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Growth of high quality ZnSe epitaxial layers on transparent substrates CaF_2 by atmospheric pressure metallo-organic chemical vapour deposition

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Abstract

High quality ZnSe epitaxial layers (epilayers) on $CaF_2(111)$ transparent substrate have been successfully fabricated for the first time by atmospheric pressure metallo-organic chemical vapour deposition, using dimethylzinc and H_2Se as sources. The double-crystal X-ray diffraction pattern (111) shows a little shift of ZnSe diffraction peak towards a small diffraction angle, and the full width at half-maximum of the diffraction peak value from its (111) face is about 0.20°. The optical and electrical characteristics of ZnSe epilayers were measured by photoluminescence, scanning electron microscopy and the Van Der Pauw method; the epilayers exhibit a high crystallographic quality and reveal an even mirror surface. All epilayers have high resistivities of up to 10^7 Ω cm. From the analyses on the energy shift of the luminescence line, a compressive stress has been found in the epilayer sides of these heterostructures. This is consistent with the stresses predicted for a lattice mismatch between the ZnSe epilayer and the CaF_2 substrate.

1. Introduction

Much attention has been paid to the wide-band-gap II–VI compound semiconductors ZnSe and ZnS as materials suitable for blue-light-emitting and optoelectronic devices at room temperature. Recently, attention has been focused on the optical bistability [1–3] in ZnSe. It is difficult to etch a window for II–VI group materials on a GaAs substrate. In order to investigate the bistability of ZnSe epitaxial layers (epilayers) or strained-layer superlattices (SLSs) with a ZnSe well, it is necessary to look for suitable transparent substrate materials. Etienne and Bougnot [4] obtained ZnSe epilayers on a CaF_2 substrate using the vapour-phase epitaxy (VPE) method and the growth temperature was above 650 °C. This method does not favour overcoming the environmental pollution and self-compensation of ZnSe crystals. In this paper, we report the results of investigations concerning the interface stress of ZnSe/CaF_2 and ZnSe/GaAs heterostructures grown by the atmospheric pressure metallo-organic chemical vapour deposition (MOCVD) technique.

2. Experimental details

2.1. Sample preparation

Epilayers were grown in a horizontal atmospheric pressure MOCVD system; the growth conditions have been reported previously [5]. In order to avoid destructive gas-phase pre-reaction an r.f.-heated reactor with a water-cooling sheath was used. The H_2-carried dimethylzinc (DMZ) and H_2Se passed through the central nozzle and inner tube respectively and met at a distance of 2.5 cm from the substrates. The electronic grade DMZ source was contained in a stainless steel bubbler placed in a temperature-controlled bath; the mole fraction of DMZ was adjusted using the temperature of the cooling bath and the flow rate of the carrier gas H_2; the H_2Se was employed as the source of selenide. All reagents were delivered into the reactor in purified palladium-diffused H_2 gas. Typical flow rates were 9.9×10^{-6}–2.4×10^{-5} mol min^{-1} for DMZ and 4.3–8.4×10^{-5} mol min^{-1} for H_2Se with a ratio of $J(Zn)/J(Se) = 1/4.5$; the total flow rate of hydrogen was 1.0–1.5 l min^{-1}. The substrates were placed in an organic susceptor in the growth area after having been cleaned in organic solvents and etched in a 5:1:1 H_2SO_4:H_2O_2:H_2O solution, as described previously. After being loaded into the reactor, the substrates were heated in a pure H_2 stream at 600 °C for about 10 min for heat cleaning; then the substrate temperature was maintained at 280 °C. The growth rate is about 2–3 μm h^{-1}. To avoid the effects of lattice mismatch and thermal stress, the temperature was reduced slowly to about 3 °C min^{-1} after growth.

2.2. Photoluminescence and X-ray diffraction measurements

Samples were immersed in liquid nitrogen in a cryostat with a quartz window. A model QJD-9 nitrogen

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pulsed laser was used as the excitation source with $\lambda = 337$ nm, $\tau = 10$ ns, $f = 10$ Hz and $I_{max} = 3$ MW cm^{-2}. The photoluminescence (PL) measurements were carried out with a model 44 W spectrometer and a RCA-C 31034 photomultiplier. A model D/Max-RA CN1518B1 scan double-crystal goniometer made by Rigaku Corporation of Japan was used for the X-ray diffraction measurement.

3. Results and discussion

Resistivity measurements were made at temperatures ranging from 77 K to room temperature. The results show that the ZnSe epilayers have a high resistivity $\rho > 10^7\ \Omega$ cm. The scanning electron microscopy (SEM) photographs show the even surface, while the epilayer thickness is below 2 μm, as seen in Fig. 1. Figure 2 shows the pattern of the double-crystal X-ray rocking curve of a ZnSe (1.0 μm) layer on CaF$_2$(111) and GaAs(100) substrates. The ZnSe epilayers on CaF$_2$(111) and GaAs(100) substrates all present a cubic structure. From the figure we can calculate the lattice parameters $a_{(111)}{}^{\perp} = 0.6860$ nm normal to the surface for a CaF$_2$ substrate and $a_{(100)}{}^{\perp} = 0.6685$ nm for a GaAs substrate. On the basis of the results it is assumed that the lattice suffers tetragonal distortion. Since the interface misfit in ZnSe/GaAs is smaller (0.27%), the X-ray diffraction measurement demonstrates that the lattice parameter normal to the surface is similar to that of the stress-free crystal, indicating that the epilayer properties are the same as those of the bulk single crystal when the epilayer thickness is greater than 1 μm. As the misfit of ZnSe/CaF$_2$(111) is 3.6%, a compressive strain is introduced parallel to the surface of the ZnSe layer. The full widths at half-maximum (FWHM) of the X-ray diffraction peak of ZnSe layers are 180″ and 720″ for GaAs and CaF$_2$ substrates respectively. The dislocation defect density d can be estimated from the following equation [8]:

$$d = 410(\mathrm{fwhm})_{\text{X-ray}}{}^2 \qquad (1)$$

The result calculated from eqn. (1) indicated that the density $d_1 = 2.1 \times 10^8$ cm^{-3} for ZnSe/CaF$_2$(111) is larger than $d_2 = 1.3 \times 10^7$ cm^{-3} for ZnSe/GaAs (100).

Information about the interfacial strain can also be obtained from PL spectra. Figure 3 shows the PL spectra of ZnSe/CaF$_2$ and ZnSe/GaAs epilayers at 77 K and room temperature. As seen from the figure, the emission bands of the epilayer located at 443.1 nm for the ZnSe/CaF$_2$(111) and at 445.9 nm for the ZnSe/GaAs(100) structures were attributed to the free-exciton recombination following scattering from free electrons in the conduction band [9], and no longer-wavelength emission bands were observed at a high excitation level. The PL spectra at room temperature showed a strong emission interelation to the excitons,

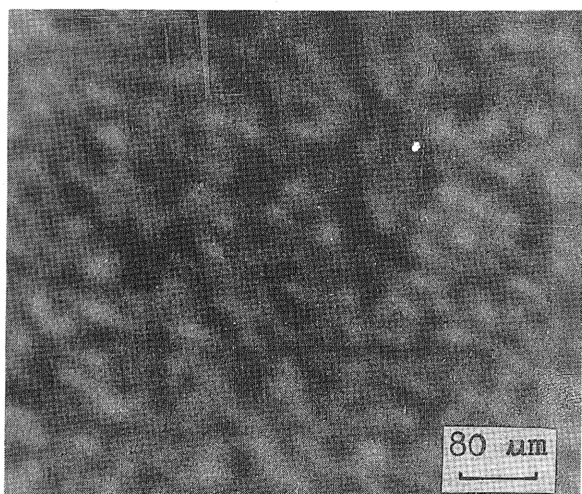

Fig. 1. SEM photograph of a ZnSe epilayer (thickness $t = 1.5$ μm) on a CaF$_2$(111) substrate.

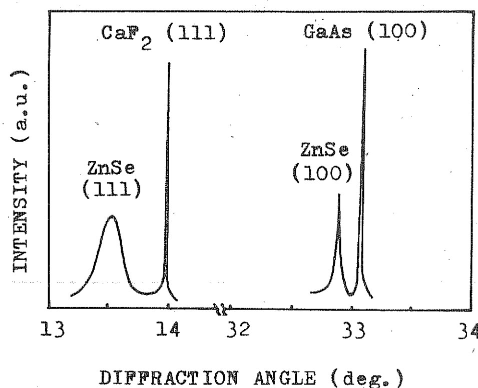

Fig. 2. Double-crystal X-ray diffraction of ZnSe epilayers on CaF$_2$(111) and GaAs(400) substrates: a.u., arbitrary units.

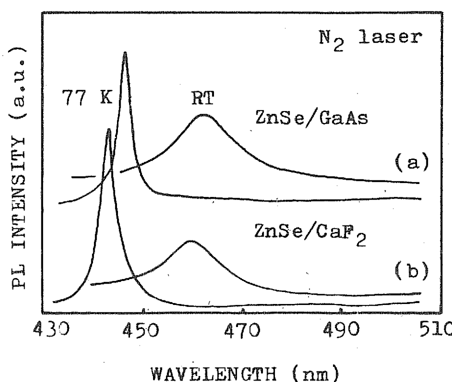

Fig. 3. PL spectra of ZnSe layers on GaAs(100) substrates (curve (a)) and CaF$_2$(111) substrates (curve (b)) at 77 K and room temperature: a.u., arbitrary units.

indicating that samples grown on CaF_2 substrates are of good optical quality like those on GaAs substrates. The difference between the positions of the two PL peaks mentioned above is considered to be due to the contribution of the strain. The ZnSe bulk lattice parameter exceeds that of CaF_2 at room temperature. Therefore for the coherent epitaxial growth of ZnSe on CaF_2, the ZnSe must experience a compressive elastic strain in the plane of the interface and, because of the assumed resulting tetragonal distortion of the lattice, a uniaxial tension strain normal to this plane. The energy gap shifts with strain parallel to the (111) direction in zincblende-type materials; the calculated shift in the $K=0$ band gap is given by [10]

$$\Delta E = \left(-6a + \frac{3^{1/2}}{2} d \frac{C_{11}+2C_{12}}{C_{44}}\right) e_{xx} \qquad (2)$$

where a is the hydrostatic deformation potential, d is the shear deformation potential, C_{ij} are the elastic constants and e_{xx} determines the magnitude of the strain components using [11]

$$a'' = a_0 - \frac{a^{\perp} - a_0}{A} \qquad (3)$$

and

$$A = \frac{2C_{11}+4C_{12}-4C_{44}}{C_{11}+2C_{12}+4C_{44}}$$

The parameters appropriate for ZnSe have been listed in Table 1; from the geometric relation we can easily obtain

$$e_{xx} = \left[\frac{2}{3}\left(\frac{a''}{a_0}\right)^2 + \frac{1}{3}\left(\frac{a^{\perp}}{a_0}\right)^2\right]^{1/2} - 1 \qquad (4)$$

Using eqns. (2)–(4), ΔE is calculated to be about 22 meV; this is similar to the value of the energy shift ΔE in PL spectra of 18 meV. In the $ZnSe/CaF_2$ structure, owing to the difference between the linear coefficients of expansion for these two materials ($\alpha_1 = 7.2 \times 10^{-6}$ °C^{-1} for ZnSe, and $\alpha_2 = 19.7 \times 10^{-6}$ °C^{-1} for CaF_2) the thermal strain and the mismatch strain are in the same direction; so the energy shift has two parts. We can calculate the thermal strain contribution using the two-dimensional model of a bimetallic strip [12]. In our samples the substrate thickness and epilayer thickness are $t_{sub} = 300$ μm and $t_{lay} = 1.0$ μm respectively. So the relationship can be simplified into the following form:

$$e = 2\nu(\alpha_1 - \alpha_2)(T_G - T_R) \qquad (5)$$

where α_1 and α_2 are the linear coefficients of expansion of the epilayer and substrate respectively, T_G and T_R are the growth temperature and the room temperature respectively and ν is Poisson's ratio. In the above sample the thermal strain contribution is about 50% ($\Delta E = 14$ meV). If the temperature has been reduced sufficiently slowly from T_G to T_R, the lattice parameter for the epilayer will change gradually and the epilayer will remain intact. When the temperature was reduced too quickly, the epilayer broke because of the thermal strain and the lattice mismatch strain in the same direction. Thus a lower growth temperature and a slower rate of reducing the temperature are very important for the $ZnSe/CaF_2$ system.

TABLE 1. Values of the material parameters for ZnSe used in calculations which are described in the text

Parameter	Value	Ref.
C_{11}	8.72×10^{10} N m^{-2}	6
C_{12}	5.24×10^{10} N m^{-2}	6
C_{44}	3.92×10^{10} N m^{-2}	6
a	−4.25 eV	7
d	−3.8 eV	13
υ	0.38	14
a_0	0.56686 nm	15
a_1	7.2×10^{-6} °C^{-1}	15

4. Conclusion

ZnSe single crystals could be obtained by MOCVD at atmospheric pressure on transparent substrates CaF_2. Thermal and mismatch strain analyses were presented and it was shown that the thermal strain plays an important role in the PL spectra. The experimental results were in good agreement with the theoretical calculation. Furthermore it is important to grow ZnSe–ZnS/CaF_2 SLSs to research the properties of optical bistability.

Acknowledgments

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