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## Radiative centers in layered semiconductor GaS doped with Zn

S. Shigetomi<sup>a,\*</sup>, T. Ikari<sup>b</sup>

<sup>a</sup>Department of Physics, Kurume University, 67 Asahi-machi, Kurme, Fukuoka 830-0011, Japan <sup>b</sup>Department of Electrical and Electronic Engineering, Miyazaki University, 1-1 Gakuenkibanadai, Miyazaki 889-2155, Japan

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#### Abstract

The radiative recombination mechanisms of the Zn-doped GaS have been investigated using photoluminescence (PL) measurements. In these undoped and Zn-doped samples, the five emission bands at 2.570, 2.555, 2.534, 2.521, and 2.480 eV are related to the indirect band exciton with phonon emission. The PL spectrum (at 77 K) related to the impurity level is dominated by the new emission band at 1.85 eV. The temperature dependences of the PL intensity, peak energy, and full-width at half-maximum are characterized by the recombination mechanism of the configurational coordinate model. It is found that the1.85 eV emission band is related to the acceptor-vacancy complex center. © 2004 Elsevier B.V. All rights reserved.

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### 1. Introduction

The layered semiconductor compound, GaS, is a material with an indirect band gap of about 2.5 eV at room temperature. Much interest has recently been focused on the optical and electrical properties of GaS [1–8] because of its potential application in photoelectronic devices in the visible range [9]. It is considered to be very useful to have detailed information on the impurity levels for fabricating high-quality devices. For the electrical

E-mail address: shigeto@med.kurume-u.ac.jp

(S. Shigetomi).

measurements, the impurity levels in undoped n-GaS have been investigated using photoinduced-current-transient spectroscopy, the spacecharge-limited-current, and the Hall effect [4,5]. It was found that the impurity levels are located at 0.17, 0.45, 0.52, and 0.56 eV below the conduction band. On the other hand, the six trap levels at 0.05, 0.06, 0.12, 0.63, 0.71, and 0.75 eV were found using the thermally stimulated current of undoped p-GaS [6]. The photoluminescence (PL) spectra of the undoped n-GaS showed three emission bands at 2.22, 2.02, and 1.59 eV (at 9 K) [7]. These emission bands originate from the donor–acceptor pair recombination processes. The donor and acceptor levels of the 1.59 eV emission band were

<sup>\*</sup>Corresponding author.

due to the point defects. The radiative transitions of the Cu-doped GaS have been studied using PL and electroluminescence measurements [8]. The two emission bands were observed at 2.12 and 1.80 eV. It was found that the impurity levels due to Cu atoms are localized at 1.23 and 1.48 eV in the forbidden band. However, the radiative transitions in the Zn-doped samples have not yet been investigated.

In this paper, we present the PL spectra related to the impurity level in Zn-doped GaS. The recombination mechanism is deduced from the temperature dependences of the PL intensity, peak energy, and full-width at half-maximum (FWHM).

#### 2. Experiment

Single crystals of GaS were grown by the conventional Bridgman technique with a stoichiometric mixture of Ga (5N pure) and S (5N pure) as the source materials. Doping by Zn (5N pure) was performed at 0.1 and 1 at% in the stoichiometric melt of GaS. The samples were prepared by cleaving an ingot parallel to the layer, which was perpendicular to the *c*-axis. The surfaces were mirror-like and no further etching treatment was necessary to make the optical measurements.

The conduction type of the undoped sample was the n-type. After doping the stoichiometric melt with Zn, the conduction changed from n-type to ptype. To study the electron and hole concentrations of the undoped and Zn-doped samples, the Hall coefficient measurement was carried out using the Van der Paw method. The Hall contact formed by evaporating In was nearly ohmic for the undoped and Zn-doped GaS samples with a high resistivity. The electron concentration of the undoped sample was about  $2 \times 10^{13}$  cm<sup>-3</sup> at 373 K. On the other hand, the hole concentration of the Zn-doped sample was about  $1 \times 10^{13}$  cm<sup>-3</sup> at 373 K.

The PL measurements were made at 77 K by immersing the samples in liquid nitrogen and at temperatures of 85-210 K using a cryostat. Excitation was usually made with a semiconductor laser operating at a wavelength of 405 nm with  $0.5 \text{ W/cm}^2$ . The intensity of the laser beam changed from 0.005 to  $5 \text{ W/cm}^2$  for the dependence of the PL intensity and peak energy on the excitation intensity. The PL spectra from the *c*-plane were analyzed using double and single grating spectrometers and detected with the cooled R943-02 and 7102 photomultipliers employing lock-in technique.

#### 3. Results and discussion

Fig. 1 shows the PL spectra of the near exciton region for the undoped and Zn-doped GaS samples at 77 K. The initial Zn concentrations in the growth solutions, which are hereafter denoted as [Zn], are also given in the figure. For the undoped sample, the three emission bands denoted by PA, PB, and PC were observed at 2.570, 2.555, and 2.534 eV, respectively. Moreover, the two emission bands denoted by PD and PE appeared at 2.521 and 2.480 eV, respectively, in the Zn-



Fig. 1. Photoluminescence (PL) spectra of the undoped and Zn-doped GaS samples near the exciton region at 77 K. The initial Zn concentrations [Zn] in the growth solutions are indicated in the figure.

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