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Li-doped *p*-type ZnS Grown by Molecular Beam Epitaxy

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Abstract : Li-doped ZnS layers were grown by molecular beam epitaxy. It was found that relatively low growth temperature is suitable for effective incorporation of Li acceptors. The layers grown under optimized conditions exhibited photoluminescence spectra dominated by neutral-acceptor-bound excitons. Such layers also showed electrically *p*-type behavior in capacitance-voltage characteristics. The net acceptor concentration is estimated to be approximately 3×10^{15} cm^{-3}.

Key words : Li-doped ZnS, Net acceptor concentration, Molecular beam epitaxy

1. Introduction

ZnS has a large band gap energies about 3.7eV at room temperature[1] and is known as a host crystal for efficient phosphors. In addition, by using alloys such as ZnSSe[2] and ZnMgS[3],[4], one can construct heterostructures[5]-[7] necessary for optical devices. Thus, ZnS-based material systems seems to be one of candidates for semiconductor short wavelength optoelectronic devices. In particular, ZnS has a large exciton binding energy of about 37 meV. Therefore, ZnS is a fruitful candidate to realize excitonic optical devices at room temperature. In order to realize ZnS-based light-emitting devices, it is essential to grow high-quality ZnS epitaxial layers and control its electrical conductivities. However, it is very difficult to achieve *p*-type conduction in this material, and thus practical semiconductor devices have not been realized using ZnS-based materials. The difficulty in *p*-type doping stems from carrier compensation by residual donor-like impurities and defects.

To date, there have been several reports on *p*-type conduction in ZnS, including ZnS:N[8] and ZnS:N,Ag,In[9] grown by vapor phase epitaxy, ZnS:Li grown by metalorganic vapor phase epitaxy (MOVPE)[10] and metalorganic chemical vapor epitaxy(MOCVD)[11], ZnS:N and ZnS:Li grown by MOVPE[12], Li- and Na-doped ZnS grown by molecular beam epitaxy (MBE)[13]. However, there is no established and reproducible growth technique for the

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p-type ZnS with sufficiently low resistivity and good optical property. In addition, there is no report on p-type conduction in ZnS grown by MBE, although Li doping was reported[14].

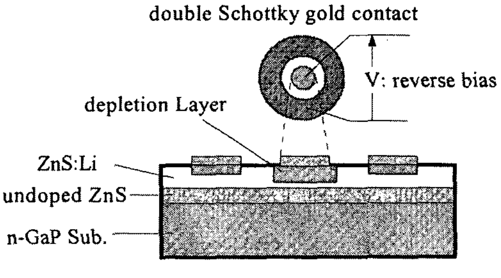
In the present work, Lithium (Li)-doped ZnS epitaxial layers are grown by MBE, and optical and electrical properties of Li-doped ZnS epitaxial layers are characterized by employing photoluminescence (PL) and capacitance- voltage (C-V) measurements by which net acceptor concentration is estimated.

2. Experimental procedures

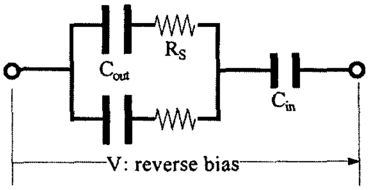
ZnS:Li epitaxial layers were grown by MBE using metal Zn and Li, under excess S beam pressure evaporated from an elemental source. The detail of the growth procedure was reported elsewhere[15].

Such a S over-pressure condition may be effective to incorporate Li into Zn site. This is one of the reason why Li is chosen as an acceptor species in this study. On a *n*-type GaP substrate, first a 0.5µm-thick undoped ZnS layer was grown for electrical isolation and for avoiding the problem related to the ZnS/GaP interface. Then a ~1.5µm-thick ZnS:Li layer was grown.

Photoluminescence (PL) spectra were recorded at 10 K using a standard lock-in technique. A Xe lamp in conjunction with a monochromator was used as an excitation light source. For electrical characterization, a pair of concentric Schottky gold contacts were fabricated on the surface of ZnS:Li layer. Fig. 1 shows the sample configuration for C-V measurement. The inner circle electrode has a diameter of 250µm, and the outer ring electrode with a diameter of 1000µm is separated by 100µm from the inner electrode. In Fig. 1(b), C_{out} and C_{in} are the capacitance of depletion layer of outer circle and inner circle, respectively, and R_S represents the resistance between these electrodes. This device is designed to measure capacitance that is in parallel with resistance. The net acceptor concentration N_A is given by



(a) Schematic diagram of device



(b) Equivalent circuit at double Schottky gold contact

Fig. 1 Sample configuration for C-V measurement

$$N_A = \left[\frac{e\varepsilon}{2} \frac{d}{dV} \left(\frac{S}{C} \right)^2 \right]^{-1}$$

where C is the measured capacitance given by

$$\frac{1}{C} = \frac{1}{C_{in}} + \frac{1}{C_{out}} \simeq \frac{1}{C_{in}}$$

C is approximately C_{in} because the area ratio between outer and inner contacts is

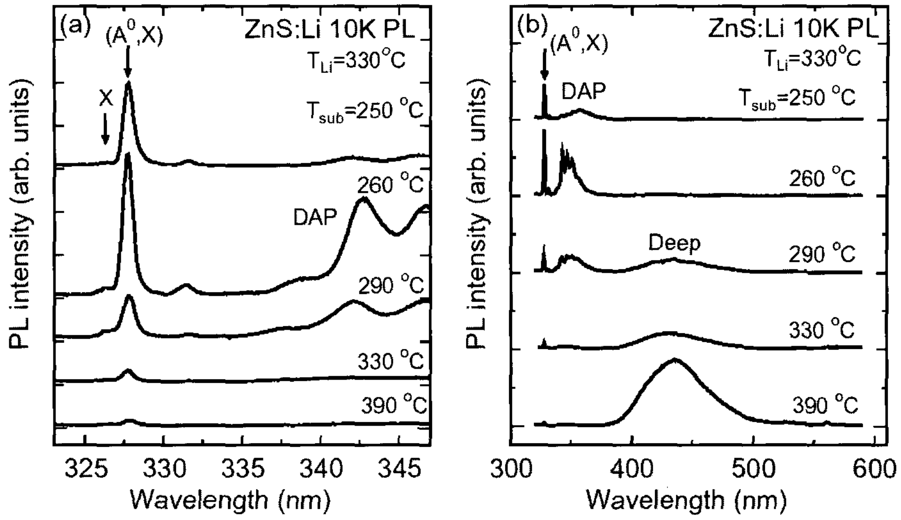


Fig. 2 PL spectra of ZnS:Li grown at different substrate temperatures, T_{sub}, for (a) band edge and (b) wide spectral range

about 14.

C-V characteristics was measured between these electrodes using C-V meter (SANWA MI-319A).

3. Results and discussion

Fig. 2 (a) shows PL spectra of ZnS:Li grown under different substrate temperatures (T_{sub}), in the spectral range corresponding to the band-edge. Each spectrum contains (A^0,X) line at 327.8nm, that is, radiative recombination of excitons bound to neutral acceptors, and donor acceptor pair (DAP) emission band with zero-phonon line at 342-343nm. As T_{sub} decreases, the (A^0,X) line becomes strong in absolute intensity as well as in relative intensity to free-exciton(X) emission at 326.3nm. This suggests an increase in the number of substitutional Li acceptors.

Fig. 2 (b) shows the PL spectra for a wider range. It is worth noting that almost no deep level emission was seen in the wavelength range of more than 400nm, for the layers grown at T_{sub}=250-260℃. The observation of DAP band suggests compensation of acceptors by intrinsic or extrinsic (e.g., interstitial Li) donor to some extent, however, the dominance of (A^0,X) line and the weakness of deep level emission shows high concentration of acceptors and low density of defects in the layers grown at T_{sub} of 250-260℃.

Fig. 3 (a) shows C-V characteristics of ZnS:Li layer grown at T_{sub}=250℃ and T_{Li}=330℃. The ZnS:Li layers at $T_{sub} \geq 290$ ℃ were high resistive. Those layers show only low capacitance, because the layers were fully depleted probably owing to a very low acceptor concentration. The voltage of horizontal axis in Fig. 3 is applied to the inner smaller electrode against the outer larger electrode. Therefore, a decrease in capacitance under positive bias voltage as shown in

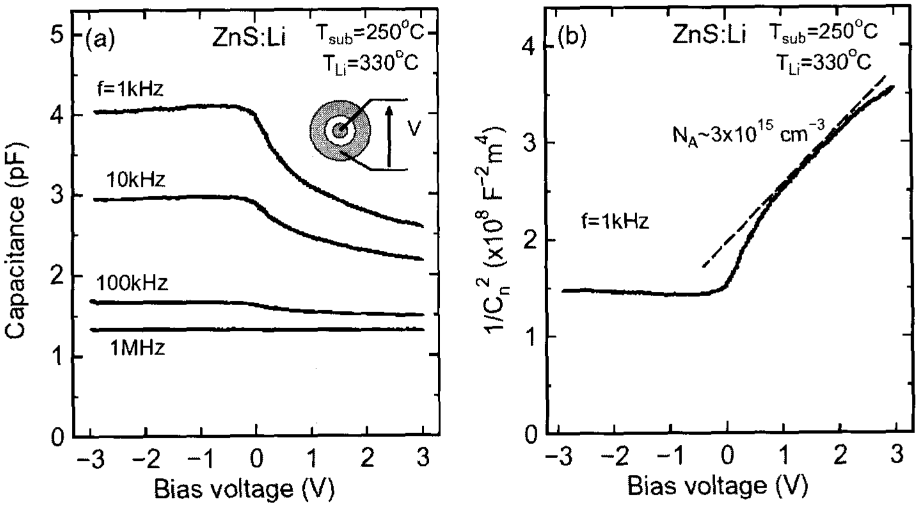


Fig. 3 (a) C-V characteristics of ZnS:Li epitaxial layer grown at T_{sub}=250℃ and T_{Li}=310℃. The inset schematically shows the shape of the Schottky contacts and the polarity of the bias voltage.
(b) Dependence of $1/C_n^2$ on bias voltage, where C_n is capacitance per unit area. Net acceptor concentration of $\sim 3\times10^{15}$cm^{-3} is obtained from the slope.

Fig. 3 (a) means an increase of depletion layer thickness beneath the inner electrode, resulting from an increase of reverse bias. Such a behavior means that the layer is *p*-type. Next, the dependence of the measured capacitance on the probe frequency *f* is discussed. The sample forms a electrical circuit, which consists of capacitance due to depletion layers and resistance due to semiconductor layer between the electrodes. The C-V measurement device used in this study assume parallel circuit of capacitance and resistance, therefore, the measured capacitance value deviates from the correct value if the series resistance cannot be neglected. This is the main reason why measured value of the capacitance decreases with increasing the probe frequency. Thus the data obtained for f=1 kHz is discussed in the following. Fig. 3 (b) shows the $1/C_n^2$-V characteristics, where C_n is capacitance per unit area. From the slope of the curve, one can determine the net acceptor concentration to be $N_A \simeq 3\times 10^{15}$cm^{-3}. This value is not enough for practical applications, however, the *p*-type samples have good luminescence properties as shown above. This seems to be important for the application for light-emitting devices. In addition, this is the first report on MBE-grown *p*-type ZnS.

4. Conclusions

ZnS:Li epitaxial layers have been grown by MBE. It was found that the growth temperature sensitively affects the doping efficiency, and relatively low growth temperature of 250-260℃ is suitable for incorporation of Li acceptors. PL spectra of ZnS:Li crystals grown at such low temperatures were dominated by strong neutral-acceptor-bound exciton emission, and almost no deep level emission was observed. These layers showed p-type behavior in C-V characteristics, giving net acceptor concentration N_A of approximately 3×10^{15} cm^{-3}.

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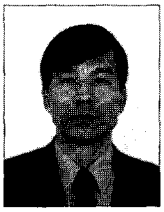

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