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Molecular-Beam-Epitaxial Growth and Characterization of High-Quality Undoped ZnSe Films

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High-quality undoped ZnSe thin films are grown by molecular beam epitaxy(MBE). The MBE ZnSe shows the largest peak intensity ratio of the near-band-edge emission to the deep center luminescence even at room temperature compared with other epitaxial techniques. From the temperature dependence of electron mobility for MBE ZnSe, we obtained the mobility value as high as 6900 $cm^2/V.sec$. This is the highest value ever obtained in epitaxial ZnSe films.

§1. Introduction

High-quality p-type ZnSe is requisite to fabricate high-efficient blue light emitting devices. There have been some attempts to grow p-ZnSe by using an ion implantation technique[1)] or epitaxial growth techniques[2,3)]. However, no successful results have been achieved. This is mostly due to electrically active impurities unintentionally incorporated into undoped ZnSe. It is highly desirable to establish growth technique for high-quality undoped ZnSe.

Device-quality ZnSe thin films have been grown by molecular beam epitaxy(MBE)[4)]. With MBE technique, as-grown low-resistivity films which emit dominant near-band-edge emission are obtained. In this paper, MBE growth and characterization of high-quality undoped lowresistivity ZnSe thin films are reported.

§2. Molecular Beam Epitaxy

The substrate used was semi-insulating (100) GaAs, which was thermally cleaned at 630 °C for 1 min before commencing growth. The substrate temperature during growth was 280 °C. The molecular beam flux ratio $k_{Zn}J_{Zn}/k_{Se}J_{Se}$ was taken to be about unity.[5)] The growth rate was about 0.6 µm/hr. The thickness of the epilayer was about 3 µm.

§3. Experimental

We measured PL spectra at room temperature by using the 3250 A line from a He-Cd laser as the exciting light with an excitation power of 200 mW/cm^2, which is considered to be a sufficiently weak excitation condition.

The resistivity and Hall effect were measured by va der Pauw method .

§4. Results and Discussion

A typical spectrum of nominally undoped, low-resistivity MBE ZnSe at room temperature is shown in Fig.1. The spectrum consists of a dominant near-band-edge emission band at around 460 nm and very weak deep emission band at around 590 nm. The deep emission is related with self-activated centers. By optimizing the growth condition, the peak intensity ratio (R) between the narrow NBE and the deep center luminescence becomes as high

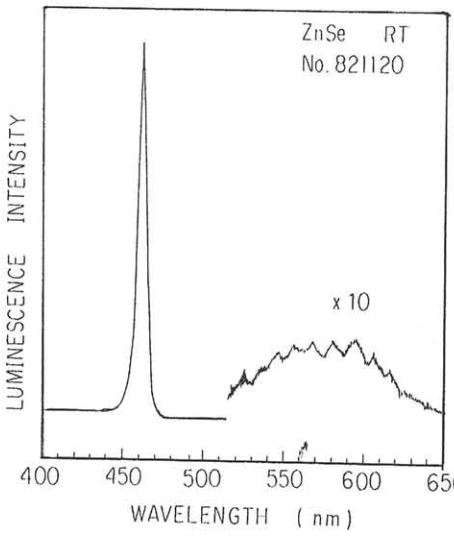

Fig.1. Photoluminescence spectrum of MBE ZnSe measured at room temperature.

as 40 even at room temperature, which is the largest value among ZnSe epilayers grown by various techniques (Table 1). The high R value indicates a low concentration of the self-activated centers.

Figure 2 shows temperature dependence of electron mobility of MBE ZnSe films. The mobility at room temperature is 530 - 550 $cm^2/V.s$. The electron mobility in ZnSe at around room temperature is dominated by polar optical phonon scattering, while the electron scattering by charged defects will dominate at low temperature. The mobility increases with lowering temperature and ha a maximum at a certain temperature. We denote the maximum mobility μ_{max} and the temperature T_{max} at which the mobility reaches the maximum value. With decreasing concentration of charged defects (N_I), the μ_{max} value increases and the T_{max} value is lowered. The μ_{max} values in MBE ZnSe are as high as 4.7 - 6.9 x 10^3 $cm^2/V.s$, and the T_{max} values are 30 - 40 K. The slight difference in μ_{max} for the two MBE ZnSe films is attributed to a slight difference in the actual growth conditions.

Table 1 shows the reported μ_{max} values and T_{max} values for epilayers grown by various epitaxial techniques. MBE ZnSe shows the highest value ever obtained in epitaxial ZnSe films.

The solid line in Fig.2 shows the calculated mobility via polar optical phonon scattering (μ_{PO}), scattering by charged defects (μ_I), and the resultant mobility. The μ_I values were calculated by using the Conwell and Weisskopf formula[6)]

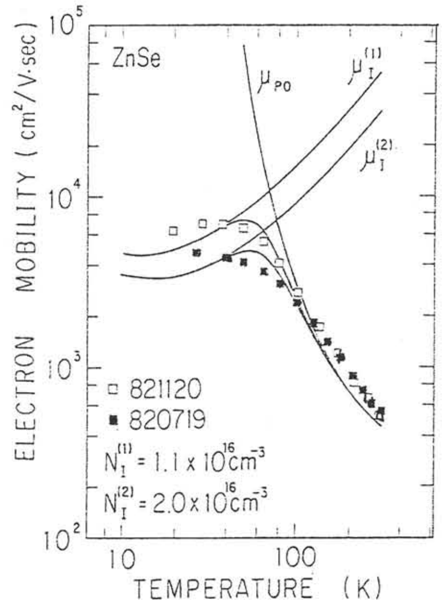

Fig.2. Temperature dependence of electron mobility of MBE ZnSe thin films and calculated mobility.

assuming singly charged defects. The concentration of charged defects (N_I) were chosen so as to make the calculated mobility values fit the experimental values. The obtained N_I values are tabulated in Table 1 together with estimated values from the μ_{max} values for MOCVD, LPE, and CVD ZnSe films. It is noted that the N_I value of MBE ZnSe is extremely small, as low as 1 - 2 x 10^{16} cm^{-3}, while those in MOCVD, CVD and LPE films are larger than 1 x 10^{18} cm^{-3}. This indicates that MBE grown ZnSe films are of extremely high quality.

Why can MBE grow such high quality ZnSe films?

TABLE 1. R and μ_{max} values in ZnSe films grown by various epitaxial techniques.

	T_{sub} (°C)	R ($\frac{NBE}{deep}$)	μ_{max} ($\frac{cm^2}{V.sec}$)	T_{max} (K)	μ_{RT} ($\frac{cm^2}{V.sec}$)	n_{RT} (cm^{-3})	N_I (cm^{-3})	Ref.
L P E	850-1050	2	?	?	100	10^{17}	$2x10^{19}$	(7)
C V D	750	0.1[10)]	220	RT	210	$1.5x10^{16}$	$4x10^{18}$	(8)
MOCVD	350	?	400	RT	400	$6.5x10^{17}$	$1x10^{18}$	(9)
M B E	280	40	$6.9x10^3$	30	550	$1.1x10^{16}$	$1x10^{16}$	present study

This is mainly due to the low growth temperature in MBE growth. As shown in Table 1, the substrate temperature of MBE is the lowest among the epitaxial growth techniques. It is noted that with decreasing growth temperature the μ_{max} value increases and the N_I value decreases. We have found that the μ_{max} value of MBE ZnSe decreases with the increase of the substrate temperature above 280 °C.

The advantage of the low temperature are summarized as follows : (1) Out-diffusion of impurities from substrate material is reduced. (2) Generation of contaminant impurities from the back ground is suppressed. (3) Concentration of native defects as V_{Zn}, for instance, is reduced, and the concentration of the self-activated centers is reduced. All of the above mentioned points are effective for growing high-quality epitaxial films.

§5. Conclusions

High-quality and -purity undoped ZnSe thin films have been grown by MBE technique with low substrate temperature. It is expected that the MBE technique will contribute to growing high quality p-type ZnSe.

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