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Surface process and lattice relaxation in growth of $\text{ZnS}_x\text{Se}_{1-x}$ epilayers on GaAs substrate by VPE

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Successful vapour phase epitaxial (VPE) growth of $\text{ZnS}_x\text{Se}_{1-x}$ on (100) GaAs substrate is reported. The solid composition x can be controlled by varying the substrate temperature. This result is discussed in terms of adsorption and desorption processes at the vapour-solid interface. An activation energy of $E = 24.3$ kcal/mol is deduced for the S/Se mixture in the solid. The effect of lattice relaxation is investigated. The perpendicular relative mismatch ($\Delta a^\perp/a$) is measured and a maximum value of -6×10^{-3} is found for $x > 0.2$. The emission from exciton-exciton interaction was observed in $\text{ZnS}_x\text{Se}_{1-x}$ ($x = 0.1, 0.2$) epilayers at 77 K for the first time. It indicates that high quality $\text{ZnS}_x\text{Se}_{1-x}$ epilayers have been grown by VPE method.

1. Introduction

The VPE $\text{ZnS}_x\text{Se}_{1-x}$ epilayer is one of the most promising materials for optoelectronic devices for use in the region between blue and ultraviolet, so that most of the interest has been focused on the growth and photoluminescence (PL) of VPE $\text{ZnS}_x\text{Se}_{1-x}$ epilayers [1,2]. Composition control and, thereby, control of the lattice constant is crucial for most heterostructure devices. Hence, it is necessary to obtain a better understanding of the process governing the growth of alloys.

In the growth of $\text{ZnS}_x\text{Se}_{1-x}$ by VPE, it is often found experimentally that the composition in an epilayer differs strongly from the composition in the gas phase, and the composition in the solid changes significantly with growth temperature (T_{sub}). This phenomenon is similar to that in the $\text{GaAs}_{1-x}\text{P}_x$ growth system [3]. It means that a process with an activation energy exists in the $\text{ZnS}_x\text{Se}_{1-x}$ growth system. The lattice relaxation in a mismatched $\text{ZnS}_x\text{Se}_{1-x}$ epilayer on a GaAs substrate can cause the formation of defects which have a serious influence on the electrical and optical properties of the layer. For epilayers with a certain thickness, we found that lattice relax-

ation takes place only if the composition x is larger than a critical composition (x_c). This result shows that the layers with x less than x_c should be of high quality. In this work, we have determined the activation energy for the $\text{ZnS}_x\text{Se}_{1-x}$ growth system by the method given in ref. [3]. The effect of lattice relaxation was investigated. In an unrelaxed (i.e. coherently strained) epilayer, i.e. the composition x in the layer less than x_c , spontaneous and stimulated emission due to exciton-exciton interaction ($E_x - E_x'$) is for the first time reported at 77 K.

2. Experimental procedure

ZnSe and ZnS powders are used as growth sources. There are three regions in the reaction tube of the VPE apparatus. In region I, ZnS and ZnSe sources were arranged separately in the inner reaction tubes and they react with hydrogen gas independently to form gas sources which flow into region II, where they mix and react with each other. Region III is a growth region where $\text{ZnS}_x\text{Se}_{1-x}$ deposits on the growth surface. Palladium diffusion H_2 is used as a carrier gas. The

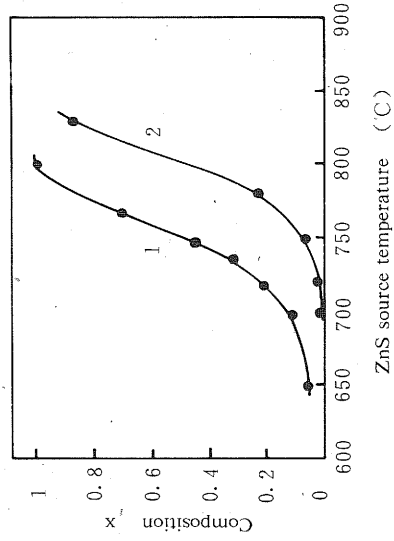


Fig. 1. Variation in the solid composition x with ZnS source temperature for VPE ZnS_xSe_{1-x} epilayers; $T_{sub} = 550^\circ C$ (curve 1) and $T_{sub} = 650^\circ C$ (curve 2).

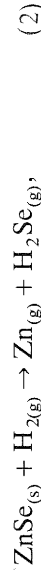
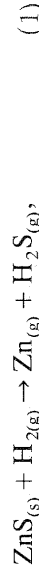
ZnSe source temperature ($T_{ZnSe} = 850^\circ C$), H_2 flow rate over ZnSe source ($J_1 = 50 \text{ cm}^3/\text{min}$) and ZnS source ($J_2 = 40 \text{ cm}^3/\text{min}$) are constant. The substrate used in this study is n-type GaAs, oriented in the [100] orientation. A different composition x is obtained by varying the ZnS source temperature ($T_{ZnS} = 720\text{--}850^\circ C$) and substrate temperature ($T_{sub} = 550\text{--}650^\circ C$). The x values are determined from PL spectra as reported by Stutius [4]. The PL spectra are measured with a Spex-1403 monochromator. The 337.1 nm line of a N_2 laser ($f = 15 \text{ Hz}$, $\tau = 10 \text{ ns}$), or the 435.7 nm line from a Nd:YAG laser pumped H_2 Raman frequency shifter ($f = 15 \text{ Hz}$, $\tau = 5 \text{ ns}$) is used as an excitation source. The samples are immersed in liquid nitrogen.

3. Results and discussion

3.1. Growth of VPE ZnS_xSe_{1-x}

Fig. 1 shows the variation in solid composition of S in ZnS_xSe_{1-x} with ZnS source temperature in the case of constant $T_{sub} = 550^\circ C$ (curve 1) and $T_{sub} = 650^\circ C$ (curve 2). We see that the composition of S in the solid increases with increasing T_{ZnS} . For a constant T_{ZnS} , the composition x for $T_{sub} = 550^\circ C$ is larger than that for $T_{sub} = 650^\circ C$. These results indicate that the solid composition is not only dependent on the ZnS

source temperature, but also on the substrate temperature. Obviously, surface processes, which are a function of substrate temperature, may play an important role in the growth of ZnS_xSe_{1-x} . The reaction equations in the source region are written as [1]:



where (s) and (g) express solid and gas phase, respectively. In the growth region, the gas composition (x_g) of S can be expressed as:

$$x_g = P_{H_2S} / (P_{H_2S} + P_{H_2Se}), \quad (3)$$

where P_{H_2S} and P_{H_2Se} are the partial pressures of H_2S and H_2Se in the gas phase, respectively. In fact, x_g is different from x due to the existence of the surface process. According to the study on organometallic epitaxial growth of $GaAs_{1-x}P_x$ by Samuelson et al. [3], the surface process includes adsorption and desorption processes of S and Se on the growing surface. By the analysis of the surface dynamical process, the relation between x and x_g can be expressed as:

$$\frac{x}{1-x} = \frac{\alpha}{\beta} \frac{x_g}{1-x_g}, \quad (4)$$

where $\alpha/\beta = d_{Se}k_s/k_{Se}d_s$, and d_s , k_i and d_i are the adsorption and desorption rate coefficients of atom i , respectively. Both k_i and d_i are functions of T_{sub} and therefore α/β is a function of T_{sub} . This function should be obtained from the dependence of $x/(1-x)$ on T_{sub} in the case of constant x_g , i.e. constant T_{ZnS} .

Fig. 2 shows the dependence of logarithmic $x/(1-x)$ on $1/T_{sub}$ with constant T_{ZnS} . It is found that the composition x decreases with increasing T_{sub} , and the dependence is nearly linear. From the slope of the lines in fig. 2, an activation energy $E = 24.3 \text{ kcal/mol}$ is obtained. It means that α/β can be described by:

$$\alpha/\beta = A \exp(E/kT_{sub}), \quad (5)$$

where A is a constant. The activation energy E describes the competition between S and Se on the growing surface, and the lower substrate tem-

perature is in ZnS_xSe_{1-x} and (5), we have

$$x = \frac{1}{1 + P_{H_2S}}$$

In this experiment, P_{H_2S} on 7 experimental solid compositions is reasonable. The substrate temperature is

3.2. Effect of

There is a (100) GaAs substrate. Therefore, the different from ZnS_xSe_{1-x} lattice, and thickness, the X-ray diffraction are not equal

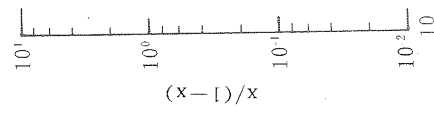


Fig. 2. Dependence of $(x-1)/x$ on $1/T_{sub}$ for ZnS source temperature.

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perature is in favour of the deposition of S in the ZnS_xSe_{1-x} growing system. From eqs. (3), (4) and (5), we have

$$x = \frac{1}{1 + P_{\text{H}_2\text{Se}}/AP_{\text{H}_2\text{S}}} \exp\left(\frac{E}{kT_{\text{sub}}}\right); \quad (6)$$

In this experiment, $P_{\text{H}_2\text{Se}}$ is considered to be unchanged because of constant ZnSe source temperature. The parameter A and the dependence of $P_{\text{H}_2\text{S}}$ on T_{ZnS} can be determined by fitting the experimental data in eq. (6). Hence, the desired solid composition can be obtained by selecting a reasonable ZnS source temperature and substrate temperature.

3.2. Effect of lattice relaxation

There is a strain in the ZnS_xSe_{1-x} epilayer on a (100) GaAs substrate, unless the x value is equal to the lattice-matching composition of 0.05. Therefore, the perpendicular lattice parameter is different from the unstrained parameter. If ZnS_xSe_{1-x} grows by exactly matching the GaAs lattice, and without lattice relaxation to the final thickness, the x values determined from (400) X-ray diffraction angles ($x_{\text{X-ray}}$) by Vegard's law are not equal to the real mole fraction of sulfur.

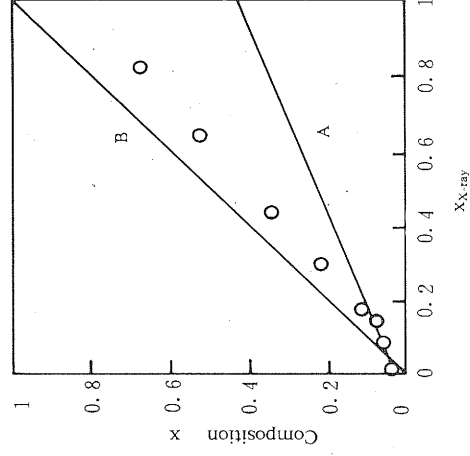


Fig. 3. Relation between x and $x_{\text{X-ray}}$. Line A shows the case of exact lattice matching. Line B shows the case of complete lattice relaxation. (O) Experimental data.

The relation between $x_{\text{X-ray}}$ and x is expressed as follows [5]:

$$x = 0.45x_{\text{X-ray}} + 0.03. \quad (7)$$

To deduce this formula, Poisson's ratios are calculated from the stiffness constants C_{11} and C_{12} , and the values of 1.20 and 1.25 were obtained for ZnSe and ZnS, respectively. Since these two values are very close, we have adopted 1.20 for ZnS_xSe_{1-x}. In eq. (7), the errors in $x_{\text{X-ray}}$ become larger with increasing x . In this work, the x values determined from PL(x_{PL}) [4] are used as the real composition. It is easy to estimate that the errors in x_{PL} are smaller than those in $x_{\text{X-ray}}$, especially for larger x values.

Fig. 3 shows the relationship between x and $x_{\text{X-ray}}$ in ZnS_xSe_{1-x} epilayers with a thickness of 0.5 μm . Line A describes eq. (7). Line B shows the other extreme case of $x = x_{\text{X-ray}}$, that is, the case of complete lattice relaxation. In fig. 3, the experimental data are close to line A around small compositions (x less than 0.2), and further depart from line A toward line B with increasing x (x larger than 0.2). It indicates that a large lattice relaxation is formed due to the large lattice mismatch with increasing x . This phenomenon is also shown in fig. 4. This figure shows the composition dependence of the perpendicular

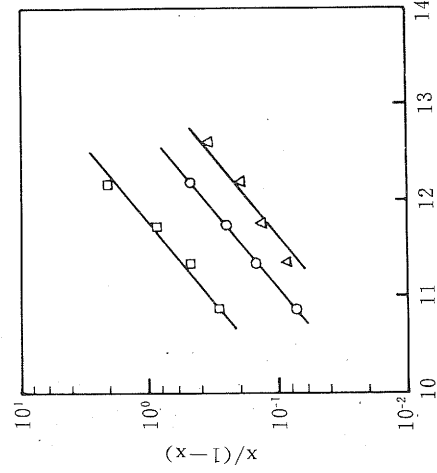


Fig. 2. Dependence of $(x-1)/x$ on $1/T_{\text{sub}}$ with constant ZnS source temperatures of 720°C (Δ), 745°C (\circ) and 783°C (\square).

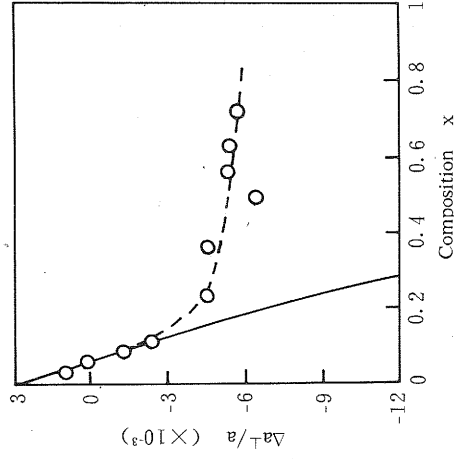


Fig. 4. Composition dependence of the perpendicular relative mismatch ($\Delta a^\perp/a$) in $0.5 \mu\text{m}$ thick VPE ZnS_xSe_{1-x} epilayers on (100) GaAs substrates. (—) Theoretical curve; (---) experimental curve.

relative mismatch, $\Delta a^\perp/a$, where a^\perp is the perpendicular strained lattice parameter, a is the unstrained lattice parameter of ZnS_xSe_{1-x} epilayers and $\Delta a^\perp = a^\perp - a$. The solid line is calculated for the case that the layer grows by exactly matching the GaAs lattice without lattice relaxation. The line is described as:

$$\Delta a^\perp/a = (2C_{12}/C_{11})(1 - a_{\text{GaAs}}/a), \quad (8)$$

where $a = a_{\text{ZnSe}} - (a_{\text{ZnSe}} - a_{\text{ZnS}})x$, and a_{ZnSe} , a_{ZnS} and a_{GaAs} are the lattice parameters of ZnSe, ZnS and GaAs, respectively. The experimental data depart from the solid line for x larger than the critical composition x_c of 0.2. This is considered to be a result of rapid lattice relaxation, while an amount of defects are formed in the layer. Therefore, the layers with $x \leq x_c$ should be perfect. In the case of x larger than 0.2, the value of $\Delta a^\perp/a$ is saturated and reaches a maximum of -6×10^{-3} . For a certain thickness (or a certain composition), there exists a critical composition (or a critical thickness) in ZnS_xSe_{1-x} epilayers on GaAs substrates. The existence of the critical thickness h_c in an epilayer was first detailed by Van der Merwe [6], and later by numerous other authors. Recently, People and Bean [7] reported a calculation of the critical layer thickness for growth of Ge_xSi_{1-x} strained

layers on Si substrates obtained by assuming that the misfit dislocation generation is determined solely by the energy balance. The equation is given by [7]:

$$h_c \approx \frac{1-\nu}{1+\nu} \frac{1}{16\pi\sqrt{2}} \frac{b^2}{a(x)} \frac{1}{f^2} \ln\left(\frac{h_c}{b}\right), \quad (9)$$

where f is the misfit between epilayer and substrate. In our work, $a(x)$ is the lattice parameter for ZnS_xSe_{1-x} layers, $\nu = C_{12}/(C_{11} + C_{12}) = 0.38$ and $b = 4 \text{ \AA}$. The values of h_c for $x = 0.2$ and 0.16 are 0.3 and $0.5 \mu\text{m}$, respectively. It is seen that the values obtained in eq. (9) closely fit the experimental data. Thus, the defects in the $ZnS_xSe_{1-x}/\text{GaAs}$ strained layers will be generated when the areal strain energy density of the film exceeds the energy density associated with the formation of a defect at a distance from the free surface equal to the layer thickness.

3.3. PL spectra

There is no lattice relaxation in the layer if $x < x_c$; therefore, few defects are in the layer and the PL spectrum of the layer should exhibit good optical properties. Hence, we selected $ZnS_{0.1}Se_{0.9}$ and $ZnS_{0.2}Se_{0.8}$ epilayers to measure their PL spectra. Fig. 5 shows the near band edge emission spectra of a VPE $ZnS_{0.1}Se_{0.9}$ epilayer at 77 K with different excitation densities (excitation line is the 435.7 nm laser line). The E band (438.5 nm) is due to free exciton recombination scattered by

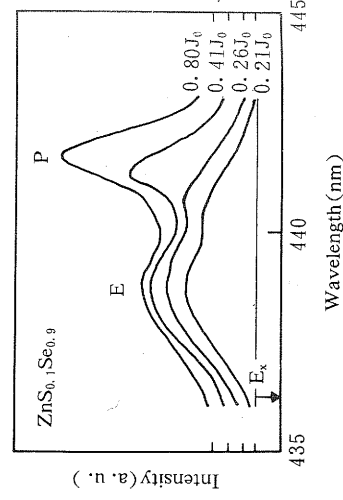


Fig. 5. Near band edge emission spectra of VPE $ZnS_{0.1}Se_{0.9}$ epilayer at 77 K with different excitation densities. The 435.7 nm laser line is used as excitation source ($J_0 = 1 \text{ MW/cm}^2$).

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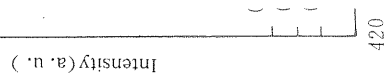


Fig. 6. N_2 laser ZnS_xSe_{1-x} PL spectra.

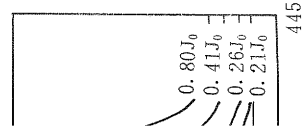
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electrons in the conduction band [8]. The P band is due to the exciton-exciton interaction [9], which is observed for the first time in epilayers of this kind at 77 K. The E band is dominant and the P band is weak in the spectrum at the low excitation density. However, the P band grows faster than the E band with increasing excitation density. The intensity of the P band (I_P) grows with a superlinear relation of $I_P \propto J^{1.8}$, which is nearly in agreement with the relation of $I_P \propto J^{1.9}$ in ZnSe crystals at 1.8 K reported by Saito and Shionoya [2], where J is the excitation density. It is also observed that the P band shifts toward the low energy part of the spectrum when the exciting light intensity increases. This phenomenon has been explained by Levy et al. [10] for CdS crystals. In fig. 5 the arrow shows the energy position of free exciton (E_x), at low excitation density, the energy separation between E_x and the P band is about 23 meV, which nearly equals the free exciton binding energy of $ZnS_{0.1}Se_{0.9}$, 22 meV, which was calculated as follows: The values of exciton binding energy of ZnSe and ZnS are about 20 and 39 meV, respectively. The exciton

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of VPE $ZnS_{0.1}Se_{0.9}$ epilayers. The 435.7 nm emission line is observed at $J_0 = 1 \text{ MW/cm}^2$.

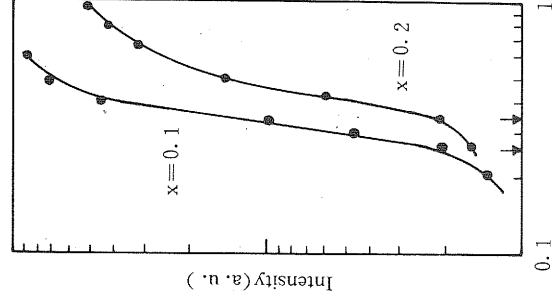


Fig. 7. Intensity dependence of lasing line (L) with pumping density in VPE ZnS_xSe_{1-x} ($x = 0.1, 0.2$) epilayers.

binding energy of ZnS_xSe_{1-x} can be determined by assuming a linear variation of exciton binding energy with composition x . The behaviour of the P band further identifies that the P band is mostly produced by the inelastic collision process of two excitons (E_x-E_x).

The stimulated emission (L line) from exciton-exciton interaction is observed in the epilayers ($x = 0.1, 0.2$) for the first time at 77 K, pumped with the 337.1 nm line of a N_2 laser, as shown in fig. 6. Fig. 7 shows the intensity dependence of the L line on pumping density. It exhibits that above the pumping density threshold (arrowed) the dependence becomes exponential, clearly indicating the stimulated character. The optical properties above show that high quality ZnS_xSe_{1-x} epilayers have been grown on (100) GaAs substrates by VPE. In the epilayers with x larger than 0.2, we have not observed E_x-E_x emission. It is perhaps caused by the large lattice relaxation in the epilayers.

4. Conclusions

The surface process, which is a function of substrate temperature, has a strong influence on

the solid composition in ZnS_xSe_{1-x} growth by VPE. An activation energy of 24.3 kcal/mol is obtained in the S/Se mixture in the solid. A large lattice relaxation is rapidly formed in 0.5 μm thick ZnS_xSe_{1-x} epilayers on (100) GaAs for x larger than 0.2, while the perpendicular relative mismatch reaches a maximum of -6×10^{-3} . PL spectra exhibit that high-quality epilayers have been grown on (100) GaAs substrate by VPE.

Acknowledgements

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