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Effect of Thermal Treatments on Fe^{3+}-Related Absorption and Infrared Photoluminescence Spectra of $CuGaS_2$

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Optical absorption and infrared photoluminescence spectra of $CuGaS_2$ single crystals, grown by chemical vapour transport and annealed in various atmospheres (under vacuum, S-vapour, and in the presence of Cu and Ga), have been studied in order to gain information on the positions of residual iron ions in the crystal lattice of $CuGaS_2$. Having analysed the results obtained, we have proven that Fe ions substitute both Cu and Al sites in the crystal lattice, forming two types of defects, i.e., Fe_{Cu} and Fe_{Ga}, the former being responsible for the infrared photoluminescence and the latter causing the green colouration of the crystals.

KEYWORDS: single crystals of $CuGaS_2$, thermal treatments, iron impurity, infrared photoluminescence, optical absorption

§1. Introduction

I-III-VI$_2$ semiconductors have been attracting much interest as new optoelectronic materials. Among them $CuGaS_2$ is one of the promising candidates of blue-light-emitting materials. However, the single crystals prepared by the chemical transport technique are usually green in colour, which has been attributed to the absorption band located in the infrared-to-red region.

From our previous studies, we know that there are two absorption peaks, A at 1.2 eV and B at 1.8 eV, in the absorption spectrum of the Fe-doped $CuGaS_2$ crystals. Because the intensities of these two absorption bands increase with Fe concentration, we concluded that these bands are caused by optical transitions from the valence band to the acceptor states caused by Fe.[1] In other words these absorption bands can be considered to originate from charge-transfer transitions related to Fe^{3+} ions. It has also been reported that the green colouration of undoped $CuGaS_2$ crystals is caused by the strong absorption band, B.[2]

On the other hand, it has been reported that undoped $CuGaS_2$ shows a sharp infrared photoluminescence (hereafter referred to as IRPL) near 2 μm.[3] The photoluminescence was assigned, on the basis of its Zeeman spectrum, to the ligand field transition between the excited multiplets $^4T_1$ and the ground multiplets $^6A_1$ of Fe^{3+} in the tetrahedral coordination. In our preceding paper,[4] we reported that we had observed the Fe^{3+}-related IRPL in solid-solution crystals with different compositions of two group-III elements (i.e., in $CuGa_xAl_{1-x}S_2$ with x varying between 0 and 1), and we explained the spectra in terms of the local atomic arrangements surrounding the Fe^{3+} ion. From this analysis, we also found that the Fe^{3+} ion associated with the IRPL can only be assigned to the one that substitutes the Cu-site. In addition, from the excitation spectrum measurements, we found that the

IRPL can only be excited by low-energy peak A of the two absorption bands observed in the absorption spectrum of $CuGaS_2$:Fe.[1]

Moreover, judging from the fact that no IRPL was observed in the samples which showed the strongest visible absorption, there seems to be no direct relationship between the IRPL line and the below-gap absorption. This fact seems to be contradictory to the effect that incorporation of the Fe impurity makes the crystals darker, as mentioned above. In order to explain that, we conducted four kinds of thermal treatments on $CuGaS_2$ crystals grown by the chemical vapour transport technique and measured the absorption and IRPL spectra of annealed crystals.

In this study, we investigate the relationship between the absorption band and the IRPL line by applying different kinds of thermal treatments to the undoped $CuGaS_2$ crystals, with particular reference to the effect of the iron impurity.

§2. Experimental

Single crystals of $CuGaS_2$ compound were grown by the chemical vapour transport (CVT) technique in a closed system using iodine as a transporting agent. The starting materials used were powders of Ga_2S_3 and Cu_2S, which were sealed in a quartz ampoule (18 mm ID and 20 cm in length, the total charge being 5 g) under a vacuum of 5×10^{-6} Torr with iodine in the concentration of 10 mg/cm^3 of inner volume of the ampoule. The ampoule thus prepared was placed in a two-zone furnace to grow the single crystals, the temperature gradient at the first stage being inverse (source zone temperature being 750°C and growth zone temperature being 900°C) for about 24 hours, which was followed by the second (growth) stage with the source zone temperature being 900°C and the growth zone temperature being 700°C for five days. The resulting single crystals were typically needle-shaped with the length of about 15 mm, the colouration of the crystals being transparent green. The crystals used for absorption measurements and for thermal treatments were mirror-polished to the thickness of 150-

250 μm using the lapping films.

The CuGaS$_2$ single crystals grown by the CVT technique were placed into quartz tubes (10 mm ID and 20 cm in length) and annealed in various atmospheres: i.e., under vacuum, S-vapour, and in the presence of Cu and Ga. Before annealing, the ampoules were evacuated up to the pressure of 8×10^{-6} Torr.

Annealing in vacuum was carried out for 2 hours at 800°C, after which the ampoule was immediately quenched by an electrical fan. After annealing in vacuum, the colour of the crystals changed to brown.

Sulphur annealing was carried out for 48 hours at 750°C, the samples having been placed into one end of the ampoule and 1g of sulphur having been placed into the other end of the ampoule. Immediately after S-annealing the ampoule was quenched in cold water to avoid segregation of sulphur, and the sulphur stuck to the samples was eliminated by washing the crystals in hot CS$_2$. This thermal treatment deepened the green colouration of the crystals.

Annealing in Cu was done for 25 hours at 700°C, the samples being placed into the ampoule together with 0.8 g of CuGaS$_2$ crystal powder and 1.2 g of Cu$_2$S powder. By this treatment, the colour of the crystals was changed to black.

Annealing in Ga was carried out for 40 hours at 800°C, the samples previously annealed in vacuum being placed into one end of the ampoule and 0.75 g of Ga into the other end of the ampoule. After this treatment the crystals became brown with a rough surface; therefore they were polished again before optical measurements.

Absorption spectra of annealed samples were measured at room temperature using the HITACHI U-3140 spectrophotometer, and photoluminescence (PL) spectra were measured at 20 K in the infrared spectral region. An Ar$^+$-ion laser was used for PL measurements, the infrared PL being excited by the 514-nm line of this laser. All measured spectra were corrected for the spectral response of the detection system.

§3. Results and Discussion

The infrared photoluminescence and absorption spectra of CuGaS$_2$ crystals annealed in various atmospheres are shown in Figs. 1 and 2. For comparison, the spectra of as-grown undoped crystals are also shown in these figures. In Fig. 1 it can be seen that only annealing in Ga leads to the elimination of the Fe^{3+}-related IRPL (Fig. 1(d)), whereas the thermal treatment in other atmospheres under investigation does not change the intensity of the IRPL peak (Figs. 1(b), 1(c) and 1(e)). On the other hand, as shown in Fig. 2, only annealing in S-vapour leads to drastic strengthening of Fe^{3+}-related A- and B-absorption bands (Fig. 2(e)), whereas thermal treatment in other atmospheres essentially does not influence the intensities of these bands (Figs. 1(b), 1(c) and 1(d)). It should be noted that in relation to the absorption spectra, the annealing of the CuGaS$_2$ crystals in S-vapour plays the same role as iron-doping of the crystals. It has also been reported that S-annealing and Fe-doping cause the same change in a visible cathodoluminescence spectrum of the compound under investigation,[5] these results having been shown by us to be valid for the PL
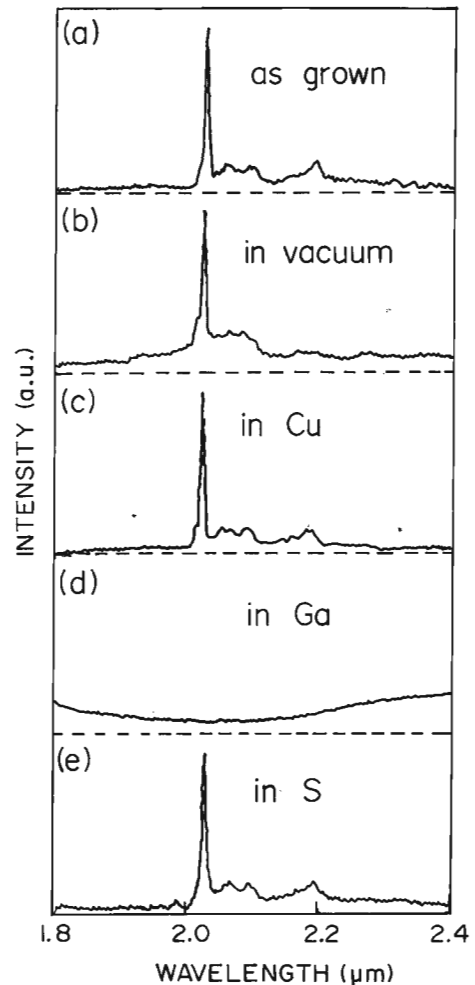

Fig. 1. Infrared photoluminescence spectra (20 K) of CuGaS$_2$ crystals, grown by CVT and annealed in various atmospheres.

spectrum in the visible spectral region as well (these PL results will be published in our following paper).

In order to interpret this phenomenon, let us consider the defect chemistry of the CuGaS$_2$ compound, taking into account residual iron ions. In theory, by applying the law of mass action and the charge neutrality condition, the concentration of all point defects in a ternary compound (such as vacancies, interstitials and defects of antisite disorder) can be accounted for in principle. However, this is a very difficult task because of the large number of possible defects in the ternary compound. This task can be simplified if we take into account the fact that the material under consideration is a close-packed one, since in this case several types of native defects (such as cation-anion antisite defects and S-interstitials) are unlikely to occur because of their high formation energies. This leaves, as defects to be considered, vacancies, cation interstitials and cation-cation antisite disorder defects, i.e., V_{Cu}, V_{Ga}, V_S, Cu_i, Ga_i, Cu_{Ga}, and Ga_{Cu}.

It has been proven by our previous investigations[4] that the Fe^{3+} ion associated with IRPL can only be assigned to the one which substitutes the Cu-site. If the triple-charged Fe ion substitutes the monovalent Cu-site, forming donor-like $[Fe^{3+}]_{Cu^+}$ defects, the effective positive charge of ionized donors in the crystal lattice will increase. In order to compensate this excessive charge, the
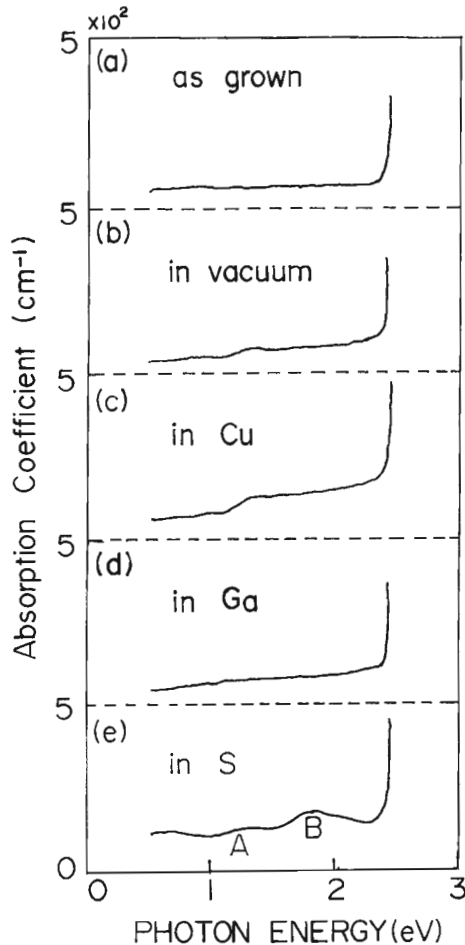
Fig. 2. Absorption spectra (300 K) of CuGaS$_2$ crystals, grown by CVT and annealed in various atmospheres.

concentration of positively charged gallium antisite defects $[Ga_{Cu}]^+$ will decrease, leading, in its turn, to the increase in concentration of negatively charged copper vacancies $[V_{Cu}]^-$. At the same time, the concentration of negatively charged gallium vacancies $[V_{Ga}]^-$ will also increase. All three of the above-considered processes will eventually lead to the compensation of the positive charge of the lattice, caused by the incorporation of Fe-ions.

Annealing in vacuum leads to the increase of concentration of sulphur vacancies $[V_S]^+$ as well as cation vacancies $[V_{Cu}]^-$ and $[V_{Ga}]^-$. Since these defects compensate each other's charge, the lattice charge in the first approximation remains zero. Therefore no change in the Fe^{3+}-related IRPL or in the absorption spectra can be expected, which corresponds well with the experimental results obtained. The same seems to be true for annealing in copper, but in this case, the increase in concentration of $[V_S]^+$ is compensated only by $[V_{Ga}]^-$ defects.

Annealing in gallium results in the increase of concentration of positively charged donor-like $[V_S]^+$ and $[Ga_{Cu}]^+$ defects and in the decrease in concentration of negatively charged acceptor-like defects such as $[V_{Ga}]^-$ and $[Cu_{Ga}]^-$. Hence, this thermal treatment will lead to the formation of excessive positive charge in the lattice, this process leading to the capture of electrons by triple-charged iron ions ($[Fe^{3+}]_{Cu} + e \Rightarrow [Fe^{2+}]_{Cu}$). Since Fe^{2+} ions at Cu-sites do not emit radiation in the measured in-

frared spectral region, the IRPL will disappear, this conclusion being in good agreement with the results obtained (Fig. 1(d)).

Thermal treatment in sulphur vapour will definitely lead to the decrease in concentration of donor-like $[V_S]^+$ defects and to the increase in concentration of acceptor-like cation vacancies $[V_{Cu}]^-$, and $[V_{Ga}]^-$, these processes being superimposed on each other and resulting in the increase of the concentration of negatively charged ionized acceptor states in the lattice. In other words this process can be interpreted as a movement of the Fermi level down towards the valence band due to the capture of electrons by newly formed acceptor-like cation vacancies. This excessive negative charge can only be compensated by the formation of cation interstitials, as well as by the change in the charge-state of iron ions, the remaining double-charged Fe ions losing their third electron and becoming triple-charged ($Fe^{2+} \Rightarrow Fe^{3+} + e$).

The increase of concentration of Fe^{3+} ions will lead to the increase of intensities of the A- and B-absorption bands, this conclusion being in good agreement with the absorption spectrum observed. On the other hand, if we assume that Fe^{3+} ions substituting Cu-sites are responsible for both absorption and PL, the intensity of the IRPL in the crystal annealed in S-vapour should increase drastically due to the increase in the concentration of Fe^{3+} ions. However, as is shown in Fig. 1(e), the intensity of the IRPL line shows no noticeable change. These results can only be explained by assuming that iron substitutes two different sites in the crystal lattice, i.e., both Cu-sites and Ga-sites with the formation of the defects Fe_{Cu}^{3+} and Fe_{Ga}^{3+}, the former being responsible for infrared PL and the latter being responsible for the absorption spectra.

§4. Conclusions

In conclusion, we have definitely proven in this paper that the Fe-related IRPL line and A,B-absorption bands in CuGaS$_2$ crystals are not optical phenomena of the same center. The iron has been found to substitute both Cu and Ga sites in the lattice, resulting in the formation of two types of optically active defects, Fe_{Cu}^{3+} and Fe_{Ga}^{3+}. The former of these defects is responsible for the sharp infrared photoluminescence line at about 2 μm, and the latter is believed to be responsible for the colouration of the crystals.

References

1) K. Tanaka, K. Ishii, S. Matsuda, Y. Hasegawa and K. Sato: Jpn. J. Appl. Phys. **28** (1989) 12.
2) T. Teranishi, K. Sato and K. Kondo: J. Phys. Soc. Jpn. **36** (1974) 1618.
3) K. Sato and T. Teranishi: J. Phys. Soc. Jpn. **37** (1974) 415.
4) K. Sato, K. Tanaka, K. Ishii and S. Matsuda: J. Cryst. Growth **99** (1990) 772.
5) S. Kobayashi, M. Koike, S. Funane, N. Tsuboi, F. Kaneko and N. Saito: Oyo Buturi **55** (1986) 507 [in Japanese].