Growth of ZnSe on GaAs(1 1 0) surfaces by molecular beam epitaxy

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Abstract

Single crystal films of ZnSe have been grown on nonpolar GaAs(1 1 0) surfaces by molecular beam epitaxy (MBE). The epitaxial films have been characterized by in situ reflection high-energy electron diffraction (RHEED), ex situ scanning electron microscopy (SEM) and X-ray diffraction. RHEED and SEM images of the surfaces reveal the formation of facets which are aligned along the [0 0 1] direction. The formation of facets indicates that ZnSe growth on the (1 1 0) surface proceeds 6°–13° off the vicinal (1 1 0) surface. Facet-free ZnSe surface has been successfully grown on a GaAs(1 1 0) 6°-off the substrate. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

ZnSe-based II–VI materials have attracted much attention in connection with the attempt to fabricate efficient emitters such as light emitting diodes and laser diodes in the blue region of the visible spectrum [1,2]. II–VI epitaxial layers are usually grown on GaAs(1 0 0) surface in order to take advantage of the natural cleavage planes which exist normal to the crystal face, and the smooth morphology of the epitaxial surface which can be obtained over a wide range of growth conditions [3–5]. However, recent studies of the interface between GaAs(1 0 0) and ZnSe indicate that the instability of the interface caused by the heterovalency between ZnSe-based alloys and GaAs(1 0 0) substrates is crucial to the life time of ZnSe-based blue–green laser diodes [6]. The inherent drawback of the ZnSe/GaAs system is the lattice mismatch of about 0.27%. This results in a considerable number of misfit dislocations and stacking faults which originate at the
interface and extend through the overgrowing layers. Furthermore, ZnSe is a II–VI compound, whereas GaAs is a III–V compound. So there exists a heterovalent problem, which also causes the generation of defects at the interface. To realize reliable II–VI blue laser diodes, these heterovalent interface problems must be suppressed. In view of the heterovalent problem, the (1 0 0) interface consists of Ga–Se and As–Zn bonds, where the former has an excess of ¼ electron per bond, while the latter is ¼ electron deficit per bond. The dominance of either type of bonds may cause interface charge, which could be compensated by the formation of defects. Alternatively, the nonpolar (1 1 0) substrate, which consists of the same number of both elements seems more insensitive to the charge neutralization problem. From this point of view, growth on GaAs(1 1 0) substrates seems to be more promising than the (0 0 1) growth [7].

During MBE growth of ZnSe on GaAs(1 1 0) surface, the surface arrangement of the atoms requires a 1 : 1 ratio of Zn and Se species to react and maintain the surface stoichiometry. Because of the different surface stoichiometries, the growth conditions for smooth (1 1 0) epitaxial layers may be different from those for (0 0 1) growth as is the case for MBE growth of GaAs on a (0 0 1) substrate [8]. Surface diffusion and faceting processes play an important role in growth on GaAs(1 1 0). Our purpose is to present new experimental data concerning ZnSe growth on the (1 1 0)GaAs surface in order to understand the growth mode.

In this paper, we investigate the dependence of the surface morphology and crystal quality of ZnSe(1 1 0) epitaxial layers on the GaAs(1 1 0) surface under various growth conditions. The surface reconstruction and topography of ZnSe(1 1 0) are characterized by in situ RHEED and ex situ SEM. The crystal quality of the layers are characterized by photoluminescence (PL) and double crystal X-ray diffraction measurements.

2. Experimental methods

MBE growth was performed on ‘epi-ready’ undoped GaAs(1 1 0) just nominally and 6°-off wafers which were degreased, etched in a solution of \( \text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 : \text{H}_2\text{O} (5 : 1 : 1) \), and mounted with indium onto a molybdenum heating block. Prior to MBE growth, the substrates were thermally cleaned at 620°C for 10 min in a growth chamber. Reflection high-energy electron diffraction (RHEED) was used to examine the surface condition of the substrate during pre-heating and epilayer growth. The growth was performed in a wide temperature range from 200 to 350°C with a beam pressure ratio \( (P_{\text{Zn}}/P_{\text{Ga}}) \) of 0.8–7 \( (1 \times 10^{-7} \text{ Torr for } P_{\text{Zn}}) \). The surface morphology of epitaxial layers was observed by scanning electron microscopy (SEM). Photoluminescence (PL) measurements were carried out at 17 K using the 325 nm line from a He–Cd laser as an excitation source. The crystal quality was characterized by an X-ray diffractometer.

3. Results and discussion

3.1. Growth rate

The measured growth rates of ZnSe films grown on a GaAs(1 1 0) and (1 0 0) substrates, where the beam pressure ratio was kept at unity, are shown in Fig. 1 as a function of substrate temperature. In agreement with earlier investigations [9,10], the growth rate decreases with increasing substrate temperature.
temperature. The growth rate on the (1 1 0) surface is almost half of that on the (1 0 0) surface.

Fig. 2 shows the epitaxial growth rate of ZnSe(1 1 0) as a function of Se beam pressure, $P_{Se}$, at different substrate temperatures, while the Zn-beam intensity is kept constant ($P_{Zn} = 1 \times 10^{-7}$ Torr). The growth rate increases with increasing Se beam pressure and tends to saturate at high Se to Zn beam pressure ratio, while it decreases with increasing substrate temperature. This temperature dependence of growth rate for (1 1 0) growth is similar to (1 0 0) growth previously reported [11].

The dependence of growth rate for (1 1 0) on substrate temperature and molecular beam pressure ratio can be interpreted based on a phenomenological model proposed for (1 0 0) growth [11]. According to this model on the surface of the film, the Zn atoms and Se atoms are bonded only to Se atoms and Zn atoms, respectively, causing each atom to form its respective sublattice. The kinetic equation for the surface concentration ($N_i$) of the constituents ($i,j$) can be written as

$$N_i \frac{d\theta_i}{dt} = -\theta_i k_{ij} J_j - \frac{N\theta_i}{\tau_{ji}} + \theta_j k_{ji} J_i + \frac{N\theta_j}{\tau_{ij}},$$

where $N$ is the surface atom concentration, $\theta_i$ and $\theta_j$ are the respective surface coverages of Zn and Se ($\theta_i + \theta_j = 1$), $k_i$ and $k_j$ are the sticking probabilities of Zn and Se, and $\tau_{ji}$ and $\tau_{ij}$ the surface life times of Zn on Se-covered surface and Se on Zn-covered surface. The growth rate is calculated to be

$$G = \theta_j k_i J_i \tau_{ji} - \theta_i k_j J_j \tau_{ji}.$$

(2)

If the growth rate is far greater than the desorption rate, i.e., $k_i J_i \tau_{ij}, k_j J_j \tau_{ji} \gg N$, then Eq. (2) reduces to

$$G = [(k_i J_i)^{-1} + (k_j J_j)^{-1}]^{-1}.$$

(3)

From the above equations, we can see that the growth rate is dependent on sticking probability and flux ratio. The decrease in growth rate at higher substrate temperatures is due to a decrease in sticking probabilities of Zn and Se on the (1 1 0) surface. We note that an incoming Zn atom, for instance, should bond surface Se atoms through a single bond on the (1 1 0) surface, while the Zn atom can bond surface Se atoms with two bonds on the (1 0 0) surface. These different configurations of adatoms could explain the reduced sticking probabilities of Zn and Se. The experimental data shown in Fig. 1 suggest the sticking probability of the constituent atoms on the (1 1 0) surface to be almost 4 of that on the (1 0 0) surface. In order to investigate if Eq. (3) can explain the observed dependence of growth rate on the beam pressure ratio, we tentatively assume for simplicity that $k_{Zn} \approx k_{Se} \approx 1$ for ZnSe growth on the (1 0 0) surface at low substrate temperature ($T_s \approx 200^\circ$C). One could fit the growth rate calculated by Eq. (3) to the observed dependence of growth rate over the (1 1 0) surface on the beam pressure ratio $P_{Se}/P_{Zn}$. In our experiments on the (1 0 0) growth, we found that $J_{Se} \approx J_{Zn}$ at $P_{Se}/P_{Zn} \approx 2.5$. If we assume that the growth rates, at an extreme $J_{Se}$ value, are 1 $\mu$m/h for $T_s = 200^\circ$C and 0.3 $\mu$m/h for 280°C and that $k_{Zn} \approx k_{Se} \approx k$ for simplicity, then Eq. (3) gives solid curves for $T_s = 200$ and 280°C. The agreement between calculation and experiment is fair. We note that $k(1 1 0)/k(1 0 0) \approx 0.45$ and $k(200^\circ$C)/$k(280^\circ$C) $\approx 4.5$. 

![Growth rate of ZnSe/GaAs(1 1 0) dependence on the beam pressure ratio ($P_{Se}/P_{Zn}$) for different substrate temperatures. The growth rate increases with increasing beam pressure ratio and increases further at 200°C.](image.png)
3.2. RHEED

Fig. 3 shows RHEED patterns of a GaAs(1 1 0) substrate thermally cleaned at 620°C (a) and a ZnSe(1 1 0) epilayer after 2 h growth at 200°C (b). The thermally cleaned GaAs surface shows well-defined (1 × 1) structure. At the very beginning of ZnSe growth, three-dimensional growth is indicated but this changes into two-dimensional growth within a few seconds. During the growth, RHEED maintains a (1 × 1) streaky pattern but there is a drop in the RHEED intensity, which suggests considerable roughening of the surface. In addition, in [1 1 0] azimuthal plane, tilted diffraction streaks are observed as shown in Fig. 3b. These tilted diffraction streaks are inclined at about 13° and indicate the formation of facets on the surface. We observe the same RHEED which shows a (1 × 1) streaky pattern over all ranges of beam pressure ratios and substrate temperatures in our experiment.

3.3. Surface morphology

Fig. 4 shows the surface morphology observed by SEM, on the ZnSe epitaxial films grown at 200 and 280°C for different beam pressure ratios. It shows that the surface morphology strongly depends on the value of the beam pressure ratio. At 200°C, the epitaxial films grown with $P_{Se}/P_{Zn} = 0.8$ show the best surface morphology. At beam pressure ratios of 2 and 5, the surface morphology is rough, indicating that the growth rate is too fast to allow smooth growth. The surface morphology of ZnSe epitaxial films grown at 280°C (in Fig. 4b) shows the formation of facets which are aligned.
Fig. 4. The surface morphologies of ZnSe epitaxial films grown at 200 and 280°C for different beam pressure ratios: (a) $T_{\text{sub}} = 200{\degree}\text{C}$ and (b) $T_{\text{sub}} = 280{\degree}\text{C}$. Facets are formed along the [0 0 1] direction and they decrease in size with increasing beam pressure ratio.

Fig. 5 shows SEM micrographs and a sketch of the geometry of a facet of ZnSe grown on GaAs(1 1 0) surface at a substrate temperature of 280°C and a beam pressure ratio of 2.5. Tilting experiments show that the front facet surfaces form an angle of roughly 35°–54° with the (1 1 0) surface and the back facet surfaces roughly 6°–13.5°. The value of 13° for the back facet angle is consistent along the [0 0 1] direction; their size decreases with increasing beam pressure ratio.
Fig. 5. Scanning electron microscopy images and schematical geometry of facets on (1 1 0) surface. Tilting experiments show that the front and back facet surfaces are inclined roughly 35°–54° and 6°–13.5° from the (1 1 0) surface.

The front facet surfaces angled at about 35°–54° from the (1 1 0) surface are (1 1 1)–(112) planes, indicating that front facet surfaces are roughly (1 1 1)Ga plane. The back facet surfaces angled about 6°–13.5° from the (1 1 0) surface are (7 7 1)–(3 3 1). The change of back facet surface angles indicates that the surface plane makes steps and grows by a step-flow mode incorporating more upper-terrace adatoms than lower-terrace adatoms. As a result, ZnSe growth on the (1 1 0) surface proceeds as growth on 6°–13° off vicinal (1 1 0) surfaces and this determines the nominal growth rate of the (1 1 0) surface. It has been shown that facet formation is characteristic of the homo-epitaxial growth of GaAs on the (1 1 0) surface under certain conditions and that the facets are aligned along the [0 0 1] direction [12,13]. Recent investigation suggests that the facet was formed on the GaAs(1 1 0) substrate in the early stage of MBE growth [14]. As a result of the charge transfer between surface Zn and Se atoms, the ZnSe(1 1 0) surface has no reaction dangle bond and the growth rate for ideal ZnSe(1 1 0) surfaces is considered to be much smaller than the nominal growth rate shown in Fig. 5. Other experiments showed that the growth rate of ZnSe on (1 1 1)Se surface is faster than that of (1 1 1)Zn surface. This indicates that (1 1 1)Zn surface is more stable than (1 1 1)Se surface. Tiny islands formed at the early stage of ZnSe(1 1 0) growth become growth nuclei. Adsorbed atoms then migrate on the (1 1 0) surface and are incorporated to the islands forming vicinal (1 1 0) surfaces and the (1 1 1)Zn facets, which have smaller surface free energies than (1 1 1)Se facet. The formation of facets are explained by these phenomena.

In a further experiment, we examined the ZnSe epitaxial growth on GaAs(1 1 0) substrates tilted 6° toward the (1 1 1)Ga plane. Fig. 6 shows the surface morphology of ZnSe layers grown on a GaAs(1 1 0) 6°-off substrate. It shows a facet free surface, thus, two-dimensional or layer by layer growth can be accomplished. Furthermore it indicates that the exposure of Ga ledges, which act as growth nuclei, is the decisive factor in obtaining facet free (1 1 0)ZnSe epitaxial layers grown by MBE.

3.4. PL and XRD

The epitaxial layers grown were characterized by photoluminescence (PL) and X-ray rocking curve.
The PL spectrum of the ZnSe layer which is grown at a substrate temperature 280°C and a beam pressure ratio of 3 exhibits strong free exciton emission ($E_x$) and suppressed deep-level emission (1/30 of $E_x$ emission). The FWHM of the X-ray rocking curves for ZnSe/GaAs(1 1 0) just nominal and ZnSe/GaAs(1 1 0) 6°-off showed 180–240 arcsec. These results further indicate that we obtain good quality epitaxial layers which grow in the same orientation as the GaAs substrate.

4. Conclusions

We have investigated the growth of ZnSe on GaAs(1 1 0) surfaces by MBE employing in situ RHEED and ex situ SEM. In the case of ZnSe on GaAs(1 1 0) just nominal substrate, we found that facets are formed over a wide range of growth conditions. These facets are aligned along the [0 0 1] direction and decrease in size with increasing beam pressure ratio. The formation of facets indicates that the ZnSe growth in the (1 1 0) surface proceeds as growth on 6°–13° off vicinal (1 1 0) surface. In the case of ZnSe on GaAs(1 1 0) 6°-off substrate, a facet free surface morphology is obtained.

PL and X-ray rocking curve results show that good quality epitaxial layers which grow in the same orientation as the GaAs(1 1 0) substrate were obtained.

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References