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OPTICAL AND ESR CHARACTERIZATION OF IRON IMPURITY IN Cu-III-VI₂ SEMICONDUCTORS

Results of characterization of iron impurity in I-III-VI₂ chalcopyrite type crystals by means of infrared optical absorption and ESR spectroscopies are described.

1. INTRODUCTION

Transition atom (TA) impurities have been known to introduce deep levels in the band gaps of semiconductors, including the ternary ones, these levels not only taking part in the processes of electrical charge compensation and, therefore, controlling the concentrations and type of conducting carriers, but also acting as activators or killers of luminescence (SATO et al.) The optical absorption and luminescence properties of ternaries depend greatly on the charge states of the TA impurities, which, therefore, can be determined from the optical measurements.

Iron is known to be a dominant residual TA impurity in the ternary compounds of the type Cu-III-VI₂, with chromium and nickel being the second and third contaminant, respectively. In this paper we report the results of the studies of the iron impurity in a row of Cu-III-VI₂ (III = Al, Ga, In, VI = S, Se) ternary compounds by both optical and ESR methods. Both divalent and trivalent states of Fe ion have been detected, the relative concentrations of Fe²⁺ and Fe³⁺ being determined by the energy position of the Fermi level relative to the band gap edges of the host compound.

2. EXPERIMENTAL

Single crystals of the ternary compounds were grown by the chemical vapor transport (CVT) technique in a closed system using iodine as a transporting agent, as well as, only in the case of CuInSe₂, by the normal freezing method (ENDO et al.) The powders of the corresponding compound, obtained by the direct melting of the constituent elements in a BN crucible held in a sealed quartz ampoule, were used as source materials for CVT.

Thermal annealings of the as-grown crystals in vacuum, chalcogen vapor and in the presence of Cu were carried out for 50 hr at 650°C. The obtained samples were characterized by the thermal probe and four-probe methods to determine their resistivities and conductivity type.

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respectively, as well as by the electron probe microanalysis (EPMA) to determine their composition.

Optical absorption measurements were carried out at room temperature (RT) by using a BOMEM Type MB100 Fourier Transform IR spectrometer for middle-IR region and a HITACHI Type U-3410 Spectrophotometer for near-IR to visible wavelengths. ESR spectra were taken at 4.2 - 300 K with a JEOL JES-RE2X X-band spectrometer with the microwave power of 5 mW.

3. RESULTS AND DISCUSSION

3.1 IR absorption

The IR absorption spectra of the CVT-grown crystals have been found to exhibit no remarkable features in all the compounds investigated. Annealing of the crystals in vacuum, however, results in an appearance of broad IR bands in CuInSe_2 , CuInS_2 , and CuGaS_2 crystals as shown in Fig. 1. The absorption is peaked at about 3300 cm^{-1} in CuInSe_2 , 4000 cm^{-1} in CuGaS_2 , and is split into two partially resolved subbands peaked at 3200 cm^{-1} and 3900 cm^{-1} in the case of CuInS_2 . The absorption bands, shown in Fig. 1, have been attributed to the Fe^{2+} impurity occupying Cu or group-III sites in the crystal lattice of the ternaries. This assumption is supported by the results of the previous studies of the binary semiconductors, where the Fe^{2+} ion has been found to exhibit a broad absorption centred, for example, at about 3400 cm^{-1} for ZnS (VOGEL et al.). Taking into account also the ESR results, which will be discussed below, we attribute the IR absorption bands to the intrasystem optical transitions ${}^5E \Rightarrow {}^5T_2$ in the Fe^{2+} ion having $3d^6$ electronic configuration.

Since the point symmetry surrounding the Fe^{2+} ion in chalcopyrite lattice is regarded as D_{2d} , the energy levels of the ion can be obtained from the Hamiltonian as

$$H = H_0 + H_{\text{CF}}(T_d) + H_{\text{CF}}(D_{2d}) + H_{\text{LS}} \quad (1)$$

where H_0 is the free ion Hamiltonian, $H_{\text{CF}}(T_d)$ and $H_{\text{CF}}(D_{2d})$ represent the energy of the cubic and tetragonal components of the crystal field, respectively, and H_{LS} is the energy of the spin-orbit interaction. For the Fe^{2+} ion we have

$$H_0(\sim 10^4 \text{ cm}^{-1}) > H_{\text{CF}}(T_d) > H_{\text{CF}}(D_{2d}) > H_{\text{LS}}(\sim 10^2 \text{ cm}^{-1}). \quad (2)$$

We believe that the energy of the low symmetry crystal field $H_{\text{CF}}(D_{2d})$ for Fe^{2+} is greater than that of the spin-orbit interaction since, if the energy H_{LS} had been greater than $H_{\text{CF}}(D_{2d})$, the spin-orbit interaction would have resulted in the non-Kramers singlet ground state of the system. (LOW et al.) Therefore, we would not have any ESR signal from the Fe^{2+} ion, which is contrary to our experimental results discussed below.

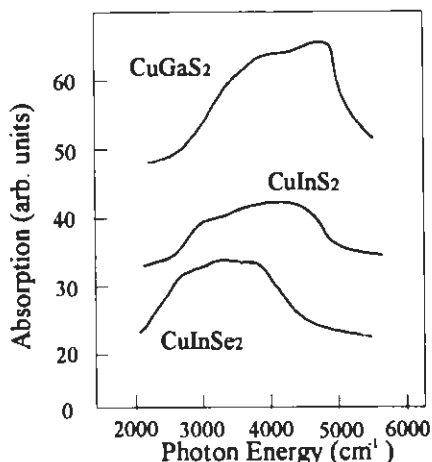


Fig. 1 IR absorption spectra in vacuum-annealed Cu-III-VI₂ crystals

Consequently, we consider the effect of various interactions on the Fe^{2+} ion in the order of (2), with the resulting splitting of the lowest free ion term 5D of Fe^{2+} shown in Fig. 2. For the Fe^{2+} ion we can expect only one spin-allowed ligand-field transition from the ground state 5E to the first excited state 5T_2 , with all the other higher energy transitions being spin-forbidden and, therefore, of much less probability. From the spectral position of the baricenters of the IR absorption bands due to Fe^{2+} (Fig. 1) we can get a rough estimate of cubic crystal-field parameters Dq as being 330 cm^{-1} for CuInSe_2 , 350 cm^{-1} for CuInS_2 , 400 cm^{-1} for CuGaS_2 , which are close to the value of Dq estimated for CuAlS_2 (360 cm^{-1}) from the ESR measurements (KAUFMANN, 1976)

3.2 ESR

The ESR spectra for the Fe^{3+} impurity in all S-containing compounds studied (Fig. 3) exhibit a well-known 5-line fine structure transitions of an ion with $3d^5$ -configuration, occupying lattice sites of the tetragonal symmetry (the spin Hamiltonian contains the terms corresponding to the cubic and axial components of the crystal field). (BRANDT et al.)

To the contrary, the Fe^{3+} -originated signal of Se-containing compounds (Fig. 4) exhibits several anisotropic lines with $g \sim 2 - 6$ together with a nearly isotropic line at $g \sim 4.3$, resulting from transitions within three Kramers doublets split from the sixfold-degenerate ${}^6S_{5/2}$ ground state of Fe^{3+} due to the effect of a strong noncubic crystal field containing both axial and rhombic components. (HOLTON et al.)

The Hamiltonian of the Fe^{3+} ion in the non-cubic crystal field reads

$$H = g \beta H S + D[S_z^2 - 1/3S(S+1)] + E(S_x^2 - S_y^2) \quad (3)$$

where D and E are parameters of the axial and rhombic components of the crystal field, respectively.

Both the axial and rhombic components of the ligand field cause the splitting of the sixfold-degenerate ground state ${}^6S_{5/2}$ of Fe^{3+} into three Kramers doublets, resulting in the possibility of observation of the ESR signal. The solutions of the above Hamiltonian depend on the parameter $\lambda = E/D$, describing the relative strength of the axial and rhombic terms of the crystal field. If $E \gg D$, we should observe a nearly isotropic signal near $g = 4.3$, which is in accordance with our results and has also been observed for Fe^{3+} -X pairs in AgGaS_2 . (VON

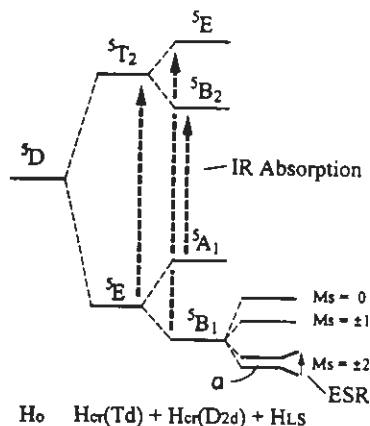


Fig. 2 Energy diagram of $3d^6$ system in chalcopyrite lattice

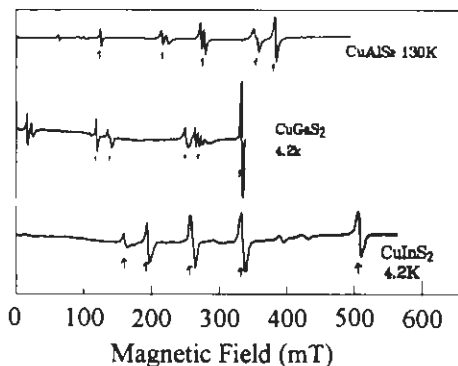


Fig. 3 ESR spectra of Fe^{3+} in Cu-III-S₂ crystals

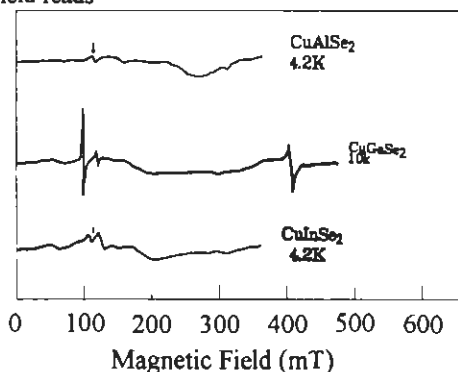


Fig. 4 ESR spectra of Fe^{3+} in Cu-III-Se₂ crystals

BARDELEBEN et al.) For the second limiting case, when $E \ll D$, we may expect an anisotropic signal consisting of several lines with g -values in the range 2 – 6, which has also been detected in our CIS crystals.

Annealing of the crystals in vacuum results in a quenching of the Fe^{3+} -originated signal and in an appearance of a highly anisotropic signal as shown in Fig. 5 for the case of CuInSe_2 . The annealing in the presence of Cu partly quenches the Fe^{3+} -related signal and also leads to an appearance of the I-signal, whereas annealing in Se-vapor results in quenching of the I-signal and reappearance of the Fe^{3+} -related signal.

The highly anisotropic I-signal with the peak-to-peak line width $\Delta H_{pp} = 4$ mT, the effective g -factor of which takes its maximum value of $g_{\text{eff}} = 9.5$ (CuAlS_2), $g_{\text{eff}} = 14.5$

(CuInS_2) and $g_{\text{eff}} = 28.7$ (CuInSe_2) when the tetragonal c -axis of the crystal is parallel to the external magnetic field ($g_{\text{eff} \perp} \sim 0$ for this signal), has also been observed by other authors in both CuAlS_2 (Kaufmann 1976) and CIS (TCHAPKUI-NIAT et al.), and has been attributed to the substitutional divalent iron impurity, the signal originating from the magnetically allowed microwave transitions $+2 \leftrightarrow -2$ within the lowest $M_S = \pm 2$ non-Kramers doublet in Fe^{2+} . Crystal-field theory predicts the value of $g_{\parallel} = g_e - 8k\lambda_0/10Dq$, where k is the covalency reduction factor and g_e is the free electron g -factor. Therefore, we can obtain the values of g_{\parallel} using the value of Dq from the IR absorption results, discussed in the previous section. With $k=0.8$ and $\lambda_0 = -100 \text{ cm}^{-1}$ we find $g_{\parallel} = 2.194$. This value is quite consistent with the values of g_{\parallel} obtained from g_{eff} using an expression $(h\nu)^2 = (4g_{\parallel}\beta H)^2 + \alpha^2$ for the transition within the $M_S = \pm 2$ doublet, (ABRAHAM et al.) the resulting values of g_{\parallel} being 2.19, 2.20 and 2.19 for CuAlS_2 , CuInS_2 and CuInSe_2 , respectively.

The observed changes in the optical and ESR spectra of the crystals, caused by thermal treatments in various atmospheres, can be explained by the annealing-induced motion of the Fermi level relative to the energy bands edges. The Fe impurity whose energy is near the position of the Fermi level in the band gap of a semiconductor will gain or lose electrons as the Fermi level passes through the demarcation level delineating Fe^{2+} and Fe^{3+} of this defect, thus leading to the change in the charged state, which in turn introduces changes in optical and ESR spectra. (AKSENOV et al. 1992)

References

- ABRAHAM, A. and PRYCE, H.M.L.: Proc. R. Soc. London Ser. A **205** (1951) 135.
 AKSENOV, I. and SATO, K.: Jpn. J. Appl. Phys. **31** (1992) 2352.
 BRANDT, G., RAÜBER, A. and SCHNEIDER, J.: Solid State Commun. **12** (1973) 481.
 ENDO, S., IRIE, T. and NAKANISHI, H.: Solar Cells **16** (1986) 1.
 KAUFMANN, U.: Solid State Commun. **19** (1976) 213.
 HOLTON, W. C., DE WIT, M., ESTLE, T. L., DICHER, B. and SCHNEIDER, J.: Phys. Rev. **169** (1968) 359.
 LOW, W. and WEGER, M.: Phys. Rev. **118** (1960) 1119.
 SATO, K., TSUNODA, H. and TERANISHI, T.: Proc. 7th Int. Conf. Ternary & Multinary Compounds, Snowmass, 1986 (Mater. Res. Soc., Pittsburgh, 1987) p. 459, and references therein.
 TCHAPKUI-NIAT, J.M., GOLTZENE, A. and SCHWAB, C.: J. Phys. C: Solid State Phys. **15** (1982) 4671.
 VOGEL, E. E., MUALIN, O.M., DE ORUE, A. and RIVERA-IRATCHET, J.: Phys. Rev. **B 44** (1991) 1579.
 VON BARDELEBEN, H.J., GOLTZENE, A., SCHWAB, C. and FEIGELSON, R.S.: Phys. Rev. **B 5** (1980) 1757.

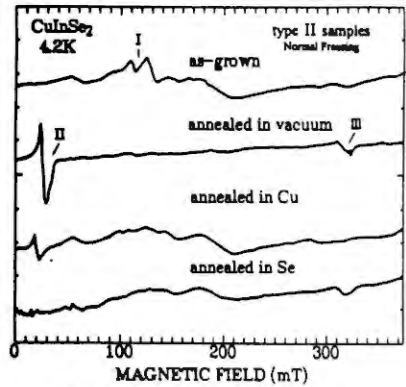


Fig. 5 Variation of ESR spectra by annealings