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〈연구논문〉

Photoluminescence Properties of Ni-doped and Undoped $CdGa_2Se_4$ Single Crystals

Chang-Dae Kim, Hae-Mun Jeong, Dong-Ho Shin and Wha-Tek Kim*

Department of Physics, Mokpo National Univeristy, Mokpo 534-729, Korea
**Department of Physcis, Chonnam National University, Kwangju 500-757, Korea*
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Ni-Doped $CdGa_2Se_4$ 및 Undoped $CdGa_2Se_4$ 단결정의 광발광 특성

김창대 · 정해문 · 신동호 · 김화택*

목포대학교 자연과학대학 물리학과, *전남대학교 자연과학대학 물리학과
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Abstract—PL and PLE spectra of Ni-doped and undoped $CdGa_2Se_4$ single crystals grown by the iodine transport technique have been investigated. In the PL spectra of undoped $CdGa_2Se_4$ two emission bands with the maxima at energies 2.13 and 1.20 eV are observed. The emission band at 2.13 eV is attributed to radiative transitions from quasi-continuously distributed traps below the bottom of the conduction band to an acceptor level at 0.07 eV above the valence band. Also, the emission band of 1.20 eV is assigned as DA (donor-accptor) pair recombination between a deep donor level and an acceptor level at 0.12 eV above the valence band. The emission band of 1.48 eV observed in Ni-doped $CdGa_2Se_4$ is due to intracenter transitions of Ni^{2+} ions from the excited state $^3T_1$ (^3P) to the ground state $^3T_1$ (^3F). The proposed energy band model permits ıs to explain the radiative recombinatiin processes in $CdGa_2Se_4$.

요 약—Iodine 화학수송법으로 성장한 Ni-doped $CdGa_2Se_4$와 undoped $CdGa_2Se_4$ 단결정의 PL 및 PLE 스펙트럼을 조사하였다. Undoped $CdGa_2Se_4$ 단결정의 PL 스펙트럼에서는 전도대아래 준연속적으로 분포된 electron trap과 deep donor level, 그리고 가전자대 위 0.07 eV, 0.12 eV에 있는 acceptor level 사이의 전자전이에 의한 2개의 emission band를 2.13 eV와 1.20 eV 영역에서 관측하였으며, Ni-doped 단결정에서는 Ni^{2+} 이온의 여기상태 $^3T_1(^3P)$와 바닥상태 $^3T_1(^3F)$ 사이의 전자전이에 의한 emission band를 1.48 eV 영역에서 관측하였다. 이러한 결과로부터 제안된 $CdGa_2Se_4$의 energy band model은 본 연구의 PL mechanism을 설명하는데 가능함을 보여주었다.

1. Introduction

In earlier papers[1-3], we reported some results of optical absorption and photoconductivity on $CdGa_2Se_4$ single crystals.

$CdGa_2Se_4$ is a wide-gap material with the direct-band gap of 2.33 eV[1] at room temperature and shows n-type conductivity[3]. The dark resistivity is equal to $\sim10^{10}\Omega\cdot cm$ at 300 K[1]. Also this compound belongs to a tetrahedrally coordinated semiconductor crystallizing in the so-called thiogallate or defect chalcopyrite structure, which may be derived from the crystal structure of zincblende by the incorporation of an ordered array of vacancies, located in cationic sublattice sites[4]. It has been reported that such structural defects have a great influence on the photoconductivity and luminescence properties of this compound[5, 6] and may result in quasi-continuously distributed states within the forbidden band gap[6]. A generally accepted model of the energy levels and recombination processes in defect chalcopyrite semiconductors such as $CdGa_2Se_4$ has been proposed by Guzzi and Grilli [7]. A few papers on the photoluminescence of $CdGa_2Se_4$ have been reported[6, 8-10]. We also have investigated photoluminescence spectra related with deep levels of $CdGa_2Se_4$[11]. However, a study on the nature of localized states in the forbidden band gap of $CdGa_2Se_4$ has been made insufficiently.

The purpose of the present work is to investigate photoluminescence (PL) and photoluminescence excitation (PLE) spectra for both as-grown and annealed $CdGa_2Se_4$ single crystals in order to identify the origin of the localized states in $CdGa_2Se_4$. In addition, PL spectra of $CdGa_2Se_4$ single crystals doped with nickel-transition metal are also presented.

2. Experimental Procedure

Single crystals of $CdGa_2Se_4$ and $CdGa_2Se_4$: Ni (0.01 mole%) have been prepared by the iodine transport technique[1]. A part of these single crystals were annealed in selenium vapour at 510℃ for 1 h [12]. The PL spectra were obtained by means of the PL measurement system consisting of monochromator (Spex 1702, f=0.75 m) with 1200 grooves /mm gratings balzed at 500 and 1000 nm, PM tube (RCA, C31034), and Ge detector (North Coast, EO-817). For PL, the excitation was provided by the 488 nm-line of Ar ion laser (Spectra Physics, 2025-05). The PLE spectra were obtained by employing a 150 W xenon lamp. All the PL and PLE spectra were corrected for the spectral response of the optical system. Appropriate filters were employed in order to eliminate spurious Rayleigh-scattered light.

3. Results and Discussion

Fig. 1 presents the PL spectrum at 9 K of as-grown $CdGa_2Se_4$ single crystals. As shown in Fig. 1, two emission bands are observed at 2.13 eV (582 nm, A-band) and 1.20 eV (1030 nm, B-band). The A-band in the visible region shows almost an asymmetric Gaussian and has a halfwidth of 0.25 eV. It is to be noted that a similar band, which is connected with quasi-continuously distributed states below the bottom of the conduction band, has been earlier observed by Grilli and Guzzi[6]. The B-band in the near-infrared region is assigned as donor-acceptor (DA) pair recombination between a deep donor level and a shallow acceptor level[11].

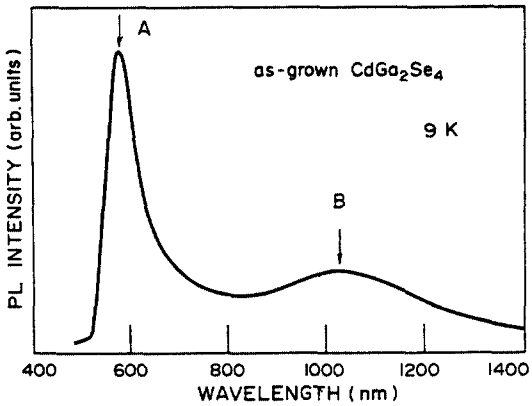

Fig. 1. PL spectrum of undoped $CdGa_2Se_4$ single crystals at 9 K in the wavelength region 400 to 1400 nm.

In order to identify the origin of the A-band with the maximum at the energy 2.13 eV, we have investigated PLE spectra of as-grown and annealed $CdGa_2Se_4$ single crystals. Fig. 2 illustrates the PL and PLE spectra of these single crystals. As we can see in Fig. 2, both the PL and PLE spectra are not affected by annealing under selenium vapour. The PLE spectra of as-grown and annealed $CdGa_2Se_4$ show one excitation band with the maximum at 2.43 eV (510 nm). The energy 2.43 eV of its maximum shows a good agreement with the band gap energy of 2.48 eV at 9 K[1]. It is also seen that the PLE spectra have a low energy exponential tail of the excitation band. These facts imply that electron traps are distributed quasi-continuously below the bottom of the conduction band. The presence of the quasi-continuously distributed electron traps has also been evidenced by photo-

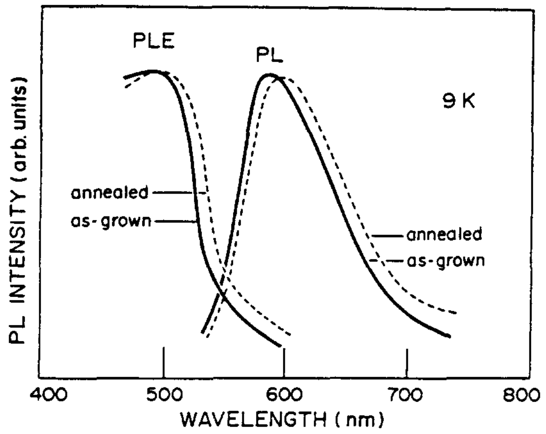

Fig. 2. PL and PLE spectra of as-grown and annealed $CdGa_2Se_4$ single crystals at 9 K.

conductivity measurements[5].

The temperature dependence of the emission intensities of the A- and B-band is shown in Fig. 3. A rapid thermal quenching of the two bands is observed above the temperature region of $T_1=70$ K for the A-band and of $T_2=100$ K for the B-band. In the high temperature regions of $T_1>70$ K, and of $T_2>100$ K, we can derive the activation energies of the PL thermal quenchng using the following relation[13]

$$I(T)=A \exp(\Delta E/kT)$$

where k is Boltzmann constant and ΔE is an activation energy. The values are then given by $\Delta E_A=0.07$ eV for the A-band and $\Delta E_B=0.12$ eV for the B-band, respectively.

On the basis of the observed results, we can propose a simple energy level scheme and electron transitions for the radiative recombination in $CdGa_2Se_4$ as shown in Fig. 4. In Fig. 4, quasi-continuously distributed electron traps T are presented below the bottom of the conduction band and two shallow acceptor levels A_1 and A_2 are given at 0.07 eV and 0.12 eV above the valence band. Thus it is explained that the A-band at 2.13 eV is due to radiative electron transitions from the electron trap center T to the acceptor level A_1 at 0.07 eV above the valence band. At the same time, the B-band with the maximum energy at 1.20 eV is assigned as DA pair recombination between the deep donor level D and

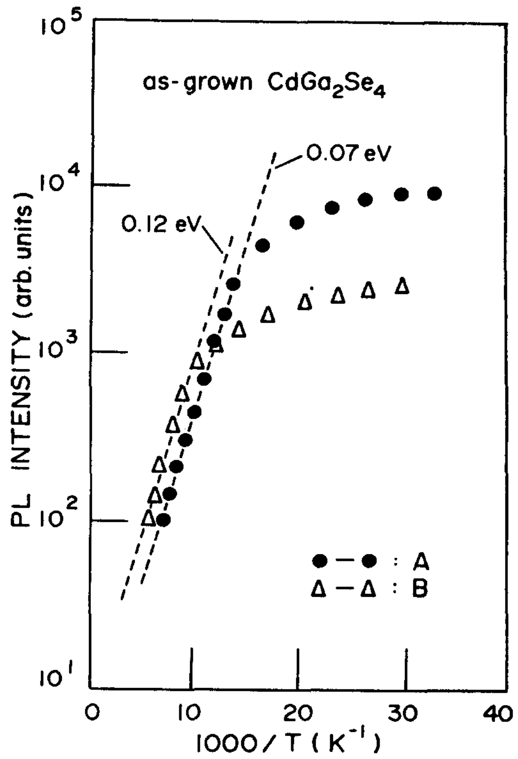

Fig. 3. Temperature dependence of emission intensities of the A- and B-band of undoped $CdGa_2Se_4$ single crystals.

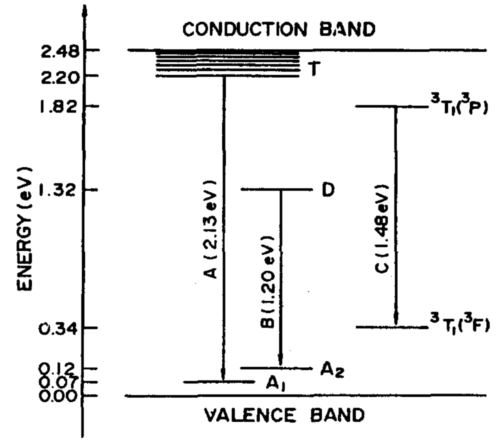

Fig. 4. Proposed energy level scheme and electron transitions for the radiative recombination in $CdGa_2Se_4$ (at 9 K).

the acceptor level A_2. It is considered that the thermal quenching of the A- and B- emission bands

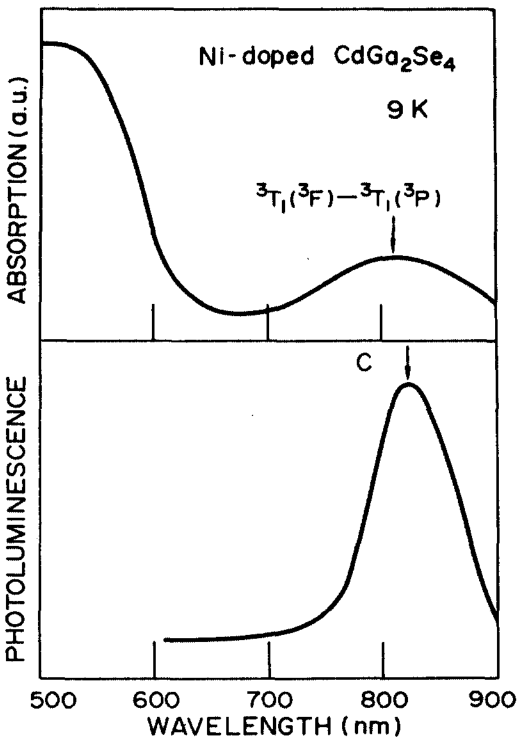

Fig. 5. PL and optical absorption spectra of Ni-doped $CdGa_2Se_4$ single crystals at 9 K.

may be originated from the thermal release of both electrons from the electron traps and holes from the acceptor levels.

Fig. 5 depicts the PL and optical absorption spectra of Ni-doped $CdGa_2Se_4$ single crystals recorded at 9 K. The optical absorption spectrum, as shown in Fig. 5, shows an abrupt optical absorption at the region of 600 nm corresponding to the band gap of Ni-doped $CdGa_2Se_4$ single crystals, and also presents a broad absorption band centered at 1.50 eV (825 nm). The absorption band is assigned to electronic transitions between the ground state $^3T_1(^3F)$ and the excited state $^3T_1(^3P)$ of Ni^{2+} ions located at T_d symmetry of the host material, comparing with the absorption bands of the Ni^{2+} ions in II-VI semiconductors[14]. In the PL spectrum of Fig. 5, only one emission band with the maximum at 1.48 eV (838 nm, C-band) is observed in the corresponding energy region of the absorption band. The intensity of the emission band was decreased on increase in the temperature, whereas its energy position was not influenced by variation of the temperature of the sample. The fact that the energy position of the emission band is independent of temperature leads us to the conclusion that the emission band is due to intracenter transitions of the Ni^{2+} ions from the excited state $^3T_1(^3P)$ to the ground state $^3T_1(^3F)$. The result of the energy level scheme in Ni-doped $CdGa_2Se_4$ is inserted in Fig. 4. As shown in Fig. 4, the ground state $^3T_1$ of the Ni^{2+} ions is located at 0.34 eV above the valence band. Observation of the energy difference between the band gap of undoped $CdGa_2Se_4$ ($E_g=2.48$ eV at 9 K[1]) and that of Ni-doped one ($E_g=2.14$ eV at 9 K) enables one to determine the level position within the gap, taking into the consideration that nickel doping in $CdGa_2Se_4$ may introduce low-energy shift of the absorption edge due to the Ni^{2+} charge state above the valence band[15]. Our results show a good agreement with the results that in CdSe the Ni^{2+} charge state exists above $E_v+0.32$ eV[15].

4. Conclusion

From the investigation of the PL and PLE spectra of undoped and Ni-doped $CdGa_2Se_4$ single crystals, we have proposed a simple energy level scheme and electron transitions for the radiative recombination. The proposed energy level scheme permits us to explain the radiative recombination processes of undoped and Ni-doped $CdGa_2Se_4$. It is concluded that two emission bands observed in undoped $CdGa_2Se_4$ are connected with quasi-continuously distributed electron traps below the bottom of the conduction band and two shallow acceptor levels above the valence band. It is also considered that the quasi-continuously distributed electron traps is the direct consequence of the heavily doped nature of $CdGa_2Se_4$ due to large densities of structural defects of cations vacancy, taking into consideration of no influence on the PL and PLE spectra by annealing under selenium vapour. The emission band observed in Ni-doped $CdGa_2Se_4$ is assigned as due to intracenter transitions of Ni^{2+} ions from the excited state $^3T_1(^3P)$ to the ground state $^3T_1(^3F)$.

Acknowledgements

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