OPTICAL CHARACTERIZATION OF TRANSITION ATOM IMPURITIES IN I-III-VI$_2$ SEMICONDUCTORS

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ABSTRACT

Optical spectra (absorption, luminescence, photoconductivity etc.) associated with several transition atom (TA) impurities in I-III-VI$_2$ chalcopyrite type semiconductors are surveyed. Recent experimental results are also presented and discussed. From these optical spectra energy levels for TA are deduced and illustrated relative to the band edges.

INTRODUCTION

Transition atom(TA) impurities have been known to introduce deep levels in band gaps of semiconductors. These levels not only control number, type and mobility of conducting carriers, but also act as activators or killers in luminescent materials.

Most of the studies on optical characterization of deep levels associated with TA-impurities have been carried out on II-VI or III-V materials[1-3]. As for TA-related levels in ternary I-III-VI$_2$ type materials, however, only a few works have been reported.

Ternary chalcopyrite crystals have several peculiarities that makes the problem more complex than binaries: The former crystals offer two crystallographically different cation sites, i.e. group I-site and group III-site, to be replaced by transition elements. Moreover, in contrast to the case of TA-doped II-VI or III-V families for which no concentrated impurity limit exists with the same crystal structure, the I-III-VI$_2$ family have their concentrated limit; i.e. CuFeS$_2$, the electronic structures of which is still in controvercy. Therefore, TA's in ternary chalcopyrite offer more important and more interesting physical problems than those in binaries. In this paper, experimental studies of TA's in I-III-VI$_2$ materials are surveyed with particular reference to their optical properties, including recent experimental results. Energy levels of TA relative to the band edges are illustrated and discussed in comparison with the case in binaries.

SURVEY AND DISCUSSIONS ON EXPERIMENTAL RESULTS

In Fig. 1 are summarized optical spectra (absorption, photoconduction and photoluminescence) of CuAlS$_2$, CuAlSe$_2$, CuGaS$_2$ and CuInS$_2$ doped with several transition atom impurities.

Two types of spectra related to TA-impurities are observed. One is so-called ligand-field transition and the other is charge-transfer transition. The former is derived from transition between atomic d^n manifolds but is modulated by hybridization with anion p-orbitals. In Table 1, crystal-field parameter 10Dq estimated from conventional analysis is listed. On the other hand, the latter transition is related to the photoionization of the impurity centers accompanied by reconstruction of the d-manifold due to the change of electronic charge. In Table 2 energies of photoionization threshold are listed for cases where the charge transfer transitions are observed.

Table 1
    Crystal field parameter obtained from ligand-field spectra of Ta in Cu-III-VI$_2$

TA	HOST	OBS. LINES	10Dq(eV)
Cr^{2+}	$CuInS_2$	$^5T_2 \rightarrow ^5E$	0.5
Mn^{2+}	$CuAlS_2$	$^6A_1 \rightarrow ^4T_1, ^4T_2, ^4E$	0.717
Fe^{2+}	$CuGaS_2$	$^5E \rightarrow ^5T_2$	0.4
Co^{2+}	$CuGaS_2$	$^4A_2 \rightarrow ^4T_1, ^4T_1$	0.533
Ni^+	$CuGaS_2$	$^2T_2 \rightarrow ^2E$	0.355

Table 2
    Photoionization threshold energy of transition atoms in Cu-III-VI$_2$ crystals.

TA	Host	Eth(eV)	REF.
Cr	$CuAlS_2$	2.50	[21]
Mn	$CuAlS_2$	2.90	[4]
	$CuGaS_2$	2.05	[4]
Fe	$CuAlS_2$	1.05	[6]
	$CuAlSe_2$	0.87	[5]
	$CuGaS_2$	1.00	[6]
	$CuInS_2$	0.80	this work
Co	$CuAlS_2$	2.36	[5]
	$CuAlSe_2$	2.17	[5]
	$CuGaS_2$	2.23	[8]
Ni	$CuGaS_2$	0.59	[24]

Iron

    Iron is the most extensively studied TA impurity in I-III-VI$_2$ compounds. Taking account of the existence of CuFeS$_2$, Fe is believed to substitute the group-III site in these comounds. EPR signals of both neutral (S=5/2) and one-electron-trapped (S=2) iron states have been observed[4,11-13]. For simplicity, the former will be denoted as Fe^{3+} and the latter as Fe^{2+} throughout this paper. But it should be noted that notation of the valency is only nominal one. Kaufmann found that the near i.r. excitation reduces the Fe^{3+} signal, while increases the Fe^{2+} signal[13].

Fig. 1 Compilation of observed absorption spectra of transition atoms in I-III-VI$_2$ chalcopyrite semiconductors.

    Strong absorption band shows up in the subgap energy region in Fe-doped crystals of CuAlS$_2$, CuGaS$_2$ and CuInS$_2$ as shown in Fig. 1[6]. Due to large oscillator strength, this absorption causes coloration of CuAlS$_2$ and CuGaS$_2$ crystals even with only 10 ppm trace impurity of Fe[14].

    The absorption band has been assigned to the charge transfer transition from the valence orbitals to the 3d-origined orbitals of Fe-atom[15]; in other words it may be interpreted as the $Fe^{3+} \rightarrow Fe^{2+}$ photoionization transition. The threshold energy of the photoionization absorption is nearly 1.0 eV indicating that one-electron trapped acceptor state in substitutional iron lies 1.0 eV above the top of the valence band. In Fe-doped CuInS$_2$ such
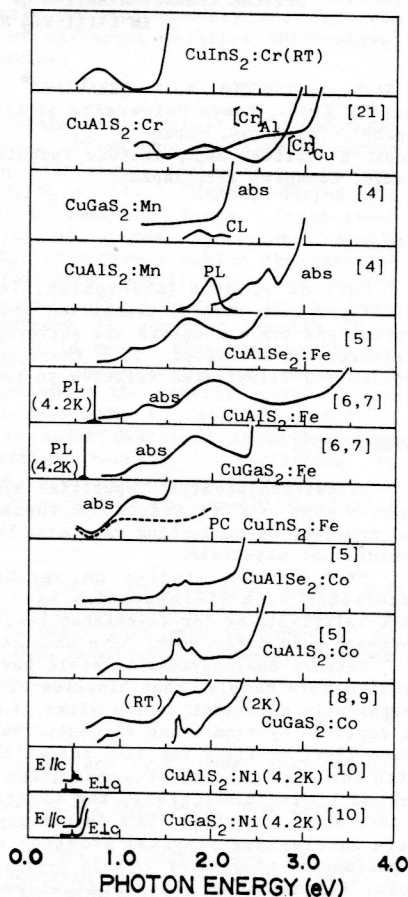
photoionization occurs at 0.8 eV. Remarkable resemblance has been observed beween optical absorption spectra of the diluted-impurity limit, e.g. $CuGaS_2$:Fe and that of the concentrated-limit, $CuFeS_2$[16].
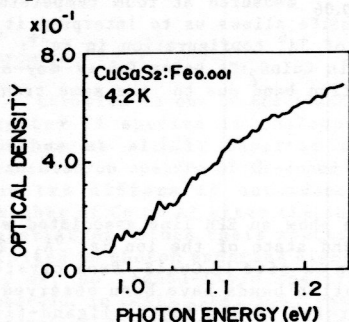

Fig. 2 Fine structures of charge-transfer absorption band oberved in $CuGaS_2$ at 4.2 K showing multiphonon character of this band.
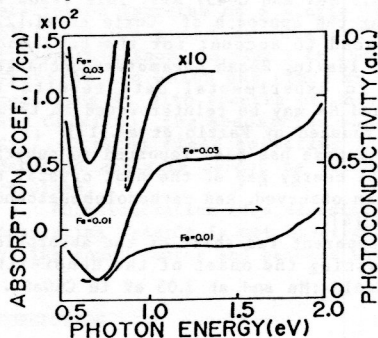

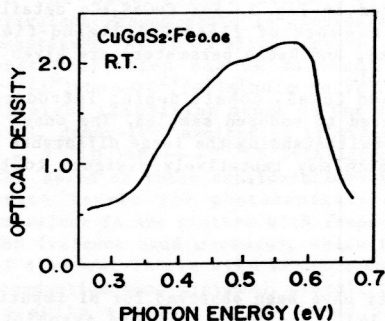Fig. 3 Absorption and photoconductivity spectra of Fe-doped $CuInS_2$.

Fig. 4 Absorption spectrum of $CuGaS_2$ doped with 6mol% Fe at room temperature.

Temperature dependence of the electrical resistivity in Fe-doped $CuInS_2$, however, locates the acceptor level at 0.076 eV above the top of the valence band. This large discrepancy may be attributed to multiplet correction[17] for the photoionization transition. The intensity of the photoionization absorption band is much reduced by annealing in vacuo. Such annealing produces cation vacancy, which raises the Fermi level above Fe^{2+} level and reduces the occupation of Fe^{3+}, which in turn decreases the $Fe^{3+} \rightarrow Fe^{2+}$ absorption. This situation is just like the case of GaAs:Cr, where Cr^{3+}/Cr^{2+} ratio depends on the position of the Fermi level[18].

The photoionization transition shows up as considerably broad absorption band indicating the importance of the coupling with lattice. This is supported by our 4.2 K absorption spectrum in $CuGaS_2$:Fe as shown in Fig. 2, in which the photoionization is accompanied by multiphonon structures[19]. .

The transition also gives rise to photoconduction as shown for the case of $CuInS_2$:Fe in Fig. 3. The threshold energy of photoconduction due to the photoionization is nearly the same as that of optical absorption.

Sharp photoluminescence(PL) peak accompanied by phonon side lines has been observed in $CuGaS_2$ and $CuAlS_2$ doped with Fe at about 0.6 eV and 0.7 eV, respectively[7]. Well-defined sixfold-split Zeeman spectrum observed in $CuGaS_2$:Fe has been explained in terms of $^4T_1$ to $^6A_1$ transition in $3d^5$ multiplets. However, the PL energies for $^4T_1$ are too low compared with the energy (about 2 eV) of $^4T_1$ in Mn^{2+} in $CuAlS_2$.

The reduction of the transition energy in $CuGaS_2$:Fe was explained by Kambara and his colleagues in terms of configuration interaction between the ligand-field multiplets and the charge transfered states[9]. On the other hands, in $CuAlS_2$:Mn, configuration mixing is negligible because photoionization excitation band is far apart

in energy.

As stated in the previous section EPR experiment has revealed that iron can also be divalent in $I-III-VI_2$ host. Fig. 4 illustrates an infrared absorption spectrum observed in $CuGaS_2:Fe_{0.06}$ measured at room temperature. Similarity of the spectrum with that of ZnS:Fe allows us to interpret it as due to the transition between multiplets of $3d^6$ configuration in Fe^{2+}: $^5E \rightarrow ^5T_2$. The increase of absorption observed in $CuInS_2$:Fe below 0.6 eV may also be associated with the tail of the absorption band due to the same transition.

Manganese

Manganese in $CuAlS_2$ has been known to show an EPR line associated with the divalent manganese indicating the ground state of the ion is $^6A_1$ [21]. The Mn^{2+} ion is believed to substitute the Cu-site in $CuAlS_2$ from crystal-radii consideration. Several weak absorption bands have been observed as shown in Fig. 1. These have been interpreted as due to the ligand-field transitions associated with Mn^{2+} center: $^4T_1$ at 2.21 eV, $^4T_2$ at 2.38 eV and $^4A + ^4E$ at 2.59 eV[4]. Strong red photoluminescence band has been observed with a peak at 1.96 eV, whose excitation spectrum agrees with the weak absorption bands. Conventional ligand-field theory provides crystal-field and Racah parameters as follows: 10Dq=0.717 eV, B=41.5 meV and C=437 meV. This leads to an unusually large value of C/B. Following the approach of Curie et al.[22] reduction factors Nt and Ne was introduced to account for the covalency effect, by which one can fit the spectrum leaving Racah parameters unchanged from their free ion values. Best fit to experimental data results in 10Dq=0.744 eV, Nt=0.926 and Ne=0.966. Nt and Ne may be reinterpreted in terms of the orbital deformation parameters introduced by Fazzio et al.[17].

On the other hand, in $CuGaS_2$:Mn, manganese has been reported to substitute both Cu and Ga sites[23]. Due to small energy gap of the host crystal no ligand-field absorption spectra has been observed. Red cathodolumunescence possibly due to $^4T_1 \longrightarrow ^6A_1$ shows up instead[4].

These absorption spectra exhibit an apparent red shift of the absorption edge amounting as large as 0.3 eV, suggesting the onset of the donor-like photoionization transition at 2.9 eV in $CuAlS_2$:Mn and at 2.05 eV in $CuGaS_2$.

Cobalt

EPR analyses suggest Co is also divalent in $CuAlS_2$ and $CuGaS_2$ crystals; i.e. the ground state is $^4A_2$[24]. Typical ligand-field absorption spectra have been observed as illustrated in Fig. 1. For $CuGaS_2$:Co detailed analysis has been performed in the framework of classical ligand-field theory, from which crystal-field parameter and Racah parameters are given as 10Dq=0.533 eV, B=62 meV and C=310 meV[8,9].

In either of $CuAlSe_2$[5], $CuAlS_2$ and $CuGaS_2$ cobalt doping introduces large red shift of absorption edge compared to undoped samples. The onset of absorption begins around 2.2-2.3 eV notwithstanding the large difference of energy gaps in these three crystals, which may tentatively assigned to the donor-like photoionization threshold.

Nickel

Both monovalent and trivalent states have been observed for Ni impurity in chalcopyrite by EPR measurements[10,24]. Absorption spectra associated with ligand-field transition have been reported for $CuAlS_2:Ni^+$, $CuGaS_2:Ni^+$ and $AgGaS_2:Ni^+$[10]. Broad structureless absorption band extending between

0.59 and 1.9 eV has been observed in $CuGaS_2$:Ni. This transition may be assigned to $Ni^{3+} \longrightarrow Ni^{2+}$ photoionization transition in Ni substituting Ga-site.

Chromium

Chromium is one of the least investigated TA species in chalcopyrites. Donohue et al.[21] reported optical transmission spectra of Cr-doped $CuAlS_2$. Spectra differs in accordance with whether of Cu or Al sites the chromium substitutes. Since their spectrum was limited to photon energies higher than 1.2 eV, no ligand-field spectra were observed. In $CuAl_{0.99}Cr_{0.01}S_2$ sample an absorption threshold is observed at 2.5 eV which may be assigned to the onset of donor-like transition associated with Cr.

Recently, we measured an optical absorption spectrum on a single crystal of $CuInS_2$:Cr grown by chemical vapor transport method. In Fig. 5 is shown the spectrum, in which one finds an absorption band with a peak at 0.7 eV. By comparing it with spectra of chromium-doped II-VI compounds, eg. ZnS, ZnSe and CdTe[25], the absorption band is assigned to $^5T_2 \longrightarrow ^5E$ transition in Cr^{2+}. Crystal field splitting is estimated to be around 0.5 eV although detailed analysis cannot be performed because no fine structures have been resolved.

Photoionization edge associated with $Cr^{3+} \longrightarrow Cr^{2+}$ as seen in p-type semi-insulating GaAs:Cr is not observed. This indicates that Cr acts as a compensating donor center and becomes divalent in this material.
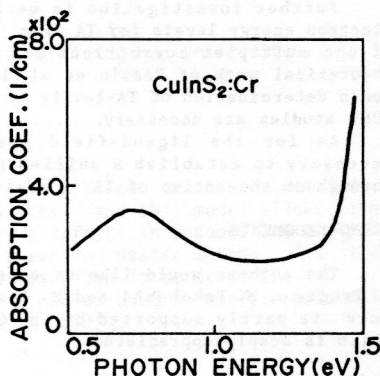
Fig. 5 Absorption spectrum of $CuInS_2$ doped with 1mol% Cr at room temperature.

CONCLUSION

In Fig. 6 TA-related levels in (a)$CuAlS_2$ and (b)$CuGaS_2$ obtained from the experiments are illustrated relative to the band edges. Since TA with trivalent ground state is considered to substitute Al or Ga site, acceptor-like photoionization can be assumed; i.e. $T^{3+}(A^0)+h\nu \longrightarrow T^{2+}(A^-)+(\text{hole in VB})$. For divalent transition atom, on the other hand, donor-like excitation is expected; i.e. $T^{2+}(D^-)+h\nu \longrightarrow T^{3+}(D^0)+(\text{electron in CB})$. Based on these considerations final state levels for photoionization of trivalent TA are plotted with respect to VBM (valence band maximum), while those of divalent TA are with respect to CBM (conduction band minimum). Overall trend is quite similar to the trend of TA levels in GaP[3] as well as the trend of donor levels predicted theoretically for CdS by Vogl[26].
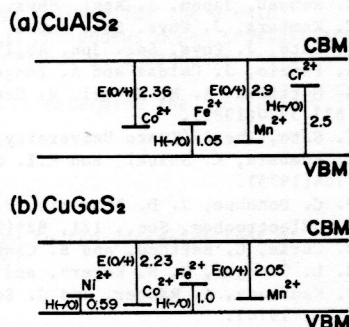
Fig. 6 Location of gap-levels introduced by transition atom impurities in (a)$CuAlS_2$ and (b)$CuGaS_2$ determined from optical measurements.

We, therefore, conclude that TA levels in I-III-VI$_2$ chalcopyrite semi-conductors are quite similar to those in binary semiconductors despite some peculiarities inherent to ternary materials.

Further investigation is necessary to calculate the effective one-electron energy levels for TA from these experimental levels, taking account of the multiplet corrections and Mott-Hubbard correlations just as the theoretical work of Fazzio et al.[17]. From experimental view point unambi-guous determination of TA-levels by other means such as DLTS, ICTS, DLOS and ODMR studies are necessary.

As for the ligand-field spectra further theoretical studies are necessary to establish a unified picture for the evaluation of covalency throughout the series of TA in chalcopyrites.

ACKNOWLEDGMENTS

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