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Growth of Low-Resistivity ZnS Films by MOCVD

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Low-resistivity ZnS films have been grown by a low-pressure MOCVD using TMAl and HCl as donor dopant sources. For Al-doped films, the resistivity is as low as about $l \ \Omega$.cm. From PL properties, it was found that the SA emission intensity increases with a decrease in resistivity. Furthermore, the activation energy of Al-donor was found to be about 60 meV. In the case of Cl-doping, such low-resistivity films as 0.2 Ω .cm can be grown. It was found, however, that when the HCl flow rate is relatively high the crystallinity tends to be poor, because of the reaction between HCl and Zn-source material.

1.Introduction

ZnS has potentially useful applications in visible light emitting devices, especially in blue light emitting diodes (LEDs), since it has such a wide directtransition bandgap as 3.66 eV at room temperature. In order to fabricate Metalinsulator-semiconductor (MIS) structure blue LEDs from ZnS, it is necessary to obtain low-resistivity ZnS crystals with blue emission centers. However, the resistivity of as-grown ZnS crystal is generally very high and it is difficult to reduce the resistivity impurity doping by in conventional high-temperature growth techniques, because a lot of native defects are easily introduced into the ZnS crystal due to the "self-compensation effect" at high temperatures. In order to achieve the resistivity control by impurity doping, it is important to obtain high-quality undoped ZnS films by low-temperature growth techniques, such as Metal-Organic Chemical Vapor Deposition (MOCVD).

In this report, low-resistivity ZnS films are grown by donor impurity doping in

a low-pressure MOCVD and electrical and optical properties of the donor doped films are examined. Al and Cl are used as donor impurities. Because, since both Al and Cl 2-5) can be a shallow donor in ZnS , it is expected that the low-resistivity ZnS films can be obtained by Al or Cl doping. Furthermore, these impurities introduce self-activated (SA) centers, which act as blue emission centers in ZnS. Thus, Al and Cl may be suitable donor impurities for fabricating the MIS type ZnS blue LEDS.

2.Experimental procedures

ZnS films were grown by a low-pressure 6,7) MOCVD system reported previously. The flow rates of DMZn and H S, which are source materials, were 4 x 10 and 2 x 10 mol/min, respectively. The flow rates of TMA1 and HC1, which are doping materials, were $1.0 - 6.0 \times 10^{-7}$ and $0.3 - 2.0 \times 10^{-7}$ mol/min, respectively. The reactor pressure was maintained at 1 Torr. Semi-insulating (100) GaAs was used as a substrate.

The PL spectrum was measured at 15 K and a He-Cd laser (λ =3250 A) was used as

an exciting light source. The resistivity was measured by the van der Pauw method at room temperature using Hg-In alloy as ohmic contacts.

3.Results and discussions

Figure 1 shows the dependences of the resistivity of both Al- and Cl-doped ZnS films on the substrate temperature. The resistivity of Al-doped films grown at 300 °C is as low as about 1 Ω .cm. The resistivity tends to be high at temperatures below and above 300 °C. Especially, the resistivity of the film grown at 345 C is as high as that of undoped one (>10 Ω .cm). It seems that Al-donors in the films grown at 345 °C







Fig.2 Dependences of the resistivity of both Al- and Cl-doped films on each dopant gas flow rate.

are compensated by acceptor-like defects. Furthermore, it was found that the resistivity of Cl-doped films grown at 300°C under the condition of HCl flow rate of 6 x $^{-8}$ nol/min, which is less than that of TMA1, is lower than that of Al-doped one.

Figure 2 shows the dependences of the resistivity of both Al- and Cl-doped films each on dopant gas flow rate. The resistivity of Al-doped films is very high under the conditions of TMA1 flow rates below 2 x 10 mol/min, but it becomes low eventually at the TMA1 flow rate of 2 x 10 mol/min. Furthermore, the resistivity tends to saturate under the conditions of the TMA1 flow rates above 4 x 10 mol/min. In case of Cl-doping, low-resistivity films can be grown at the HCl flow rate of 3 x 10 mol/min. It was found that the low-resistivity Cl-doped films can be grown even when the HCl flow rates are about one order in magnitude smaller than the TMA1 flow rates. Therefore, the doping efficiency of HCl is higher than that of TMA1.

The resistivity of Cl-doped films increases when the HCl flow rates are above 6 x 10 mol/min. It was found from the full-width at half maximum (FWHM) of (400) X-ray diffraction patterns of Cl-doped ZnS that the crystallinity becomes poor under the conditions of the HCl flow rates above 6 x 10 mol/min. Therefore, it seems that the increase in the resistivity of Cl-doped films grown at relatively high HCl flow rates is attributed to the poor crystal quality. Since Cl can easily form compounds such as ZnCl with Zn, it seems that the crystal quality tends to be poor in the films grown at the relatively high HCl flow rates. Furthermore, it was found from a comparison of the FWHMs of X-ray diffraction patterns for Al- and Cl-doped films that the crystallinity of Cl-doped films grown at such a low HCl flow rate as 6 x 10 mol/min



Fig.3 Photoluminescence spectra of both undoped and Al-doped films.

is inferior to those of undoped and Al-doped ones. Since the HCl flow rate in this work is still high, it is expected that both lower-resistivity and higher-quality ZnS films can be grown when the HCl flow rate is much reduced.

Figure 3 shows the PL spectra of both undoped and Al-doped ZnS films. For the undoped film shown in Fig.3(a), a sharp emission near the band edge (3272 A) and an emission related to deep levels at 4350 A are dominant. These emissions are called "I line" and "DE emission" hereafter in this paper. It seems that the I line is an excitonic emission because of its short peak 8) wavelength and narrow FWHM . The origin of DE emission is not completely understood yet.

In the case of Al-doped films, the I line and an emission related to deep levels at 4800 A are dominant. The emission from deep levels can be considered to be an SA emission from the result of temperature dependence of the wavelength at which the emission becomes a maximum. For the highresistivity Al-doped films shown in Fig.3(b), both SA and DE emissions are observed. For the low-resistivity Al-doped films shown in Fig.3(c), however, the intensity of SA emission becomes high and the DE emission is not observed. Thus, it was found that the intensity of SA emission increases with the decrease in resistivity.

Figure 4 shows the near-band-edge emissions of both undoped and Al-doped films. The I line and other emissions, such as P and Q, are observed in the undoped films. Since the LO phonon energy of ZnS is about 43 meV 9,10) , it was found that P and are the LO phonon replicas of P and Q_0 , Q, respectively. The origin of these emissions will be discussed elsewhere. For the Aldoped films, P and Q emissions are also observed in the Al-doped films. Furthermore, the R line is observed at 3291 A only in Aldoped films. Furthermore, the intensity of R line increase with the increase in the TMAL flow rate as shown in the figure. Therefore, it is considered that the R line is closely related to the shallow Al-donor. Assuming that the R line is the emission originated from the recombination between a shallow donor and a free hole, Al-donor activation



Fig.4 Near-band-edge emissions of both undoped and Al-doped films.



Fig.5 Photoluminescence spectra of Cldoped films.

energy can be estimated as about 59 meV, using the optical bandgap energy of cubic InS at 15 K as 3,826 eV . Furthermore, examining the dependence of resistivity of Al-doped films on temperature, the Al-donor activation energy is determined as about 56 meV. Thus, it was found that the Al-donor activation energy in ZnS is about 60 2,4meV .

Figure 5 shows the PL spectra of Cldoped films. In the case of relatively low HCl flow rate condition shown in Fig.5(a), both the I line and the SA emission are observed. The intensity of I line, however, is smaller than that of Al-doped films. Furthermore, the FWHM of I line of Cl-doped films is wider than that of Al-doped ones. An emission related to a shallow Cl-donor, such as R line observed in the case of Aldoped films, is not observed in the Cl-doped films. In the case of the relatively high HCl flow rate condition shown in Fig.5(b), the I line disappears. Therefore it was found that the crystal quality of Cl-doped films becomes poor under the relatively high HCl flow rates conditions.

4.Summary

Low-resistivity ZnS films have been

grown by a low-pressure MOCVD using TMA1 and HCl as dopant sources. The resistivity of Al-doped films grown at 300°C is as low as about 1 g.cm. From the PL properties, it was found that the intensity of SA emission increases with the decrease in the resistivity. Furthermore, the Al-donor about 60 meV, which activation energy is is determined from both the near-band-edge emission related to the shallow Al-donor and the temperature dependence of resistivity. case of Cl-doping, Tn the such low resistivity films as about 0.2 p.cm can be grown. It was found, however, that when the HC1 flow rate is relatively high the crystallinity tends to be poor, because of reaction between HCl and Zn-source the material.

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