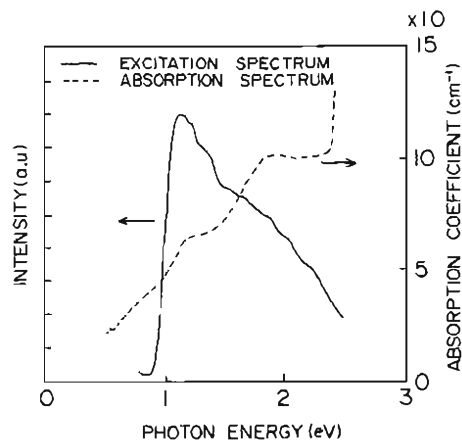


Fig. 6. Excitation spectrum for 0.61 eV luminescence at 20 K of undoped CuGaS_2 (#1) indicated by a solid curve. Absorption spectrum of the same sample is also shown by a dotted curve.

spectrum of the same sample is illustrated by a dotted curve in the figure. The excitation band of this emission corresponds to the low-energy peak, A, in the strong absorption band observed in Fe-doped CuGaS_2 .

To determine the crystallinity of the undoped single crystal, the PL spectrum near-band edge region was also measured in undoped samples supposed to contain Fe impurities. A sharp edge emission which can be ascribed to bound exciton transition was observed. However, broad emission bands which may be caused by a D-A pair and SA center were also observed. Comparison of the relative intensities between these near-edge emission bands and the Fe-originated infrared emission has not been carried out, since different types of detectors are used in each experiment.

§4. Discussion

Quantitative chemical analysis using absorption spectrophotometry shows that undoped CuGaS_2 contains an iron impurity of 0.01~0.03 mol% concentration. Undoped CuGaS_2 shows similar absorption peaks which correspond to the absorption peaks A and B in $\text{CuGaS}_2:\text{Fe}$ assigned to the charge transfer transition.⁷⁾ The absorption band of B in the red region together with the absorption band edge in the blue region results in coloration of undoped CuGaS_2 . Therefore, the green color of this material is not intrinsic to the crystal but is induced by Fe impurities. In addition, the broad absorption band caused by the Ni impurity may be responsible for the darkening of the undoped crystals as well. Direct detection by chemical analysis of Ni impurities in the undoped samples should be carried out to make this argument more definite. This is planned for future investigations.

We suspect that these Fe and Ni impurities arise from Cu metals in the starting materials and from iodine; they may also be introduced during the preparation process.

Polarization dependence of absorption spectra in $\text{CuGaS}_2:\text{Fe}$, which reflects the valence band splitting, was only observed in the absorption edge region and not in the broad absorption band. This does not agree with the polarization-dependent absorption spectrum predicted

by a molecular-orbital calculation in a 17-atom cluster with Fe in the center.¹⁰ This suggests that the absorption band is not solely caused by the charge-transfer transition relating to the Fe atom.

According to the calculated one-electron energy levels¹¹ of substitutional 3d impurities in Si and GaP, there are three main 3d impurity-induced states, denoted t_2^{CFR} (CFR: crystal-field resonances), e^{CFR} and t_2^{DBH} (DBH: dangling bond hybrid). In tetrahedral crystal-field symmetry, these states have relative energy positions as follows: the t_2^{CFR} level is lower than the e^{CFR} level and the e^{CFR} level is lower than the t_2^{DBH} level. The t_2^{CFR} level is always located in the valence band, whereas the e^{CFR} level emerges into the band-gap region as the atomic number Z becomes lower. The e^{CFR} is well localized and has mostly d-like character. The t_2^{DBH} level starts near the top of the valence band, and becomes higher in the gap as Z decreases. The t_2^{DBH} is not only d-like but also has p character and a wave function extended in the crystal and which become localized as the levels locate deeper.

In absorption spectrum of $\text{CuGaS}_2\text{:Ni}$, the energy position where the intense absorption band assumes a maximum value is 1.86 eV. This energy position is very close to the energy position of 1.84 eV of absorption band B in $\text{CuGaS}_2\text{:Fe}$. Assuming that these peaks are associated with DBH, the energy position of band B may correspond to the transition from the valence band (VB) to t_2^{DBH} , rather than that from t_2^{DBH} to the conduction band (CB), since the $\text{VB} \rightarrow t_2^{DBH}$ transition (an allowed $p \rightarrow d$ excitation) would have a higher intensity than the $t_2^{DBH} \rightarrow \text{CB}$ transition (a forbidden $d \rightarrow s$ excitation). The DBH is an antibonding state formed from the hybridization of t_2 orbitals of transition atoms and of t_2 orbitals of the host dangling bonds of the group VI element which occurs when Ga is removed. This state acts as the vacancylike defect and has a possibility of forming an intense absorption band. This assumption is also supported by the fact that the Fe^{3+} photoluminescence (PL) is excited strongly by absorption peak A but only weakly by absorption peak B. If absorption peak B is related to the DBH level, the luminescence would be quenched due to the nonradiative recombination process through the multiphonon process. Additionally, the absorption band A would act as the CFR and the energy position of absorption band A would also be related the transition of $\text{VB} \rightarrow e^{CFR}$. These transitions are schematically shown in Fig. 7.

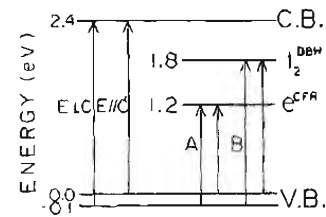


Fig. 7. A schematic view of the energy band in $\text{CuGaS}_2\text{:Fe}$.

§5. Conclusions

Optical absorption spectra, quantitative chemical analysis of Fe impurity and infrared PL measurements have elucidated that unintentionally doped Fe and Ni impurities are responsible for the green coloration of the undoped CuGaS_2 . We have also shown that the absorption band in 1.8 eV of $\text{CuGaS}_2\text{:Fe}$ and $\text{CuGaS}_2\text{:Ni}$ can be associated with deep levels caused by the dangling bond state hybridized by 3d-orbitals of transition atoms.

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