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Optical Characterization of High-Quality ZnS Epitaxial Films Grown by Low-Pressure Metalorganic Chemical Vapor Deposition

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Abstract

High-quality ZnS epitaxial layers were grown on (100)-oriented GaAs substrates by a low-pressure metalorganic chemical vapor deposition (MOCVD) method. Dependence of Ⅵ/Ⅱ flow ratio on the 4.2K photoluminescence (PL) properties of undoped ZnS layers was particularly investigated. The PL spectrum of the excellent sample grown under optimum conditions was dominated by the radiative recombination of free and donor-bound excitons. The I_1 line appears at 332nm and becomes intense in the sample grown at relatively high Ⅵ/Ⅱ ratio. We tentatively suggest that the I_1 line which originates from a deep-acceptor bound-exciton transition may be related to Zn vacancies.

1. Introduction

The next generation of high-density optical recording and the bio-medical engineering using short wavelength light sources of semiconductors, are the two driving forces for development of the ultraviolet light-emitting diodes (LEDs) and laser diodes (LDs).1,2) Recently, GaN-based wide band gap Ⅲ-Ⅴ compounds have been commercialized for blue LEDs by Nichia Chemical Industries.3) However, the active layer of LED made from an InGaN/AlGaN double heterostructure includes large densities of extended crystal defects.4)

Alternative promising material for UV light sources is the direct band gap ZnS-based Ⅱ-Ⅵ compound.5) For high performance of UV LEDs and LDs, the growth of high-quality ZnS epitaxial layers and the fabrication of quantum wells are essential. In spite of many reports6,7,8) appeared on the growth and characterization of ZnS epitaxial films so far, it has been well-known that growth of molecular-beam epitaxy (MBE) is difficult to obtain high-quality layers because elemental S could not be supplied sufficiently. Therefore, metalorganic chemical vapor deposition (MOCVD) is generally accepted for the growth of ZnS films.5)

In order to obtain high-quality epitaxial layers of undoped ZnS on GaAs substrates, the optimum growth conditions in the MOCVD process are extensively investigated through photoluminescence measurements.

In this paper, we will describe the photoluminescence characterization at 4.2K of not

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-intentionally doped ZnS epitaxial layers as a function of either growth temperature or Ⅵ/Ⅱ flow ratio. The ZnS epitaxial layers were grown on (100) GaAs substrates using low-pressure MOCVD method.

2. Experimental procedures

Cubic-structured ZnS epitaxial films were grown on (100)-oriented GaAs substrates by a low-pressure MOCVD technique using hydrogen sulfide and dimethylzinc as S and Zn sources, respectively. In our MOCVD, metalorganic alkyle source was diluted in a He gas cylinder, namely, dimethylzinc (DMZn, with a concentration of 1.06%) and hydrogen sulfide (H_2S) with a concentration of 10.8% in H_2 gas was used. The bubbling system was not used in the present MOCVD. Their gases are supplied to a reaction chamber directly through the piezo valves of mass flow controllers and air operated valves. The flow control is considerably easy compared with the case of the bubbling system. The growth conditions are as follows : a growth pressure of 0.4 Torr, a growth rate of about 700 nm/h and growth temperatures between 300 and 450℃. The flow ratio of Ⅵ/Ⅱ was selected between 2.5 and 40. Thermal cleaning of the substrate was carried out at 550℃ for 10 minutes before growth. Photoluminescence (PL) spectral measurement was performed at 4.2 K using an Xe-Cl excimer laser (a peak wave-length of 308 nm and an excitation power density of 4.7 kW/cm^2) as an excitation source capable of causing band-to-band excitation. Because there is a doubt that the observation of free-exciton recombinations in the photoluminescence may be attributed to high-density excitation according to the Xe-Cl excimer laser excitation, the PL measurements were done at the excitation power densities as low as possible. The effect of high-density excitation is much reduced in the present experiment. Optical reflectance and X-ray diffraction measurements were also performed.

3. Results and discussion

Figure 1 shows the photoluminescence spectra obtained at 4.2K of the different epitaxial layers (thickness of about 2μm) grown at temperatures of 300,350,400 and 450℃, respectively. The Ⅵ/Ⅱ flow ratio was 18.5 (DMZn=11sccm, H_2S=20sccm). This figure gives us information on the growth temperature dependence of the excitonic emission lines and of the self-activated blue (SA) emission.[6)] Usually, the SA blue emission[6,8)] appears in the vicinity of about 460nm at 4.2K in the epitaxial layers. It is found that with increasing growth temperature the SA emission band is dramatically reduced in intensity. The excitonic emissions become predominant in the sample grown at 400℃.

Figure 2 shows the detailed spectra of excitonic emissions of the same samples as used in Fig. 1, where a line X is due to a radiative recombination of n=1 free-exciton (a peak locating at 326.27nm), a line I_2 is due to a recombination of exciton bound to a neutral-donor (a peak locating at 327.04nm), a line I_1 is a transition of exciton bound to a neutral-acceptor (a peak locating at 332.09nm). A line X-LO at 329.75nm shows a phonon replica of the line X, Although an energy separation between the X line and the I_2 line can not be observed in the sample grown at 300℃, we can observe a clear

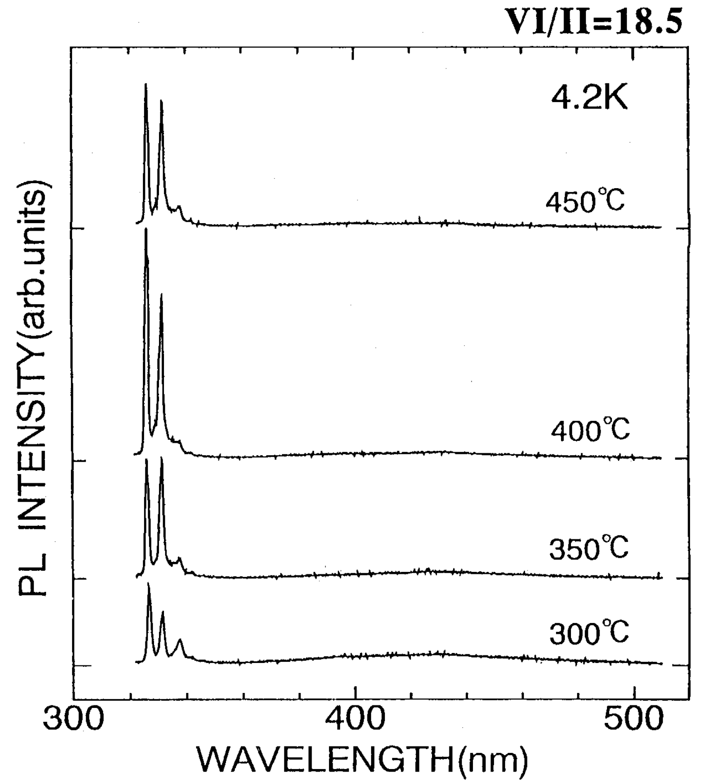

Fig. 1. Photoluminescence spectra at 4,2K of the four different ZnS epitaxial layers grown at temperatures of 300, 350, 400 and 450℃.

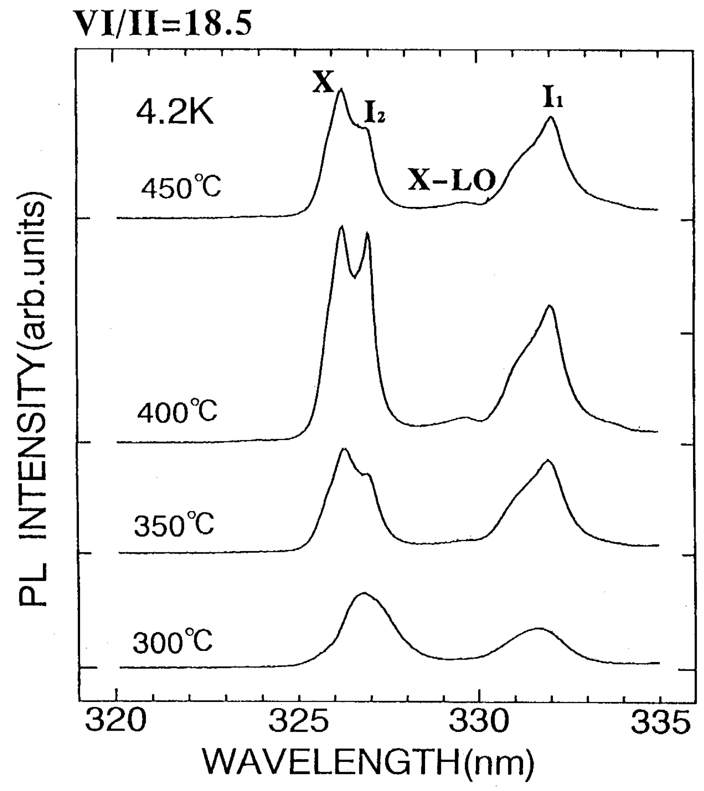

Fig. 2. Excitonic emission spectra at 4.2K of the four different ZnS epitaxial layers grown at temperatures of 300, 350, 400 and 450℃.

splitting between them with increasing growth temperature.

The crystallographic quality is very good in all samples grown at temperatures between 350 and 450℃ because the free-exciton emission (line X) is clearly observed and in the X-ray spectrum $K_{\alpha 1}$ and $K_{\alpha 2}$ peaks are clearly resolved. It is therefore considered that the epitaxial films grown at 400℃ indicate the best PL spectrum. Judging from the experimental results mentioned above, the best growth temperature is determined to be 400℃ in the present MOCVD growth.

Figure 3 shows the PL spectra obtained at 4.2K of the different ZnS epitaxial layers grown at Ⅵ/Ⅱ flow ratio of 15.7, 18.5, 22.6 and 29.1, respectively, at a constant growth temperature of 400℃. As seen in this figure, the broad SA emission band is much reduced in intensity at 18.5.

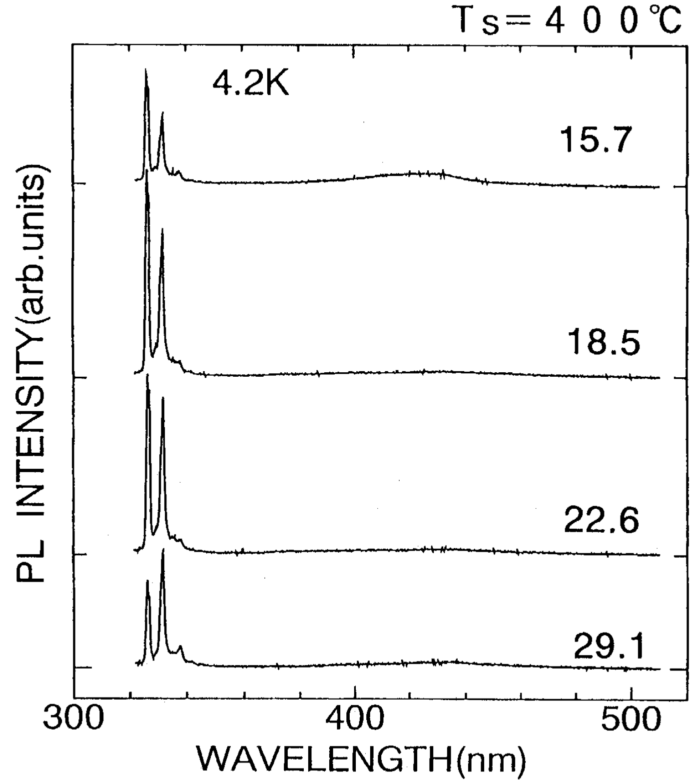

Fig. 3. Photoluminescence spectra at 4.2K of the four different ZnS epitaxial layers grown at Ⅵ/Ⅱ flow ratio of 15.7, 18.5, 22.6 and 29.1.

Figure. 4 represents the detailed spectra of excitonic emissions of the same samples as used in Fig. 3. With decreasing Ⅵ/Ⅱ ratio, the I_1 line is reduced in intensity. If a decrease of Ⅵ/Ⅱ ratio corresponds to an increase of Ⅱ element (DMZn), a number of Zn vacancies, which are related to the I_1 line, may be decreased by a sufficient supply of Zn gas. It is therefore expected that the I_1 line has a similar characteristic to the $I_1{}^d$ line, which has been identified to a deep-acceptor bound exciton transition associated with Zn vacancies in ZnSe.[9] However, the I_1 emission line still appears even though the

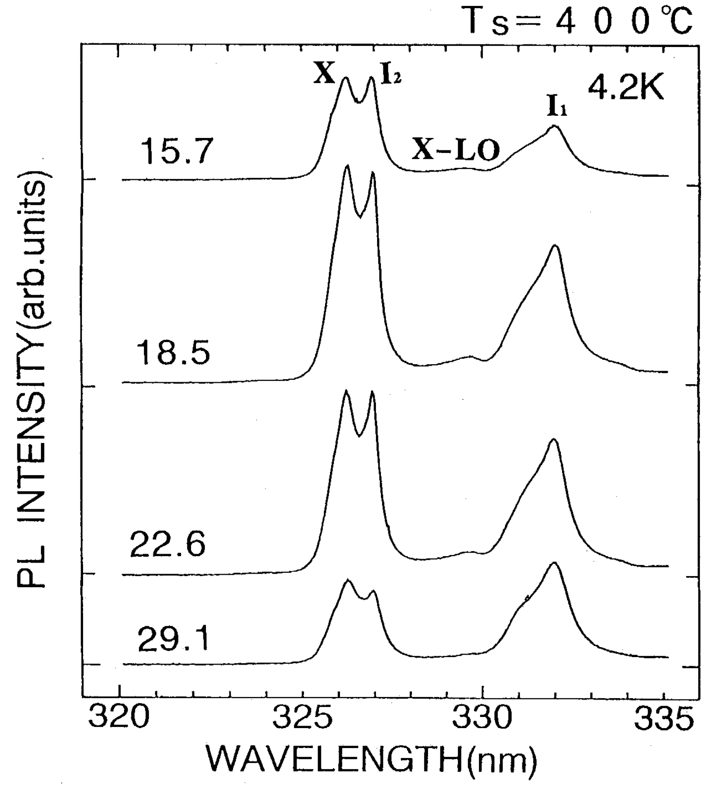

Fig. 4. Excitonic photoluminescence spectra at 4.2K of the four different ZnS epilayers grown at Ⅵ/Ⅱ flow ratio of 15.7, 18.5, 22.6 and 29.1.

Ⅵ/Ⅱ ratio is further reduced, so that the quantities of II element which can react with Ⅵ element are limited. The I_1 emission intensity is relatively stronger at the Ⅵ/Ⅱ ratio of 22.6 and 29.1, but weaker at 15.7 and 18.5. The free-exciton emission can be always observed among the four different samples. It is suggested from the results mentioned above that the best Ⅵ/Ⅱ flow ratio is estimated to be about 18.

Figure 5 shows the enlarged reflectance (upper trace) and excitonic (lower trace) spectra obtained at 4.2K of the same sample (Ⅵ/Ⅱ =18.5) used in Fig. 4. As shown in this figure, the line X indicates the $n=1$ ground state free-exciton emission. Furthermore, an excited state $n=2$ of the free-exciton is clearly observed. From the difference in energy between the $n=1$ and $n=2$ states, a binding energy of the free -exciton is calculated to be 36.3 meV.

From the dependence of growth temperature and of flow ratio on the PL spectra, it is suggested that the best growth conditions are a temperature of 400℃ and a Ⅵ/Ⅱ flow ratio of about 18.

Finally, we discuss the relationship between the I_1 line and the SA emission band. Assuming that the I_1 line has the same properties as the I_1^d line, the localization center which can bind excitons may be related a Zn vacancy. It has been well-known[6] that the SA emission band is formed by a Zn vacancy (V_{Zn}) and a donor (D) which can be replaced at either the nearest neighbor Zn site or the next nearest neighbor S site. Fig. 6 shows the correlation of the emission intensities between the I_1 line and the SA band

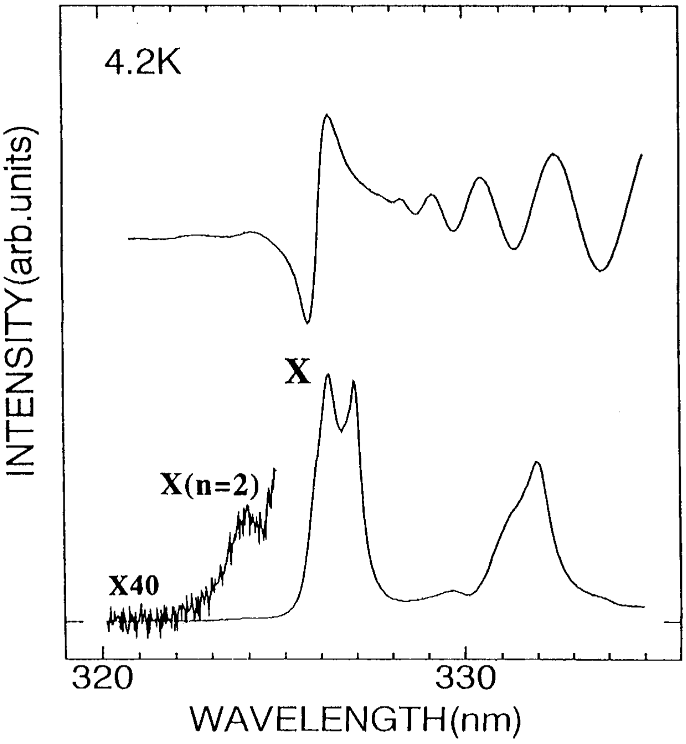

Fig. 5. Reflectance and photoluminescence spectra at 4.2K.

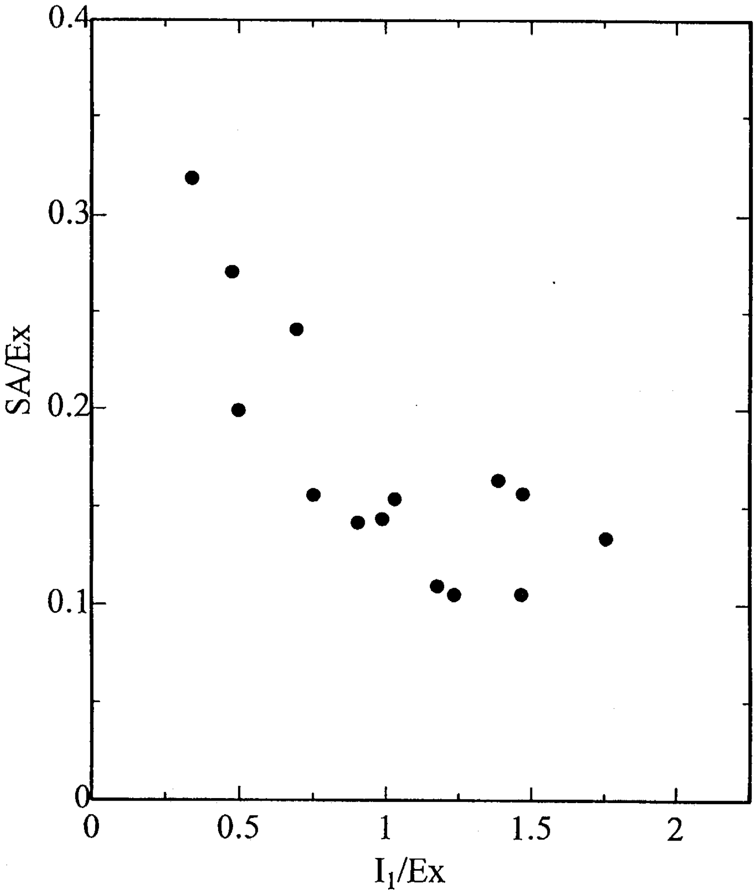

Fig. 6. Correlation between the I_1 deep-accepter bound-exciton transitions and the SA emission. (Each intensity of both the I_1 line and the SA emission band is normalized by the firee-exciton intensity (E_x))

where each emission intensity is normalized by the intensity of the free exciton (E_X). As was seen in Figs. 1 and 3 , the I_1 emission intensity becomes weak inversely as the SA emission intensity becomes strong. The localization energy of the I_1 bound-exciton line is calculated to be about 660meV using the effective mass argument.[10] This energy value corresponds to the deep-acceptor level associated with a Zn vacancy and may coincide with that of the complex-acceptor ($V_{Zn}D$) involved in the SA emission. We therefore speculate that the Zn vacancy is related to the formation of both the I_1 bound exciton line and the SA emission band.

4. Conclusions

We have shown the photoluminescence and reflectance properties of ZnS epilayers grown on (100)GaAs substrates by MOCVD. It has been revealed by the 4.2K photoluminescence spectra that the ZnS epitaxial films were high-quality. The best growth condition is determined to be the growth temperature of 400℃ and Ⅵ/II flow ratio of about 18. The binding energy of free-exciton is estimated to be 36.3 meV from the excited states of the free-exciton emission. It is found that the emission intensity of the I_1 line is much decreased with decreasing Ⅵ/II flow ratio. We tentatively suggest that the origin of the I_1 line may be related to Zn vacancies.

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