Pressure Dependence of Photoluminescence Spectra in CuAlS₂ Doped with Lanthanide

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Pressure and temperature dependence of photoluminescence(PL) spectra of ternary compound semiconductor $CuAlS_2$ doped Er and Fe are measured. Under hydrostatic pressures, PL peaks originated in transitions of 4f electrons in Er shift to lower energy and new sharp peaks appears. These results are discussed in terms of crystalline fields and spin-orbit interaction. The broad peak assigned as self-activated (SA) PL shifts to high energy under high hydrostatic pressures which coefficient is the same sign and order as that of band gap of chalcopyrite type $I-III-VI_2$ compounds. This result indicates that SA PL is related to Bloch bands.
[chalcopyrite, $CuAlS_2$, Er, photoluminescence, high pressure]

1. Introduction

Ternary compound semiconductors $I-III-VI_2$ of chalcopyrite type have been intensively investigated as candidates for host materials of solar-cells, nonlinear-optical-materials and full-color emitting diode. Among the chalcopyrite, $CuAlS_2$ is stable and its band gap is in the ultraviolet region as 3.49eV(at RT). The lanthanide elements are expected to be guest materials for full-color electro-luminescence devices.

In PL spectra of chalcopyrite doped lanthanide there are two types. One of them is originated in intra-atomic transitions between 4f-multiplets in lanthanide and the other is originated in extended states or impurity levels associated with Bloch electrons. The former is resulting from the electronic dipole transitions between 4f-multiplet states with LS coupling and crystalline fields in lanthanide ions [1,2,3].

In these materials broad photoluminescence(PL) and sharp one exist at the same energy region. And the relative intensities are very sensitive to the excitation energy and their observation temperatures. In order to investigate the origin of these PL and the energy relaxation in the excited states, we measure the pressure and temperature dependence of PL spectra in $CuAlS_2$ doped Er or Er and Fe.

2. Experimental

Two different type of samples are prepared. One ($CuAlS_2$:Er) is doped Er only and the other ($CuAlS_2$:Er Fe) is doped two elements of Er and Fe. In $CuAlS_2$ there are often Fe impurities without intentional doping. In the later, Fe is doped intentionally to compensate for the lack of charge neutrality resulting from the Er^{3+} states of Cu^+ site by changing the valence of Fe ion occupying Al site from trivalent to divalent. The former single crystal is prepared by direct melting of $CuAlS_2$ and Er, and the latter is grown by chemical vapor transports.

They are polished to thin slice of about 0.1mm and cracked into small pieces of about 0.3mm square. One of them is placed in diamond anvil cell together with ethanol-methanol mixed solution and a small piece of ruby. The applied pressure is measured by ruby scale. As excitation sources, we use lights (mainly 365nm) of 150W super-high-pressure Hg lamp with UV-pass filter. The excitation energy of 365nm is a little lower than band gap of $CuAlS_2$. The incident lights are focused on (1,1,2) surface of the thin plate. We use backscatering configuration. For detection, we use a double monochromator and photon counting system. The experimental results are obtained up to 2.7GPa and 4.2K.

3. Results and Discussion

Figure 1 shows typical PL spectra of $CuAlS_2$:Er and $CuAlS_2$: Er Fe at RT and 1 atm. The trivalent ion Er^{3+} in $CuAlS_2$ has 11 electrons in 4f-shell. In the region of Fig.1, PL spectra consist of a broad peak and two groups including several sharp lines. This broad peak is so called SA PL. And sharp PL lines in these groups are considered to originate in transitions between energy levels of intra-4f-shell. One around 2.34eV is named as A and the other around 2.26eV is as B. From Dieke diagram [4], A is assigned as $^2H_{11/2}-^4I_{15/2}$ transitions and B as $^4S_{3/2}-^4I_{15/2}$ transitions[3].
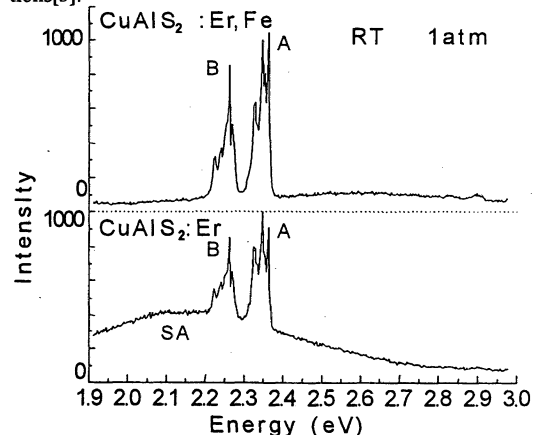

Fig.1.   Photoluminescence   spectra   of $CuAlS_2$:Er   and $CuAlS_2$:Er,Fe

In the case of $CuAlS_2$:Er,Fe, SA PL is very weak and the PL intensity of A and B is stronger than in $CuAlS_2$:Er. The reason of this fact is considered that content of Er is large and intentionally doped Fe act as center of nonradiative and infrared transition. [3]

a) Emissions of intra-4f-shell transitions

Figure 2 shows PL spectra under various pressures. At 1atm. Here four sharp peaks exist mainly in the group A (A1, A4, A5, A6), and six peaks are in the group B(B1 to B6). Details of the structures are shown in Fig. 3. Generally, as the origin of sharp lines we can consider phonon side bands and split levels by crystalline fields. As the interaction between 4f electrons and phonons is very weak in semiconductors, almost of the observed PL lines relating to 4f electrons are zero phonon lines. Thus the observed fine structures of PL are considered as PL between levels split by crystal fields of host material and by LS coupling. But the contribution of phonons is not disregarded as some of phonon energy of $CuAlS_2$ is close to the interval of sharp peaks [5] and broader lines are mixed in the structure.
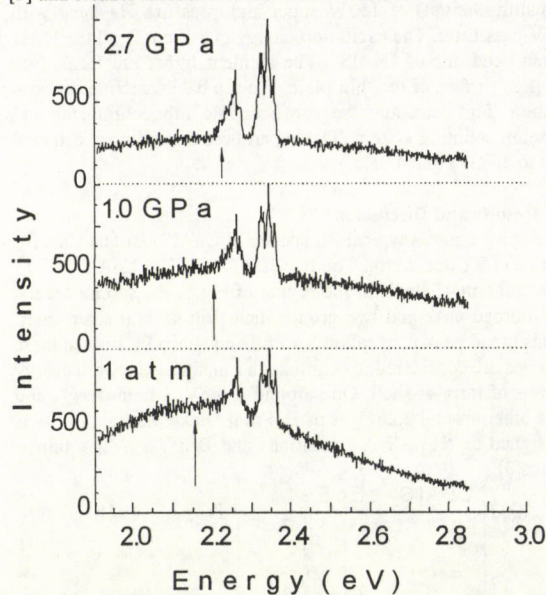

Fig.2. Photoluminescence spectra of $CuAlS_2$:Er under various pressures at room temperature.

From D_{2d} symmetry around Er ion in $CuAlS_2$ lattice, $^4I_{15/2}$ splits into 8 levels (4 Γ^6 + 4 Γ^7), $^2H_{11/2}$ splits into 6 levels (3 Γ^6 + 3 Γ^7), and $^4S_{3/2}$ splits into 2 levels (Γ^6 + Γ^7). The optical transitions between all split levels are allowed for the polarization of PL lights parallel to z axis, and between Γ^6 and Γ^7 for the polarization perpendicular to z axis. Then 48 peaks are expected in the group A, but it is considered that some of these lines overlap each other. Increasing applied pressures, these sharp peaks shift to low energy and some new sharp peaks (A2,A3) appear. Similar features are also observed in the group

B.

The obtained pressure coefficients of sharp peaks are -0.6 ± 0.1 meV/GPa for A4 and -0.5 ± 0.1 meV/GPa for B5 under hydrostatic pressures. At 2.7Gpa, spectral line width differs clearly from that of other pressure. We consider the host lattice around Er distorts strongly from the inhomogeneity of pressures above 2GPa. The obtained negative pressure coefficient is caused by the effect of crystalline fields and spin-orbit coupling of 4f-electrons in Er.
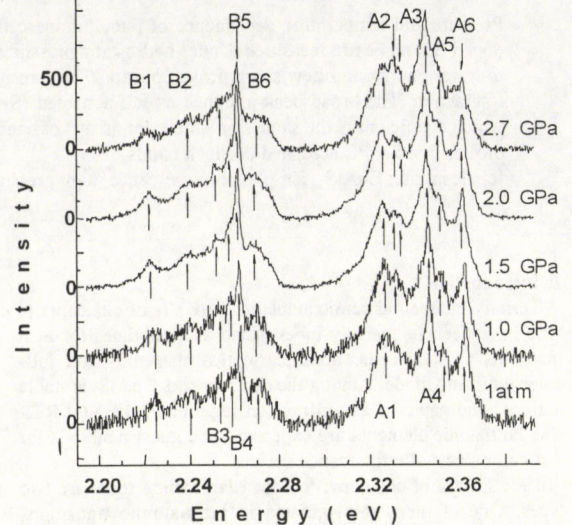

Fig.3. Detail photoluminescence spectra of the groups A and B of $CuAlS_2$:Er under various pressures at room temperature.

According to the theory of Judd and Ofelt [6,7], intensity of emission of intra-4f-shell transitions is given by next formula.

$$\Sigma_{\lambda=2,4,6} T_\lambda \, \nu \mid < \Psi_{\text{excited}} \parallel U^{(\lambda)} \parallel \Psi_{\text{ground}} > \mid^2 / (2J+1)$$

In this formula, $U^{(\lambda)}$ is tensor operator depending on crystalline fields, T_λ is a constant which characterizes Er , and ν is a function of number characterizing spherical functions. For the group A, three terms of $\lambda=2$, $\lambda=4$ and $\lambda=6$ have non-zero values. but for the group B, only one term of $\lambda=6$ has non-zero value. As the operator $U^{(2)}$ depends more strongly on crystalline fields than $U^{(4)}$ and $U^{(6)}$, we consider that one of the reasons for appearance of new peaks as A2 and A3 is lattice distortion around Er ions under high pressures.

Figure 4 shows PL spectra of $CuAlS_2$:Er,Fe at RT. and 4.2K under 1atm. At 4.2K, the intensity of peaks of A decreases and all peaks disappear almost, but many peaks are observed at the region of peaks B1 to B5. Peak B5 increases its intensity but the peak B6 is not observed at 4.2K. At RT. the peaks B1 to B4 is considered that they consist of a few peaks overlapped each other. The line width of B5 is less than 0.1meV at 4.2K, but two peaks at B1 is 0.5meV and 0.8meV. The number of peaks observed at 4.2K is not less than 20 but it is larger than number of

zero phonon lines 16 estimated from group theory. It is concluded that the group B consists not only zero phonon lines of $^4S_{3/2}$-$^4I_{15/2}$ transition.

At low temperatures PL of the group A disappears but the group B's one becomes stronger relatively. It is considered that the nonradiative transition from $^2H_{11/2}$ is efficient as the transition energy is close to the energy difference of donor and acceptor states.
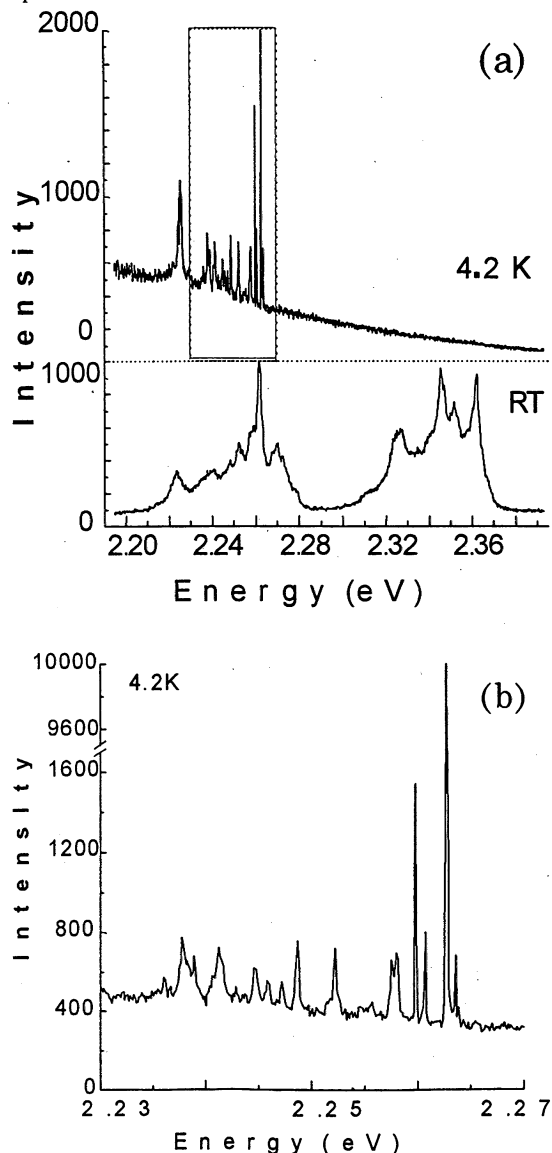

Fig.4. (a)Photoluminescence spectra of CuAlS$_2$:Er,Fe under 1atm at 4.2K and RT.
(b) The detail spectrum of the part enclosed by rectangular

in the upper Fig. (a) at 4.2K.

b) Self-activated photoluminescence

The origin of SA PL is estimated as donor-acceptor pair recombination because peak of excitation spectra lies at band gap and time resolution spectra shifts lower energy as time [8,9]. As the broad PL overlaps with sharp PL peaks, we subtract sharp emission lines from data and fit its line shape to Lorentzian for determination of its peak position. Increasing applied pressures, the peak shifts to high energy and decrease its intensity compared to 4f emissions. The pressure coefficient of SA PL is 24±4meV/GPa. This value is almost the same sign and magnitude as that of energy gaps of I-III-VI$_2$ compounds of chalcopyrite structure [10]. The energy levels relating to SA PL shift with energy gap of host crystal. The decrease of this PL intensity is caused by the energy shift of band gap to high energy under high pressures. The separation of exciting energy and band gap energy becomes large and the band gap excitation is ineffective but the intra-4f-shell transitions has almost no change.

4. Conclusion

We measured pressure and temperature dependence of photoluminescence of CuAlS$_2$:Er and CuAlS$_2$:Er,Fe. The spectra consist of SA PL and emissions A and B associated with intra-4f-shell transition. From red shifts of peaks of A and B, and appearance of new sharp peaks under high pressures, it is considered that crystalline fields and spin orbit coupling are varied by pressures. At least 20 peaks are observed in the region of emission B at 4.2K, and this shows the emission B is not consists of all zero phonon lines of $^4S_{3/2}$-$^4I_{15/2}$ transitions. And from the pressure coefficient of peak energy of SA PL , it is confirmed that the broad peak is related to the band gap of host chalcopyrite.

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