

Growth of High-purity ZnSe Single Crystals and Characteristics of MOCVD Homo-Epitaxially Grown ZnSe Films

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High-purity and large single crystals of bulk ZnSe, exhibiting excellent excitonic characteristics, have successfully been grown by recrystallization travelling-heater-method (THM) at about 850°C using a fine grained polycrystalline ingot. Effect of uniaxial stress on the I_1^d line (a deep acceptor-bound exciton) reveals that the line splits into three components along $\langle 111 \rangle$ direction due to reduction in symmetry from T_d to C_{3v} . The binding energy of Na acceptor ground state was estimated to be 102 meV from two-hole transitions in Na-doped crystals. ZnSe homoepitaxial layers have been grown using metal-organic chemical-vapour-deposition (MOCVD) onto the present ZnSe substrates. The effects of substrate temperature and orientation on photoluminescence spectra were presented.

1. Introduction

ZnSe is a very promising material for the fabrication of blue light-emitting diode (LED) because of direct band gap of 2.7 eV at room temperature. However, because p-n homojunctions have not been successfully fabricated on ZnSe bulk and film, the blue LED technology has not matured to the point of successful commercial realization.¹⁾

Several heteroepitaxial growth techniques have been reported for the ZnSe/(100) GaAs and Ge using MOCVD and molecular-beam epitaxy (MBE) at low temperature around 300 °C. Such epitaxial layers exhibit strong principal donor-bound excitons (BE), I_2 and I_x lines. It has been suggested that, for example, Ga out-diffusion from the GaAs substrate is most probably responsible for the presence of a donor BE.²⁾ It has thus been pointed out that both spectral shape and position of the BE lines are much affected by a local lattice strain due to misfit dislocations resulting from lattice mismatch and the difference in the thermal expansion coefficient between them.³⁾

Recently, homoepitaxial growth of ZnSe has been shown using MBE and MOCVD methods.^{4,5)}

Although ZnSe substrate has no problems on its lattice constant and thermal expansion coefficient for the growth of ZnSe epitaxial layers, it has been difficult to obtain large area and high-quality single crystal of bulk ZnSe.

This paper will describe the growth and characterization of high-purity single crystal of bulk ZnSe by recrystallization "Travelling-heater-method (THM)" using a fine grained polycrystalline ingot. In particular, we are concerned in this paper with the origins of the acceptor BE lines (I_1^d at 2.783 eV and I_1^{Na} at 2.7929 eV at 4.2 K), and with homoepitaxial ZnSe growth and evaluation which are studied by low-temperature photoluminescence (PL) as a function of substrate temperature and orientation.

2. High-purity ZnSe by recrystallization THM

The present growth system is schematically described in Fig. 1. The feed material was in the form of a fine grained polycrystalline plate (approximately size, 7x7x50mm³) produced by CVD from Zn vapour and H₂Se gas on a carbon substrate at 700 °C in controlled Ar carrier gas. The growth ampoule including

this feed ingot was first evacuated to about 10^{-6} Torr and then high-purity Ar gas was introduced up to 1 Torr. The temperature zone was kept about 850 °C, where a sharp zone of about 1 cm was acquired by a RF heating (400 kHz) and its temperature was precisely controlled by an auto frequency feedback circuit within ± 0.2 °C. The ampoule lowering speed was about 1-3 mm/day. After 2-3 weeks, the fine grained ingot was changed to a single crystal in terms of, presumably, grain growth mechanism. The large cleaved face, about $8\text{ mm}^2 \phi$, was easily obtainable as shown in Fig. 2.

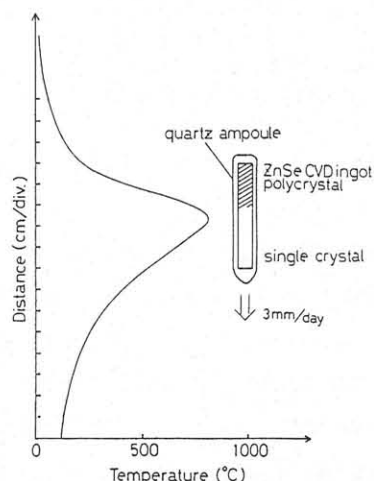


Fig. 1 Temperature profile of the RF furnace by THM and a schetch of the ampoule.

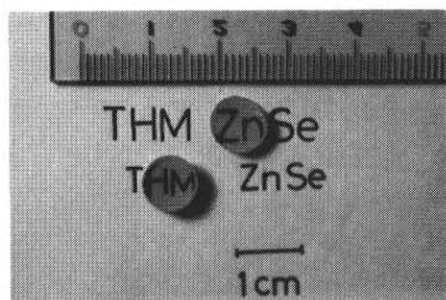


Fig. 2 The obtained ZnSe crystals at 850 °C.

3. PL characterization

3.1 As-grown crystal

As-grown crystal exhibited a high-resistivity above $10^8 \Omega\text{cm}$ at RT. Figure 3 shows the PL spectra obtained at 4.2 K of (110) ZnSe crystal. There appears a very strong I_1^d line having associated with 5-LO phonons. The insert shows the excitonic-emission lines

; the E_X^L lower polariton at 2.802 eV and the E_X^U upper polariton at 2.8036 eV are clearly observed. however, donor BE line, denoted by the I_2 at about 2.796 eV was extremely weak in intensity compared to that of free-exciton line. Such features have never been reported until now. It is therefore suggested that the large recrystallization THM crystal exhibits excellent and well-resolved excitonic emissions. After Zn extraction at 910 °C for 140 h, the excitonic-emission spectrum was drastically changed; the I_2 line at 2.796 eV becomes intense and is tentatively assigned to a Ga impurity involved in Zn metal.⁵⁾

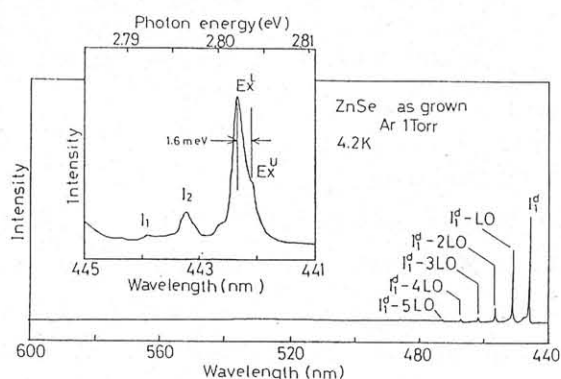


Fig. 3 PL spectra at 4.2 K of (100) ZnSe crystal and excitonic lines

3.2 Effect of uniaxial stress on the I_1^d line and Na acceptor

The I_1^d line has already been ascribed to excitons bound to a neutral acceptor, originating from either Zn vacancy or Cu impurity on Zn lattice site. However, there is nothing report concerning the spatial symmetry of the localized states which bind excitons, so far.

Fig. 4 shows the uniaxial stress measurement on the I_1^d line at 4.2 K along $\langle 111 \rangle$ direction. With increasing compressive stress, the line splits into three components, all of them being allowed for both polarization (2σ and π lines). The I_1^d line complex consists of two holes from the Γ_8 valence band and an electron from the Γ_6 conduction band. Using one-electron wavefunctions for both the holes and

the electrons, and stress Hamiltonian,⁶⁾ the three energy splittings can be obtained for the $\langle 111 \rangle$ direction,

$$E_{1,2} = a(S_{11} + 2S_{12})P \pm \frac{d}{2\sqrt{3}} S_{44}P$$

$$E_3 = a(S_{11} + 2S_{12})P$$

where S is elastic compliance coefficient, a is the hydrostatic pressure deformation potential and d is the exciton deformation potential. The solid lines in Fig. 4 yield the best fit of the above equations to the experimental results with $a=5.2$ eV and $d=4.3$ eV. It is apparent the I_1^d line is reduced in symmetry from T_d to C_{3v} under $\langle 111 \rangle$ axial stress.

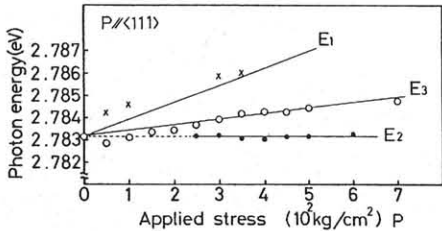


Fig. 4 Uniaxial stress effect on the I_1^d line along $\langle 111 \rangle$ direction.

Let us next briefly discuss the fine spectral feature related to Na acceptor. The Na impurity was doped with Na_2Se and Se from the vapour phase at 500 °C into (110) ZnSe.

Fig. 5 shows the Na acceptor BE emissions locating at 2.7937 eV and 2.7929 eV at 4.2 K. These three components may be originated from J-J coupling effect; namely, all dipole-allowed transition from $J=1/2, 3/2$ and $5/2$ exciton-excited states to $j=3/2$ acceptor-ground state.

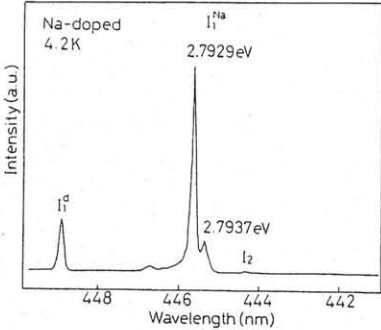


Fig. 5 Na acceptor bound-exciton line at 4.2 K.

It should be noted that the 4-LO phonon lines appear as shown in Fig. 6. With decreasing temperature, the highest line at 2.7937 eV

becomes very weak in intensity obeying to the Boltzman law. Because of no donor-acceptor pair band around 460 nm, the two-hole transition lines resulting from $2P_{3/2}, 2S_{3/2}$ and $2P_{5/2}$ excited states, have for the first time been observed. The energy difference between $1S_{3/2}$ and $2P_{3/2}$ is calculated to be 68.1 meV. Providing a central cell correction to the ground state, the Na acceptor binding energy is then calculated to be 102 meV.

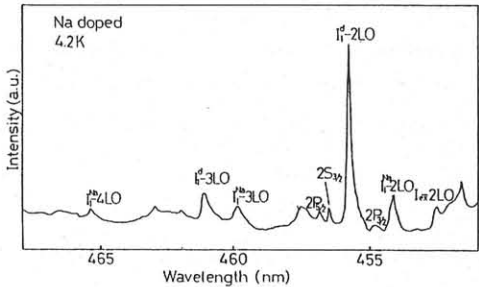


Fig. 6 Two-hole transition lines of the Na BE line.

4. Homoepitaxial ZnSe growth and characterization

ZnSe layers were homoepitaxially grown onto high-resistivity (111), (100) and (110) ZnSe substrates by low-pressure MOCVD using dimethylzinc (0.16% concentration) gas in He and 10 % H_2Se gas in H_2 .

Fig. 7 shows the PL spectral variations obtained at 4.2 K of ZnSe layers grown at 300 °C as a function of substrate orientation. Prior to growth, the substrates were heat-treated in H_2 gas at about 500 °C for 10 min. There appears I_2^M line at 2.7965 eV, locating between the I_2 and I_x lines which are usually observed in heteroepitaxial ZnSe layers onto GaAs. The origin of the I_2^M line is tentatively proposed to excitons bound to a certain donor. The linewidth (~ 5 meV) of this line is slightly broader than that of the I_2 line. The I_1^d line is also seen. The LO-phonon replicated 2.720 eV band is ascribed to a free-to-bound acceptor transition encompassing a Na acceptor lying at 100 meV above the valence band. In particular, in the case of ZnSe/(110)ZnSe, the 2.720 eV band was strong in inte-

nsity. The deep-level emissions, designated as M and SA, located at about 500 and 600 nm, respectively, were strong in intensity in ZnSe/(111)ZnSe.

Fig. 8 shows the PL spectra obtained at 4.2 K of ZnSe layers onto (110) ZnSe as a function of substrate temperature. The energy position and linewidth are not so much changed depending upon the growth temperature. At 250 °C, the SA band becomes intense, but the 2.720 eV band completely vanish at 350 °C

Fig. 9 shows the energy peak position of the I_2^M line in ZnSe/(110)ZnSe as a function of growth temperature. For comparison, the peak shifts of the I_2 and I_x lines observed in ZnSe/(100)GaAs by MBE are described.⁷⁾ Both the I_2 and I_x lines show the energy downshift with increasing growth temperature. On the

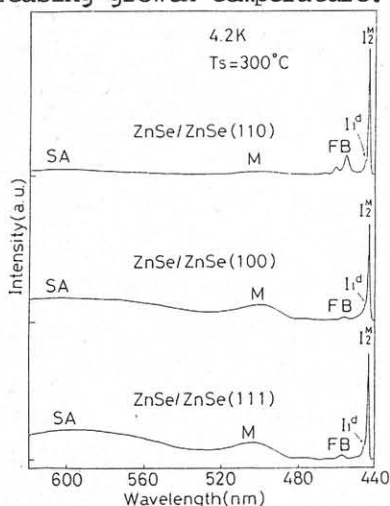


Fig. 7 PL spectra of homoepitaxial ZnSe on (110), (100) and (111) faces.

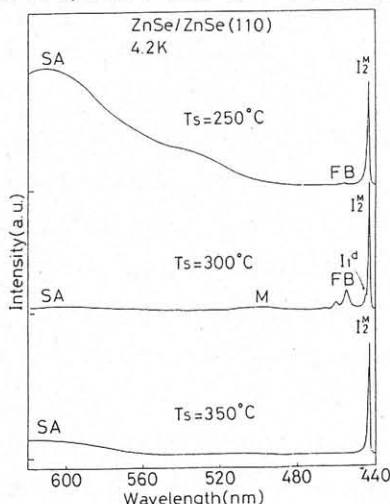


Fig. 8 PL spectra of homoepitaxial ZnSe as a function of substrate temperature.

other hand, the I_2^M line appearing in the homoepitaxial layers does not shift in the entire growth temperature. This result suggests that any kinds of strain could not be included in the homoepitaxial layers. It is therefore emphasized that the homoepitaxial ZnSe film is superior to that of heteroepitaxial ZnSe on GaAs substrate.

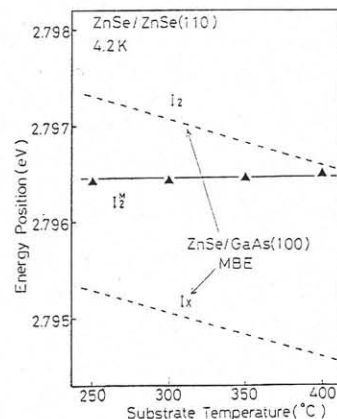


Fig. 9 Energy shifts of the I_2 , I_x and I_2^M lines as a function of substrate temperature.

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