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# ZnS Blue Light-Emitting Diodes Fabricated by MOCVD

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High-quality ZnS epitaxial layers were grown on GaP substrates at a growth temperature higher than 200°C by low-pressure MOCVD technique. Undoped ZnS electrical resistivity was as high as an insulator. Aluminum doping of about 10 ppm lowers resistivity to around $10^4$ Ωcm. Film thickness controllability is very good for this low-pressure ZnS growth. A homoepitaxial MIS structure, using undoped MOCVD-ZnS for an insulator, has been revealed to have higher emission efficiency and reproducibility, compared to a heterostructure MIS. This successful trial has resulted in a promising procedure to obtain MIS ZnS Blue LEDs on GaP substrate by low-pressure MOCVD technique.

## §1. Introduction

Based on successful massproduction in the 1970s of visible light emitting diodes (LEDs), optoelectronic device development is promissing to higher value devices area, represented by optical-fiber communication devices and other optical information signal processing devices. The demand for blue LEDs become stronger and enterprise level efforts are also increasing. However, blue LED semiconductor materials, ZnS, ZnSe, GaN and SiC, that have a wider band gap energy than 2.6 eV, have encountered serious difficulties in regarded massproducibility. Among these materials, ZnS, ZnSe and their mixed crystal ZnSSe are the most promising materials, because of their high luminescence efficiencies due to their direct band gap recombination mechanisms. Moreover, ZnS and ZnSe have been successfully grown at low temperature on GaP and GaAs by the metalorganic chemical vapor deposition (MOCVD) technique[1),2),3)], because lattice mismatch between these materials is less than 1 %. This non-thermal equilibrium deposition furnishes an opportunity to achieve low resistivity.

This paper describes low-pressure MOCVD technique to obtain high ( > $10^8$ Ωcm) and low ( < $10^4$ Ωcm) resistivity ZnS crystals on GaP substrates and a mass production procedure for blue LEDs based on metal - MOCVD insulating ZnS - semiconducting ZnS (so called MIS) devices.

## §2. ZnS Growth on GaP by low-pressure MOCVD

### 2.1 MOCVD growth

ZnS layers were grown by a low-pressure MOCVD technique developed by Stutius[1)]. ZnS source materials are dimethylzinc (DMZ) and 10 % $H_2S$ in hydrogen gas. Triethylaluminum (TEAL) was used as an n-type dopant. Reactor configuration is shown in Fig. 1.

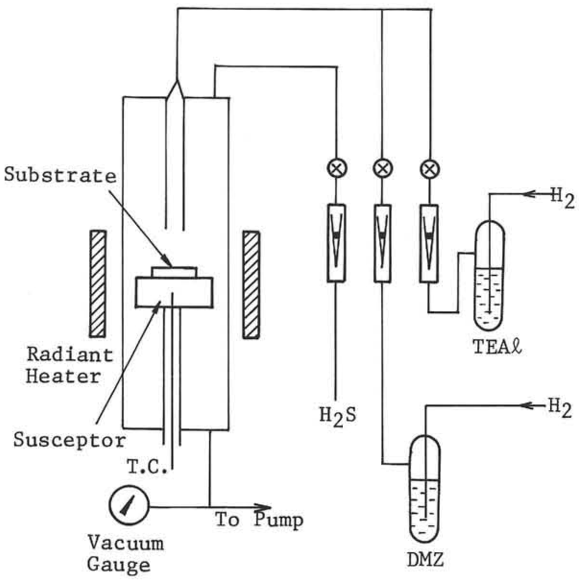


Fig. 1 MOCVD reactor diagram

$H_2S$ is introduced from the top of the reactor. A separate center tube, carrying DMZ and TEAL in $H_2$ extends up to the substrate. The reactants were kept separate because they have a tendency to react at lower temperature in the gas phase, before they arrive at the heated substrate. The SiC coated graphite susceptor is heated by infrared radiant heater. Its temperature during the deposition is held at 400°C. During the deposition, typical $1.3 \times 10^{-4}$ mol/minute flow rate for the $H_2S$ and $7.3 \times 10^{-5}$ mol/minute flow rate for the DMZ were selected. The reactor pressure was lowered to around 1∿10 Torr by a pumping system. The growth rate under this condition was about 6 μm/hour.

The surface morphology and thickness for the layers was determined from SEM measurements. The layers were generally smooth, but microhillocks appeared with increasing thickness on surface layers grown on (100) GaP substrates, as shown in Fig. 2.

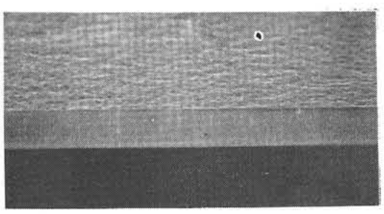


Fig. 2 ZnS/GaP surface SEM picture.

Substrate temperature ($T_G$) and flow rate for the minority reactant, i.e. the DMZ flow rate, have great influence on the growth rate. The growth rate temperature dependence is shown in Fig. 3, where DMZ/$H_2S$ mol fractions are selected as 0.6 and 0.2. Growth temperature lower than 200°C results in yielding a polycrystalline layer. As shown in this figure, growth rate has a maximum at around 250°C. At a growth temperature higher than 350°C, the growth rate decreases with increasing $T_G$, which suggests a thermal equilibrium in this deposition. It has been observed that growth rate can be suppressed to around 330 Å/minute under proper conditions and that layer thickness controllability is very good for this low-pressure ZnS growth.

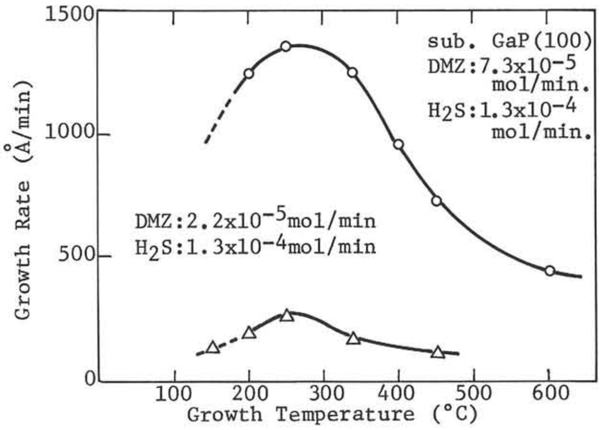


Fig. 3 Growth rate temperature dependence

## 2.2 MOCVD ZnS Crystal Quality

The grown layers crystal quality was characterized by X-ray diffraction patterns measurements. The X-ray diffraction pattern from (200) diffraction of the grown layer at $T_G$ = 340°C and 150°C is indicated in Figs. 4. (a) and (b).

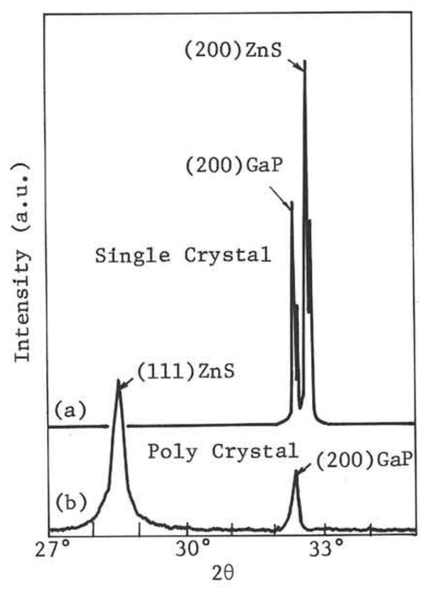


Fig. 4 X-ray diffraction pattern from (200) plane for ZnS layers on (a) (100) GaP at $T_G$ = 340 °C and (b) at $T_G$ = 150°C.

The X-ray diffraction pattern from the (111) diffracting plane, shown in Fig. 4(b), means that the deposited layer has a polycrystalline character. A narrow CuKα line doublet in Fig. 4(a) shows good ZnS epitaxial quality on GaP.

The undoped ZnS layer resistivity is quite high and no photoluminescence (PL) or cathodoluminescence (CL) had been observed at the present stage of this work. However, as TEAL was introduced together with DMZ through the center tube, the resistivity was lowered and PL and CL were observed. A typical PL spectrum of about 10 ppm Al-doped ZnS layer grown on n-type (100) GaP, measured at room temperature, is shown in Fig. 5. The PL spectrum was measured under excitation by Hg lamp at 312.6 nm wavelength. The PL spectrum has

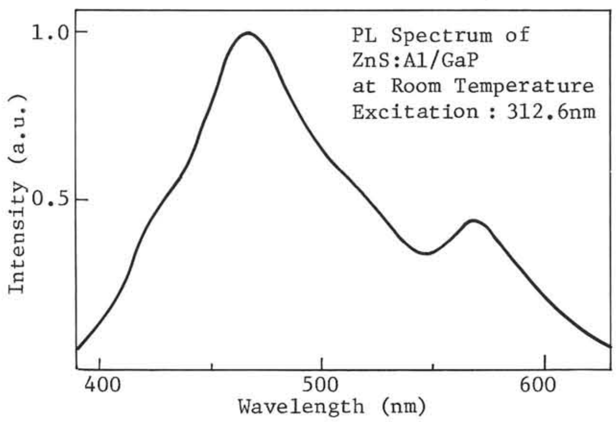


Fig. 5 ZnS:Al/GaP PL spectrum

broad peaks at 470 nm and 570 nm. The maximum at 470 nm seems to be due to the donor-acceptor pairs, probably between the isolated Al donors and the Zn vacancy-Al complex acceptors. The PL intensity at 470 nm for ZnS:Al/GaP was compared with that for Al doped ZnS crystal grown from the high pressure melt.

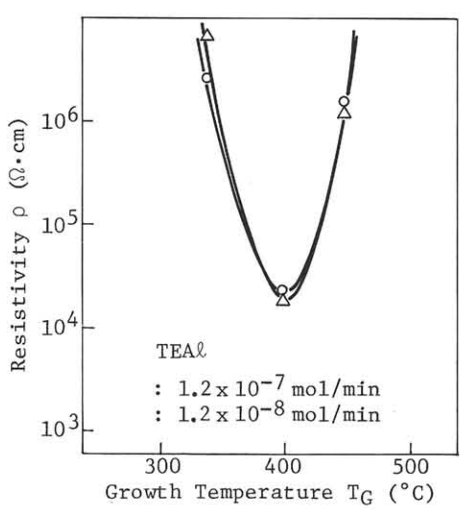


Fig. 6 Resistivity growth temperature dependence

The electrical properties of Al doped ZnS layer deposited on n-GaP substrates were measured by determining I-V characteristics for Au-(n-ZnS/n-GaP) Schottky diodes. Al doped ZnS layers resistivity shown in Fig. 6 were calculated from the series resistance of this diodes. Although a definite reason for the minimum resistivity at $T_G$ = 400°C is still unrevealed, the blue LEDs using MOCVD ZnS/GaP will be made by further crystal quality improvement in the MOCVD ZnS layers.

## §3. ZnS Blue LED Fabrication

MOCVD ZnS layer electrical resistivity decreased down to $10^4$ Ωcm. However, it is difficult to prepare a ZnS p-n junction. As an alternative to a p-n junction, another structure for minority carrier injection, MIS structure, has been studied by earlier investigators[6]. Insulating layers of MIS LEDs have been fabricated by n-type ZnS crystal heat-treatment in a vacuum or by oxidation of the crystals. However, this fabrication technique has no reproducibility. MIS structure, composed of i-ZnS/n-ZnS, seems to have stability, reproducibility and controllability. This uniform thickness i-ZnS can be grown by this low-pressure ZnS growth.

As a first stage in ZnS blue LEDs development, MIS blue LEDs using insulating ZnS single crystal, were studied[4].

### 3.1 ZnS MIS LED Structure and Fabrication Method

Fig. 7 shows a cross section for the ZnS MIS LED. Al doped low resistivity ZnS single crystals

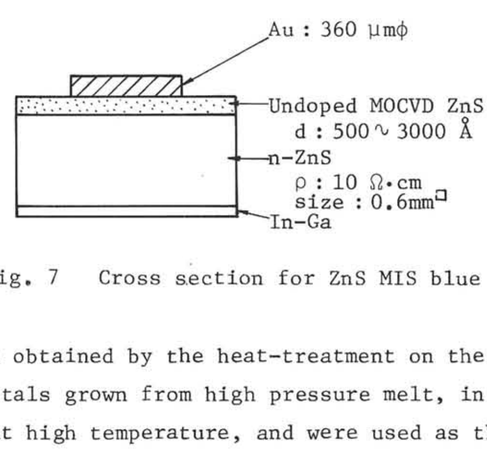


Fig. 7 Cross section for ZnS MIS blue LED

were obtained by the heat-treatment on the ZnS crystals grown from high pressure melt, in molten Zn at high temperature, and were used as the substrate. The ZnS diodes were fabricated using undoped ZnS single crystalline layers as an insulator, grown by low-pressure MOCVD. Au metal contact was attached on the insulating ZnS layer, after In-Ga ohmic contact was fabricated onto the substrate. These wafers were diced into pellets whose dimensions were $0.6 \times 0.6 \times 0.4$ mm. From the production possibility view point and diode yield controllability, three kinds of diodes have been studied, Lot a, Lot b and Lot c. Insulating layers were prepared by heat-treatment in vacuum, by ZnS oxidization in $H_2O_2$, by MOCVD ZnS deposition, for Lots a, b and c, respectively. Fig. 8 shows relations between emission intensity (L) and driving current (I), for these LEDS. L-I characteristics for Lot c are similar to those for Lot a. Lot b characteristics are not good, compared with those for Lots a and c, especially in the low operating current range. In the present work, it was found that this homoepitaxial MIS structure has higher emission efficiency and reproducibility than the heterostructure.

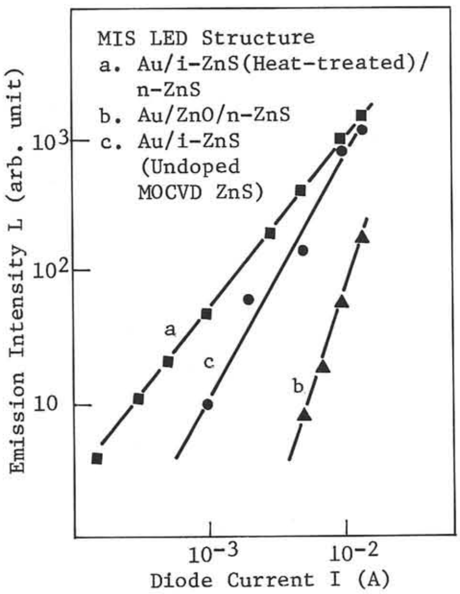


Fig. 8 L-I characteristics for ZnS MIS LEDs

## 3.2 LED characteristics

These diodes, fabricated by ZnS MOCVD, were mounted on TO-18 headers and were attached to an optical lens. Room temperature electroluminescence (EL) spectrum for ZnS blue LEDs is shown in Fig. 9. The room temperature EL wavelength has a peak at 460 nm, with showing a pure blue emission. The emission intensity-voltage (L-V) characteristics for these typical LEDs were studied. These diodes were operated in a forward drive direction at 10 mA, 5 V. Quantum efficiency obtained was typically $7 - 8 \times 10^{-5}$. Luminosity around 2 mcd was also obtained at 10 mA driving. This successful trial will be a promising procedure for low resistive ZnS crystals grown on GaP substrate by low-pressure MOCVD.

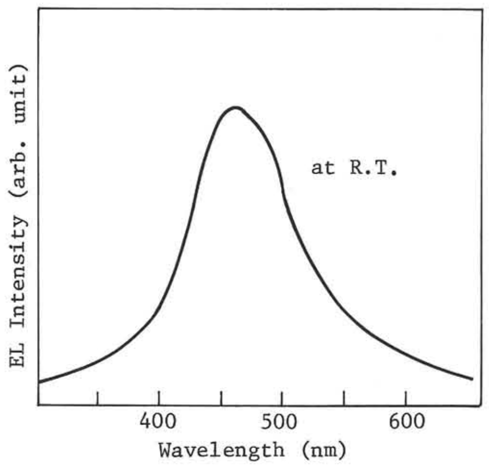


Fig. 9 MOCVD ZnS MIS LED EL spectrum

## §4. Summary

Aluminum doped ZnS crystals using low-pressure MOCVD have been shown to have a good photoluminescence property at room temperature, and have low electrical resistivity decreasing to around $10^4$ $\Omega$cm. MIS blue LEDs using insulative ZnS single crystal by MOCVD with good thin film controllability on n-type ZnS single crystal, has been revealed to have higher emission efficiency and reproducibility. These successful trials indicate a promising procedure on ZnS MIS blue LEDs fabricated on GaP substrate by low-pressure MOCVD.

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