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High crystalline quality ZnBeSe grown by molecular beam epitaxy with Be–Zn co-irradiation

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Abstract

High crystalline quality ZnBeSe epilayers with different compositions were grown on GaAs substrates by molecular beam epitaxy using Be–Zn co-irradiation of the III–V surface and a ZnSe buffer layer. A (1×2) reflection high-energy electron diffraction pattern was formed after the Be–Zn co-irradiation indicating the formation of Be and Zn dimers on the GaAs surface. A two-dimensional growth mode was observed throughout the growth of the ZnSe buffer layer and ZnBeSe epilayer. Narrow X-ray linewidth as low as 23 arcsec with the etch pit density of mid 10^4 cm^{-2} were obtained. The linewidth of the dominant excitonic emission is about 2.5 meV at 13 K for the near-lattice-matched ZnBeSe layer. For a nitrogen-doped sample, capacitance–voltage measurements showed a net acceptor concentration of 2.0×10^{17} cm^{-3}. In addition, the use of a BeTe buffer layer and of a Zn-irradiation with a ZnSe buffer layer were also investigated.

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1. Introduction

Recently, there is much interest in developing blue–green laser diodes (LD) and light-emitting diodes. Blue–green LD based on ZnSe were demonstrated for the first time in 1991 [1,2]. By introducing a ZnMgSSe quaternary alloy and ZnSSe ternary alloy lattice matched to the GaAs substrate as the cladding layer and waveguiding layer and strained ZnCdSe as the active layer, blue–green LD under continuous-wave operation with lifetimes of about 400 h have been achieved [3]. However, during molecular beam epitaxial (MBE) growth, the sulfur sticking coefficient depends strongly on the substrate temperature, making it extremely difficult to avoid composition fluctuations in the ZnMgSSe

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alloys [4]. With a small lattice constant (5.139 Å) and a large band gap ($E_g > 5$ eV), BeSe is a very good candidate to replace ZnS in the quaternary and ternary alloys. It is also important to note that MBE growth is much more controllable and reproducible when an alloy contains several metals and only a single nonmetal, rather than several nonmetals. In addition, Beryllium chalcogenides have a high degree of covalent bonding compared to other wide gap II–VI semiconductors and are expected to have higher bonding energies [5], which may further improve the device lifetime. However, in growth of II–VI alloys on III–V substrates control of the II–VI/III–V interface can be a problem. We have found that the quality of the interface is appreciably improved by performing a Zn–Be co-irradiation of the III–V surface.

The II–VI/III–V interface quality is extremely important for the growth of II–VI materials on III–V substrates. Improvement of the II–VI/III–V interface has been the main reason for the reduction of the defect density obtained in the past. In the case of the growth of ZnSe-based materials on GaAs, it is important to avoid any tendency to form a Se-(2×1) surface reconstruction [6] on the GaAs surface. On such a surface, isolated islands are easily formed, and very high density of stacking faults are produced believed to be related to the formation of Ga_2Se_3 at the interface. By using Zn-irradiation to avoid the formation of Ga_2Se_3, a reduction of etch pit density (EPD) in the ZnSe/GaAs system from 10^6 to 10^3 cm^{-2} has been reported [7].

With a few monolayers (ML) of ZnSe buffer layer directly grown on the GaAs substrate, ZnBeSe epilayers with X-ray linewidth of 27 arcsec have been demonstrated by Bousquet et al. [8]. The EPD in the ZnBeSe layers are high in the 10^6 cm^{-2} range, which is much higher than that reported in the ZnSe/GaAs system. By using a few ML of BeTe as a buffer layer, ZnBeMgSe with X-ray linewidths down to $\sim$20 arcsec and EPD below 5000 cm^{-2} was reported by Fischer et al. [9]. However, due to the high conduction band offset of about 2.3 eV between BeTe and GaAs as well as between BeTe and ZnSe the BeTe buffer may produce a very high potential barrier for electrons, possibly affecting device performance.

In this letter, high crystalline quality ZnBeSe epilayers were achieved by using Be–Zn co-irradiation before the ZnSe buffer layer growth. A (1×2) surface reconstruction was observed on the (0 0 1)GaAs surface after the co-irradiation indicating the formation of a Be and Zn surface termination layer. A two-dimensional growth mode was obtained immediately on this surface upon initiation of the ZnSe layer. In situ reflection high-energy electron diffraction (RHEED) and ex situ X-ray diffraction (XRD), EPD and photoluminescence (PL) were used to characterize the crystalline quality. p-Type doping of ZnBeSe by nitrogen was also performed. The doping level was determined by capacitance–voltage (C–V) and electrochemical C–V (ECV) measurements.

2. Experiment

ZnBeSe epilayers were grown on (0 0 1)GaAs substrates in a Riber 2300 MBE system with a III–V chamber and a II–VI chamber connected by ultra-high vacuum. Oxide desorption of the substrate was performed in the III–V chamber by heating to $\sim$580°C under an As flux, after which a 300 nm GaAs buffer layer was grown. The main shutter was closed at a substrate temperature (T_s) of 550°C to maintain a (2×4) RHEED pattern. In order to avoid the formation of Ga_2Se_3 at the III–V/II–VI interface we performed Be–Zn co-irradiation before the growth of 5 nm ZnSe buffer layer. Once the substrate with the GaAs buffer layer was transferred in vacuum to the II–VI chamber, the main shutter was opened immediately with the Zn and Be shutters open for 20 s. The RHEED pattern changes from (2×4) to (1×2) after the Be–Zn co-irradiation, indicating the formation of a new surface reconstruction on the (0 0 1)GaAs surface. Then the T_s was increased to 250°C and the ZnSe buffer layer was grown. The RHEED pattern remains streaky and the surface reconstruction changes from (1×2) to (2×1) during the ZnSe growth. After this the T_s was increased to 270°C and $\sim$1 μm-ZnBeSe epilayer was grown under Se-rich conditions using elemental Zn, Be and Se Knudsen effusion cells. The RHEED pattern remains streaky (2×1) during the ZnBeSe growth.

The p-type doping was achieved by employing an Oxford RF nitrogen plasma source. Two other approaches to control the II–VI/III–V interface were also pursued. In one, a Zn irradiation with a ZnSe buffer layer was used. Once the substrate with the buffer layer was transferred to the II–VI chamber, the substrate was heated to 250°C. When T_s was stable, the main shutter was opened with the Zn shutter open for 20–60 s. Then the Se shutter was opened to start the growth of the 5 nm of ZnSe. The RHEED pattern is streaky (2×1) with superimposed weak elongated spots evident after the ZnSe growth. After this the T_s was increased to 270°C and ZnBeSe was grown. The RHEED pattern becomes streaky (2×1) gradually as growth proceeds. In the second, a BeTe buffer layer was used. Here, once the substrate with the buffer layer was transferred to the II–VI chamber, the substrate was heated to 350°C and a few ML of BeTe were deposited under Te-rich conditions. The BeTe buffer layer was grown at 350°C instead of 250°C in order to improve BeTe crystalline quality [10]. The RHEED pattern is streaky (2×1) after the BeTe growth. Then the T_s was decreased to 270°C and ZnBeSe was grown. The RHEED remains streaky (2×1) during the ZnBeSe growth.

The ZnBeSe crystalline quality and Be composition were assessed by single and double crystal XRD measurements using a double-crystal biaxial diffractometer and Cu $K_{\alpha1}$ radiation. For EPD measurements, a solution of methanol with 0.2% Br was used at RT, which has been demonstrated to be suitable for ZnSe [11]. A solution of concentrated HCl (32%) was also used at 60°C, which has been reported to be a suitable etchant for quaternary ZnMgSSe [12] and ZnBeMgSe [9]. PL measurements were performed at 13 K using the 325 nm line of the He–Cd laser for excitation. *C–V* measurements were carried out at room temperature using a gold contact with a diameter of 0.6 mm.

3. Results and discussion

The full-width at half-maximum (FWHM) of the double-crystal X-ray rocking curves (DCXRC) of ZnBeSe epilayers grown under the three growth conditions described is shown in Table 1. The results indicate that the crystalline quality of ZnBeSe was dramatically improved by using either a Be–Zn co-irradiation with a ZnSe buffer layer or a BeTe buffer layer. Fig. 1 shows the (0 0 4) reflection DCXRC for a ZnBeSe epilayer with 3.1% Be grown with Be–Zn co-irradiation. A narrow peak related to the ZnBeSe epilayer, with a FWHM of 23 arcsec was observed indicating very high crystalline quality. From the (1 1 5) *a* and *b* asymmetrical reflection DCXRC we can obtain the perpendicular and parallel lattice constants: a_1 and a_2. The bulk lattice constant then is calculated from the equation

$$a = a_1\{1 - [2v/(1+v)][(a_1 - a_2)/a_1]\}.$$

Here v is the Poisson's ratio (we use the value of v for ZnSe of 0.28 for the ZnBeSe because of the small Be composition). Assuming that Vegard's law is valid for ZnBeSe, the Be composition can be assessed from the lattice constant. The dependence of Be composition on Be cell temperature was investigated for compositions near the lattice-matched regime. The data are plotted in Fig. 2. A near

Table 1
Properties of ZnBeSe epilayers

Growth conditions	FWHM of DCXRC (arcsec)	EPD (cm^{-2})	FWHM of PL 13 K (meV)
Zn-irradiation and ZnSe buffer layer	> 300	$> 10^6$	5
Be–Zn co-irradiation and ZnSe buffer layer	23–45	Mid 10^4	2.5
BeTe buffer layer	18–40	Low and mid 10^4	2.5

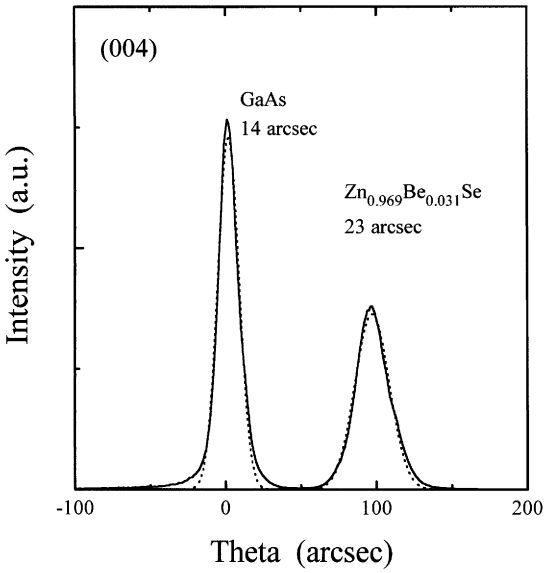

Fig. 1. (0 0 4) reflection DCXRC for an undoped $Zn_{0.969}Be_{0.031}Se$ layer grown after Be–Zn co-irradiation of the GaAs surface. The solid line is the experimental data and the dotted line is the Gaussian fit.

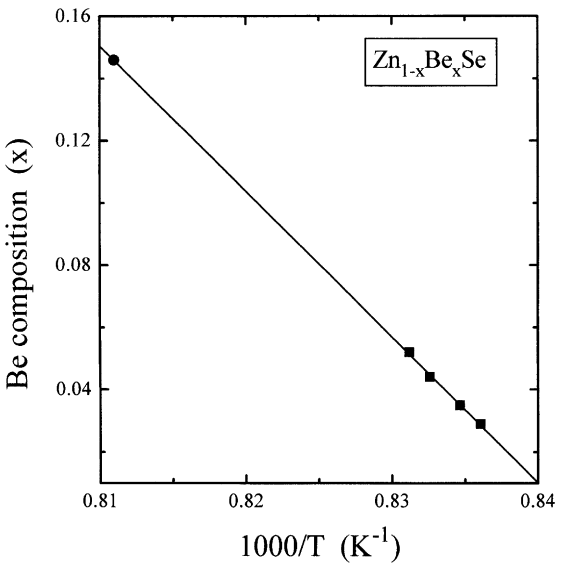

Fig. 2. Dependence of Be composition of $Zn_{1-x}Be_xSe$ alloys on the Be cell temperature during growth. Squares were calculated from the (1 1 5) *a* and *b* reflection DCXRC, and the circle was calculated from the (0 0 4) reflection single crystal XRD data assuming that the epilayer is completely relaxed.

linear dependence was observed within the small cell temperature range investigated, from 923 to 960°C, indicating a high level of compositional control in the growth of this alloy.

The results of the EPD measurements are also shown in Table 1. The EPD for the ZnBeSe epilayers grown with Zn irradiation is very high ($>10^6$ cm^{-2}), whereas that grown with Be–Zn co-irradiation or with a BeTe buffer layer is much lower, in the 10^4 cm^{-2} range. The quality of the RHEED pattern for the different growth conditions used suggests that the high EPD for the Zn-irradiation case may be related to a rough growth front of the ZnSe buffer while the lower EPD for Be–Zn co-irradiation and BeTe buffer layer cases is related to the formation of a very flat Be-based interfacial layer. Comparing the best EPD (<5000 cm^{-2}) reported in Ref. [9] (grown under a reduced Se background: 1 h growth break with Se valved cracker closed, Zn flux on and cleaned shutters), the slightly higher EPD in our ZnBeSe epilayers grown under both Be–Zn co-irradiation and/or BeTe buffer layer may be due to the higher Se background in our system since we use a normal Se K-cell and we did not perform a growth break.

Fig. 3 shows the 13 K PL spectra for undoped ZnBeSe epilayers grown using (a) Be–Zn co-irradiation with a ZnSe buffer, (b) a BeTe buffer and (c) Zn irradiation with a ZnSe buffer. The spectrum for the Be–Zn co-irradiation (case a) is quite similar to that for the BeTe buffer layer (case b): very similar emission peaks near the band gap edge (FWHM is $\approx$2.5 meV — Table 1) and negligible deep level PL are observed. However, the spectrum for the sample grown with Zn irradiation (case c) shows a broad deep level emission at $\sim$2.55 eV, and the FWHM of the band edge peak is $\approx$5 meV (Table 1). The inset of Fig. 3 is the semi-log plot of the PL spectrum near the band gap region for the sample grown with Be–Zn co-irradiation (case a) (ZnBeSe with 3.1% Be). Several sharp emission lines can be observed. The transitions at 2.894 and 2.904 eV are assumed to be related to free excitonic recombination. These are consistent with the reported values of free excitonic recombination in ZnBeSe with 2.8% Be [8]. The dominant peak at

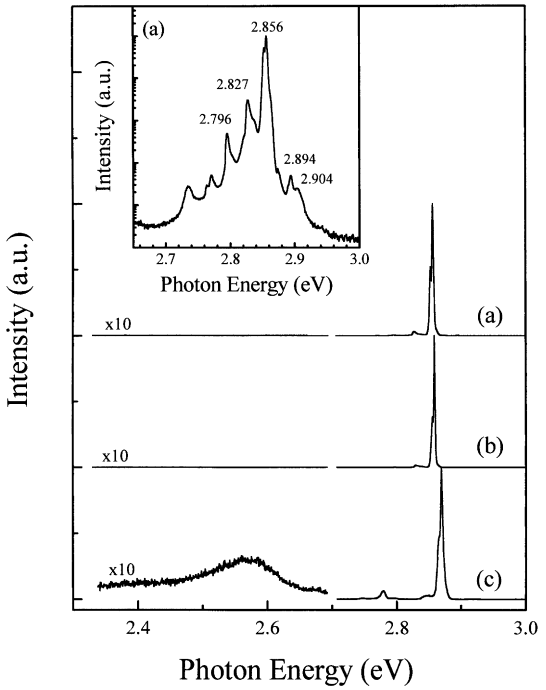

Fig. 3. Low-temperature (13 K) PL spectra for undoped ZnBeSe layers grown using (a) Be–Zn co-irradiation with a ZnSe buffer, (b) a BeTe buffer and (c) Zn-irradiation with a ZnSe buffer. The inset is the semi-log plot near the band gap region of spectrum (a).

$\sim$2.856 eV is then tentatively attributed to a deep bound excitonic recombination. The peaks at 2.828 and 2.796 eV may be phonon replicas of this dominant transition. The highly resolved PL spectrum observed supports the assessment of very high crystalline quality of this sample.

Capacitance–voltage measurements were performed on a N-doped $Zn_{0.971}Be_{0.029}Se$ epilayer. From the slope of $1/C^2$ versus V a net acceptor concentration ($n_a - n_d$) of 2.0×10^{17} cm^{-3} was obtained, which is comparable to the value obtained by ECV measurements (1.6×10^{17} cm^{-3}). This result is similar to reported doping levels [8,13]. The PL results of this sample will be reported separately.

The reasons for the quality improvement of Be-based materials by using a BeTe buffer layer have been discussed in Ref. [9]. In the case of Be–Zn co-irradiation performed here, the formation of the (1×2) surface reconstruction may play a major role in improving the ZnBeSe quality. It has been shown that the Se-rich (2×1) surface reconstruction originates from the formation of a full monolayer of Se dimers [6]. A (1×2) surface reconstruction has been proposed to be related to Zn dimers [14] on the (0 0 1)GaAs surface. However, such a (1×2) surface reconstruction has never been observed before, even after Zn irradiation of the GaAs is performed. We attribute the (1×2) surface reconstruction in our case to the formation of a full monolayer of Be and Zn dimers. Further investigations, such as scanning tunneling microscopy studies should be performed to confirm this assignment. The well-ordered Be–Zn layer on the GaAs surface avoids the formation of Ga_2Se_3, decreasing stacking faults and improving the crystalline quality dramatically. The observation of the RHEED pattern also indicates that a two-dimensional growth mode is achieved immediately and persists throughout the growth of the ZnSe buffer layer and ZnBeSe epilayer on this (1×2) surface reconstruction. Therefore, the growth front is quite flat and only the presence of a few atomic steps can induce the formation of lattice defects such as dislocations. In addition, due to the high degree of covalent bonding in beryllium chalcogenides the formation energy for a stacking fault is high at the II–VI/III–V interface and a lower density of stacking faults is expected in this Be-containing alloy.

4. Conclusions

We have investigated the MBE growth and properties of ZnBeSe epilayers with different Be compositions grown on GaAs substrates by using a new method for II–VI/III–V interface formation involving a Be–Zn co-irradiation with a ZnSe buffer layer. A (1×2) RHEED pattern was observed on the (0 0 1)GaAs surface after the Be–Zn co-irradiation, suggesting the formation of a full monolayer of Be and Zn dimers. A two-dimensional growth mode was achieved throughout the ZnSe buffer layer and ZnBeSe epilayer growth. Narrow X-ray linewidths down to 23 arcsec with a very low etch pit density, of mid 10^4 cm^{-2}, were obtained. The linewidth of the dominant excitonic

emission is about 2.5 meV at 13 K for a near lattice-matched ZnBeSe layer. For a nitrogen-doped sample, a net acceptor concentration of $2.0 \times 10^{17}\,cm^{-3}$ was obtained by C–V measurements. ZnBeSe grown with the BeTe buffer layer shows the similar crystalline quality to that grown under Be–Zn co-irradiation with a ZnSe buffer, whereas that grown under Zn-irradiation alone, with a ZnSe buffer has a much poorer quality.

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