Pergamon

Solid State Communications, Vol. 97, No. 12, pp. 1101–1104, 1996

0038–1098/96 $12.00 + .00

0038–1098(95)00728-8

PHOTOLUMINESCENCE OF Ga_2S_3 AND $Ga_2S_3:Mn$ SINGLE CRYSTALS

Jung-Soon Lee

Korea Basic Science Center, Korea Standard Research Institute, Taejeon 305-333, Korea

Young-Hee Won and Hyun-Nam Kim

Department of Physics, Ajou University, Suwon 440-749, Korea

Chang-Dae Kim

Department of Physics, Mokpo National University, Mokpo 534-729, Korea

and

Wha-Tek Kim

Department of Physics, Chonnam National University, Kwangju 500-757, Korea

(*Received* 12 *September* 1995 *by D.J. Lockwood*)

Photoluminescence spectra of Ga_2S_3 and $Ga_2S_3:Mn$ single crystals prepared by the chemical transport reaction method were investigated. We observed a relatively narrow band at 2.14 eV (514 nm) and a broad band centered at 1.81 eV (685 nm) for Ga_2S_3 at 10 K. For $Ga_2S_3:Mn$, on the other hand, a dominant emission band at 1.81 eV (685 nm) and three weak emission bands at 2.34 (530), 2.14 (579) and 1.54 eV (805 nm) are observed. The origins of the emission bands are identified on the basis of the energy-band scheme proposed from the measurements of optical absorption, TSC and PICTS. The results show that two emission bands for Ga_2S_3 are attributed to the electron transition from the donor level to the acceptor levels, and four emission bands for $Ga_2S_3:Mn$ are associated with the transitions from the excited state $^4T_1(^4G)$ of Mn^{2+} to the ground state $^6A_1(^6S)$ and the acceptor levels.

1. INTRODUCTION

Ga_2S_3, ONE OF the $A_2^{III}B_3^{VI}$-type binary semiconductors, has been expected to be a promising material for blue-light-emitting devices because of its wide direct band-gap of about 3.4 eV at room temperature. A few works on the luminescent properties of Ga_2S_3 have been reported [1, 2]. The effect of doping of transition-metal and rare-earth impurities on the physical properties of Ga_2S_3 has been studied [3–6]. However, no study on the photoluminescence properties of Ga_2S_3 doped with transition-metal ions has been made to date.

In the present paper we report the results of the investigation of the photoluminescence (PL) spectra of undoped and Mn-doped Ga_2S_3 single crystals prepared by the chemical transport reaction method. The energy-band scheme and electron transitions for the recombination processes in undoped and Mn-doped Ga_2S_3 are proposed on the basis of the measurements of thermally stimulated current (TSC) and photo-induced current transient spectroscopy (PICTS).

2. EXPERIMENTAL

Single crystals of undoped and Mn-doped Ga_2S_3 were grown by the chemical transport reaction method. A stoichiometric mixture of the constituent elements (high-purity 99.9999%) with 6 mg cm^{-3} of iodine were sealed in an evacuated quartz ampoule with a carbon coating of the inner ampoule surface.

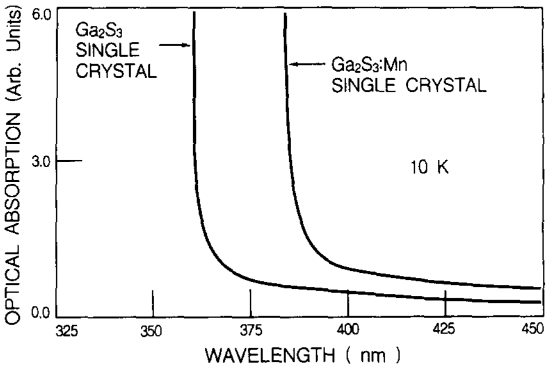

Fig. 1. Optical absorption spectra of Ga_2S_3 and $Ga_2S_3:Mn$ single crystals at 10 K.

For $Ga_2S_3:Mn$ crystals, 2 mol% of Mn-dopants was introduced. The sealed ampoules were then placed into a two-zone furnace, heated up to 900°C and held at this temperature for 24 h for a reaction. After this preheating, the temperature inversion procedure with the temperature of 600°C for the source-zone and 820°C for the growth-zone of a two-zone furnace was also performed for 24 h in order to get cleaning effects on the quartz walls of the growth-zone. For the crystal growth, finally, the source- and the growth-zone temperature was kept at 950 and 820°C for 6 days. The resulting single crystals had typical dimensions of $7 \times 10 \times 4\,mm^3$, and showed a transparent dark-white color for undoped Ga_2S_3 and a slight green color for Mn-doped one. The X-ray diffraction analysis showed that these crystals were monoclinic with α-phase.

PL spectra were obtained by means of a N_2 gas laser (Laser Photonics, 377 nm-line) as an excitation light source and a photomultiplier (RCA, C-31034) as a detector. Optical absorption was measured using an UV-VIS-NIR spectrophotometer (Hitachi, U-3501) equipped with a cryogenerator (Air Products, CSA-202B). TSC and PICTS measurements were carried out for the same sample used for the PL measurement using a 500 W tungsten–halogen lamp with appropriate filters as an optical excitation and electrical shutter to generate the light beam chopper. The temperature was swept at constant rate of $0.2\,K\,s^{-1}$ for TSC measurement and $0.05\,K\,s^{-1}$ for PICTS measurement.

3. RESULTS AND DISCUSSION

3.1. *Optical absorption of* Ga_2S_3 *and* $Ga_2S_3:Mn$ *single crystals*

Figure 1 shows the optical absorption spectra near the fundamental absorption edge at 10 K for Ga_2S_3 and $Ga_2S_3:Mn$ crystals. As can be seen in Fig. 1, the fundamental absorption edge of Ga_2S_3 locates near 344 nm, whereas Mn-doped Ga_2S_3 has the fundamental absorption edge near 386 nm shifted to the long-wavelength region. In Fig. 2, we present the energy dependent absorption coefficients of Ga_2S_3 and $Ga_2S_3:Mn$ crystals and deduce an optical energy gap by extrapolating $(\alpha h\nu)^2 = 0$. The optical energy gap is then found to be 3.42 eV for Ga_2S_3 and 3.21 eV for $Ga_2S_3:Mn$, respectively. The difference of the optical energy gap between the Ga_2S_3 and the $Ga_2S_3:Mn$ can be attributed to the Mn^{2+} acceptor levels which form a band due to heavy doping of Mn^{2+} in Ga_2S_3. It is known that the Mn^{2+} ions are incorporated into the lattice of III–V compounds on a cation site and form a shallow acceptor ($E_{VBM} + 0.4\,eV$ in GaP and $E_{VBM} + 0.14\,eV$ in GaAs) [7]. We can safely say that the doping concentration of 2 mol% of Mn^{2+} in Ga_2S_3 will

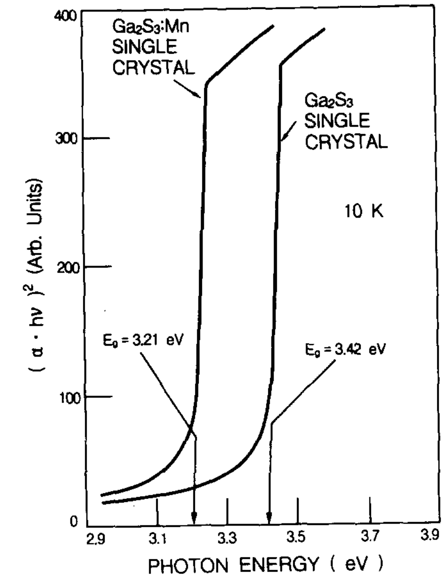

Fig. 2. Energy dependent absorption coefficients of Ga_2S_3 and $Ga_2S_3:Mn$ single crystals at 10 K.

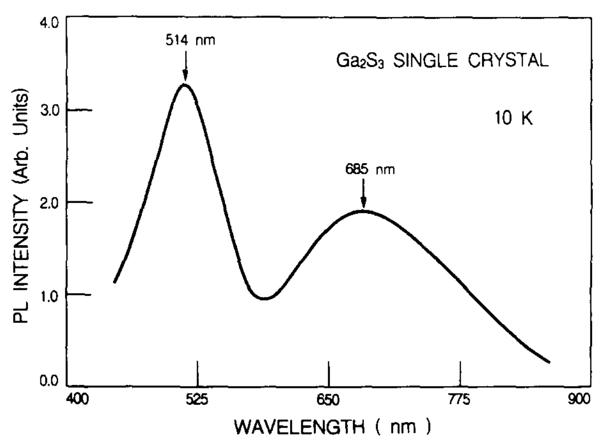

Fig. 3. PL spectrum of GA_2S_3 single crystals at 10 K.

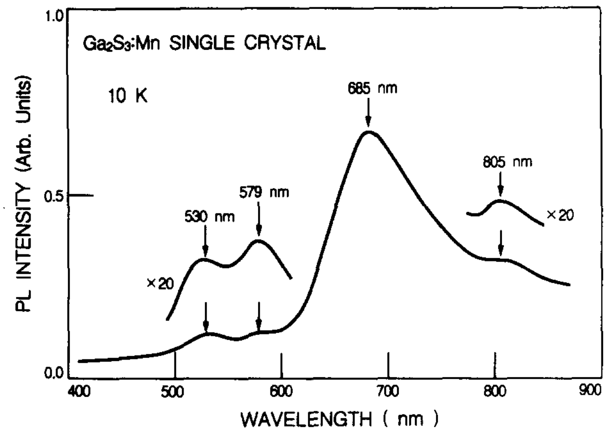

Fig. 4. PL spectrum of $GA_2S_3:Mn$ single crystals at 10 K.

cause the formation of a band due to acceptor level, and merging to the valence band. Thus we can observe the apparent shrinkage of band gap in heavily Mn^{2+}-doped Ga_2S_3. The shrinkage of band gap due to the doping of Mn^{2+} ions has also been observed in $ZnGa_2S_4:Mn$ ternary compound [8]. The Mn^{2+} substituted for Ga^{3+} in Ga_2S_3 acts as an acceptor in this crystal. The Mn^{2+} acceptor is located at 210 meV above the valence band of Ga_2S_3.

3.2. *Photoluminescence (PL) of* Ga_2S_3 *and* $Ga_2S_3:Mn$ *single crystals*

Figure 3 illustrates the PL spectrum of Ga_2S_3 single crystals at 10 K. As shown in Fig. 3, we observed a relatively narrow band at 2.41 eV (514 nm) and a broad band centered at 1.81 eV (685 nm), which are attributed to donor–acceptor

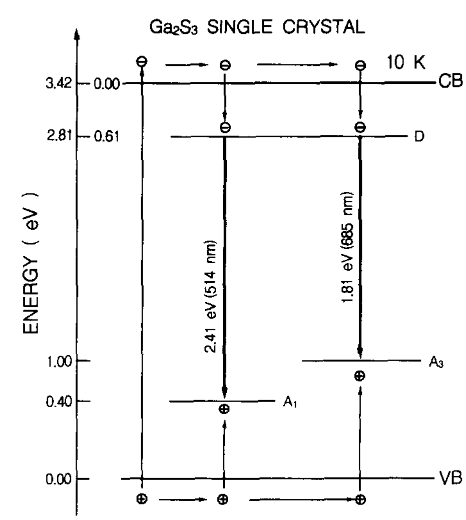

Fig. 5. Energy-band scheme and the electron transition for the recombination processes in Ga_2S_3 single crystals.

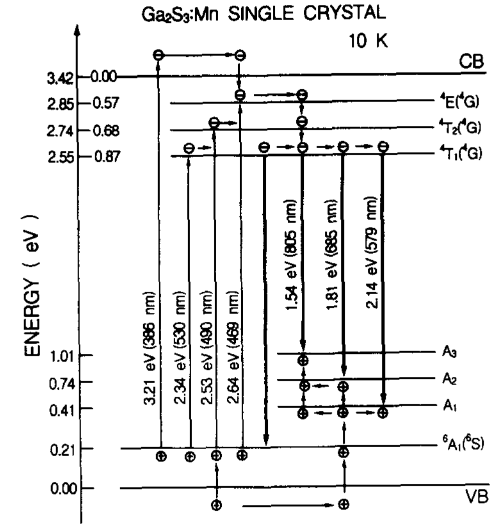

Fig. 6. Energy-band scheme and the electron transition for the recombination processes in $Ga_2S_3:Mn$ single crystals.

pair recombination [1]. The PL spectrum of $Ga_2S_3:Mn$ single crystals at 10 K is shown in Fig. 4. In the figure a dominant emission band at 1.81 eV (685 nm) and three weak emission bands at 2.34 (530), 2.14 (579) and 1.54 eV (805 nm) are observed. However, the emission bands of $Ga_2S_3:Mn$ show a different temperature dependent behavior from those of Ga_2S_3, that is, their positions are almost independent of temperature. The independent behavior of the temperature of the emission bands in $Ga_2S_3:Mn$ allows one to conclude that these bands could be associated with Mn^{2+} related levels in the forbidden band gap.

In order to clarify the origin of these emission bands, we performed TSC and PICTS measurements using the samples with ohmic contacts deposited by indium on the surface of the crystals according to the sandwich geometry, and analyzed the TSC and PICTS spectra by the initial rise, half-width and DLTS methods. In Table 1 are summarized the results of activation energy and capture cross section of deep levels in Ga_2S_3 and $Ga_2S_3:Mn$ obtained by using the TSC and PICTS measurements. The deep levels for Ga_2S_3 are found to be located at 0.40 and 1.00 eV as hole traps, and at 0.61 eV as electron traps. In the case of $Ga_2S_3:Mn$, the deep levels are located at 0.41, 0.74 and 1.01 eV as hole traps, and at 0.57, 0.68 and 0.87 eV as electron traps.

From the observed results, we now propose the energy-band scheme of Ga_2S_3 and $Ga_2S_3:Mn$. Taking account of the band gap of 3.42 eV at 10 K, the energy-band scheme for Ga_2S_3 is proposed as shown in Fig. 5, in which two acceptor levels located

Table 1. Activation energy and capture cross section of deep levels in Ga_2S_3 *and* $Ga_2S_3:Mn$ *single crystal*

TSC					
Ga_2S_3			$Ga_2S_3:Mn$		
E_t (eV)	σ (cm^2)	Type	E_t (eV)	σ (cm^2)	Type
0.40	7.35×10^{-19}	Hole	0.41	6.16×10^{-19}	Hole
			0.57	2.82×10^{-17}	Electron
0.61	5.75×10^{-17}	Electron	0.68	2.65×10^{-17}	Electron
			0.74	1.96×10^{-16}	Hole
PICTS					
			0.87	1.00×10^{-15}	Electron
1.00	1.37×10^{-17}	Hole	1.01	1.32×10^{-17}	Hole

at 0.40 and 1.00 eV above the top of the valence band are presented and a donor level located at 0.61 eV below the bottom of the conduction band is introduced. Thus two emission bands of Ga_2S_3 correspond to the electron transition from the donor level to the acceptor levels. For $Ga_2S_3:Mn$, the energy-level scheme is represented in Fig. 6. As mentioned above, the shrinkage of the band gap in Mn^{2+}-doped Ga_2S_3 implies that the ground state $^6A_1(^6S)$ of Mn^{2+} acceptor is located at 0.21 eV above the top of the valence band of Ga_2S_3. Also, optical absorption spectroscopy has revealed that the energies of inter d–d transitions of Mn^{2+} in $Ga_2S_3:Mn$ are 2.34, 2.53 and 2.64 eV [9]. Thus the excited states of Mn^{2+} can be plotted within the forbidden band gap below the bottom of the conduction band, as shown in Fig. 6, which are in good agreement with the results of the deep levels obtained from the TSC and PICTS measurements. It is concluded that the emission bands observed in $Ga_2S_3:Mn$ are associated with the transitions from the excited state $^4T_1(^4G)$ of Mn^{2+} to the ground state $^6A_1(^6S)$ and the acceptor levels.

4. CONCLUSIONS

In summary, PL study of Ga_2S_3 and $Ga_2S_3:Mn$ single crystals prepared by the chemical transport reaction method has been carried out. On the basis of optical absorption, TSC and PICTS measurements, the energy-band schemes have been proposed. The proposed energy-band schemes permit us to assign the electron transition for the recombination processes in Ga_2S_3 and $Ga_2S_3:Mn$.

REFERENCES

1. T. Aono & K. Kase, *Solid State Commun.* **81,** 303 (1992).
2. T. Aono & K.Kase, *Solid State Commun.* **83,** 749 (1992).
3. I.M. Askerov, V.F. Masterov, V.V. Romanov & K.F. Shtel'makh, *Sov. Phys. Semicond.* **23,** 813 (1989).
4. I.M. Askerov, V.F. Kobelev, V.F. Masterov, O.B. Tagiev, K.F. Shtel'makh & L.F. Likholit, *Sov. Phys. Semicond.* **23,** 814 (1989).
5. I.M. Askerov, A.O. Mekhrabov, G.K. Aslanov, B.G. Tagiev & S.M. Nakhmetov, *Phys. Status Solidi (a)* **105,** K151 (1988).
6. T. Teranishi, K. Sato & K. Kondo, *J. Phys. Soc. Jpn.* **36,** 1618 (1974).
7. A. Fazzio, M.J. Caldas & A. Zunger, *Phys. Rev.* **B30,** 3430 (1984).
8. H.L. Park, H.G. Kim, H.M. Jeong, C.D. Kim, S.H. Cheon, S.C. Hyun & W.T. Kim, *Jpn. J. Appl. Phys.* **32** (suppl. 32–3), 473 (1993).
9. W.T. Kim *et al.* (to be published).