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Photoluminescence characterization of MBE grown $Zn_{1-x}Be_xSe$

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Abstract

We report photoluminescence (PL) studies of high-quality $Zn_{1-x}Be_xSe$ films grown by molecular beam epitaxy (MBE) on GaAs substrates by use of a novel growth method of Be–Zn co-irradiation before the growth of a thin ZnSe buffer layer. Samples show double-crystal X-ray linewidth as narrow as 23 arcsec. Low-temperature (13 K) PL of undoped samples showed free exciton emission, which defined the bandgap and showed that this system gives bandgap bowing. In addition, there was dominant deep bound excitonic recombination. We also suggest that deep PL can be caused by low structural quality of films, rather than by specific impurity states. Nitrogen-doped samples (with net acceptor concentrations up to $2\times10^{17}\,cm^{-3}$) show strong impurity related photoluminescence. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Wide bandgap semiconductors are of high interest for fabricating devices emitting light in the green, blue, and UV spectral regions. However, performance of such devices depends on the adequacy of bipolar doping of the materials and on device "lifetime". It is well known that good p-type doping is still a problem for most II–VI wide bandgap semiconductors. The best devices have been fabricated lattice matched to a GaAs substrate, with ZnMgSSe as a cladding layer and ZnSSe as a guiding layer [1]. However, during molecular beam epitaxial (MBE) growth, the sulfur sticking coefficient depends strongly on the substrate temperature, making it extremely difficult to avoid compositional fluctuations [2]. Recently, the use of Be instead of sulfur in ZnSe-based alloys (i.e. $Zn_{1-x}Be_xSe$ ternary alloy) has been suggested [3]. This also increases the hardness of the material [4], which is important for improved device lifetime,

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and requires relatively small beryllium concentrations to obtain large bandgap values. In this paper, we report the results of an investigation of a series of samples of this novel material, using low-temperature photoluminescence (PL) as well as X-ray diffraction and capacitance–voltage (*C–V*) profiling. Both undoped and nitrogen-doped samples were investigated.

2. Experimental procedure

High crystalline quality ZnBeSe (1–2 μm thick) epilayers were grown on GaAs(0 0 1) substrates by MBE. The p-type doping was performed by employing an Oxford Research RF nitrogen plasma source. A novel method of Be–Zn co-irradiation, before growth of a 5 nm ZnSe buffer layer, was used in order to avoid the formation of stacking faults at the III–V/II–VI interface. A more detailed description of the growth procedure and growth parameters is given in Ref. [5]. We also examined other approaches to controlling the II–VI/III–V interface: Zn irradiation with a ZnSe buffer layer [6] and a BeTe buffer layer [7] .

The ZnBeSe crystalline quality and Be composition were assessed by double-crystal X-ray diffraction measurements using a double-crystal biaxial diffractometer and Cu $K_{\alpha 1}$ radiation. The nitrogen-doped samples were also investigated by *C–V* or electrochemical *C–V* measurements. For the *C–V* measurements a gold contact was used.

For most PL measurements, samples were kept in the He gas chamber of the second stage of a closed-cycle refrigerating system. The temperature was kept mostly at 13 K and was monitored by a silicon diode mounted in the vicinity of the sample. The 325 nm line of a He–Cd laser was used as an excitation source. The PL was dispersed through a $\frac{3}{4}$m monochromator and was detected with a low-noise photomultiplier tube, whose output was connected to a SR400 photon counter.

3. Results and discussion

The full-width at half-maximum (FWHM) of the double-crystal X-ray rocking curves (DCXRC), for most of the ZnBeSe epilayers grown via Be–Zn co-irradiation and a ZnSe buffer layer, are in the range of 23–45 arcsec, which indicates a high crystalline quality of the ZnBeSe epilayers. From the (115)a and b asymmetrical reflection DCXRC we obtain the perpendicular and parallel lattice constants: a_1 and a_2. Then the bulk lattice constant, a, is calculated from the equation [8]

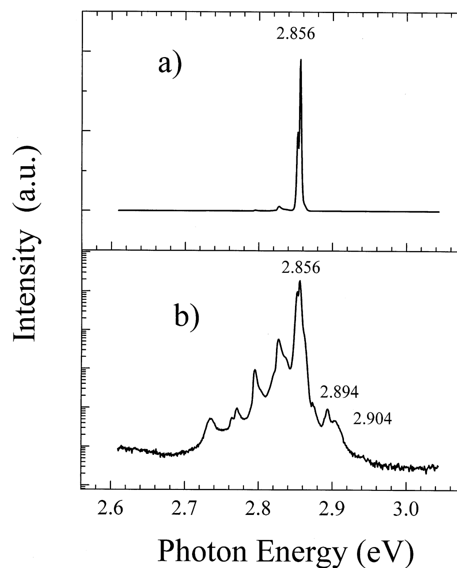

Fig. 1. Low-temperature (13 K) PL spectra of an undoped sample with 3.1% Be: (a) in linear scale; (b) in semi-log scale; a complex structure, presumably due to phonon replicas, is seen on the low-energy side of the main peak, and two free excitons at 2.894 (FX1) and 2.904 eV (FX2) are seen on the high-energy side.

$$a = a_1\left[1 - \frac{2v}{1+v}\frac{a_1 - a_2}{a_1}\right], \qquad (1)$$

where v is Poisson's ratio. We used the ZnSe value ($v = 0.28$) for the ZnBeSe alloys because of the relatively small Be concentration in all our samples. Then, assuming that Vegard's law is valid for $Zn_{1-x}Be_xSe$, the Be composition for the samples was calculated. We used the following values of the lattice constants: $a_{ZnSe} = 5.6676$ Å [9] and $a_{BeSe} = 5.139$ Å [10] .

The nitrogen-doped samples show a net acceptor concentration around $2\times10^{17}\,cm^{-3}$, which

Table 1
Sample characteristics

Sample	a (Å)	Be (%)	$N_A - N_D$ (cm^{-3})	RC FWHM (arcsec)	Main peak (eV)
A1215	5.6569	2.05 ± 0.05	Undoped	39	2.834
A1160	5.6510	3.15 ± 0.05	Undoped	23	2.856
A1158[a]	5.6504	3.25 ± 0.05	Undoped	18	2.859
A1124	5.6441	4.45 ± 0.05	Undoped	46	2.871
A1218	5.6389	5.43 ± 0.05	Undoped	145[b]	2.885
A1165	5.6527	2.82 ± 0.05	2.0×10^{17}	37	2.770
A1166[a]	5.6498	3.37 ± 0.05	2.0×10^{17}	33	2.777
A1149	5.6462	4.05 ± 0.05	1.5×10^{17}	34	2.782
A1233	5.6374	5.72 ± 0.05	2.0×10^{17}	157[b]	2.808

[a] BeTe buffer layer.
[b] Samples are partially relaxed.

corresponds to the highest values reported up to date [11]. Sample information is given in Table 1.

We now discuss results from the undoped samples. The PL spectrum from a typical undoped sample (3.1% Be) is shown in Fig. 1. This is characterized by very narrow emission peaks (FWHM < 2.5 meV) in the band-edge region, as well as by a negligible deep PL. Two adjacent peaks, 3 meV apart, peaks can be seen at 2.8524 and 2.8562 eV. Closer examination of the spectra, however, shows several additional emission lines between 2.796 and 2.826 eV (see Fig. 1b), which we attribute to phonon replicas of one or both peaks. Moreover, small peaks at 2.894 and 2.904 eV are also observed. Qualitatively similar spectra are obtained for the other undoped samples investigated (see Table 1).

Of particular interest are the two small high-energy lines. We attribute these to free excitons for two reasons. First, in four out of five samples we examined, there were two such peaks; it is known that non-pseudomorphic epitaxial ZnSe layers show two free exciton peaks [12]. Second, if one plots these peaks as a function of Be concentration, one can obtain a smooth extrapolation to the ZnSe values (Fig. 2) by assuming bowing of the gap. Moreover, we have also plotted in Fig. 2 earlier values obtained at 77 K [13]; the variation is close, over the concentration range over which our values overlap with the earlier ones. We have fitted the

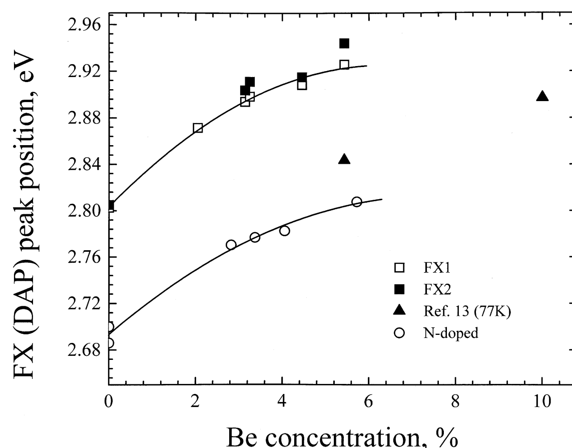

Fig. 2. Peak positions of free excitons (undoped samples) and DAP (N-doped samples) as a function of Be concentration. Solid lines are fits to Eq. (2). Literature data (Ref. [13]) is also shown.

data to a parabolic function

$$E = E(0) + \alpha x + \beta x^2, \quad (2)$$

where $E(0)$ is the appropriate peak energy in ZnSe, x is the Be concentration in %, and α and β are the bowing parameters. We have found that the latter obtained from different peaks (see Fig. 2) are the same within fitting errors; however, since impurity ionization energies can vary with composition, we take the values obtained from

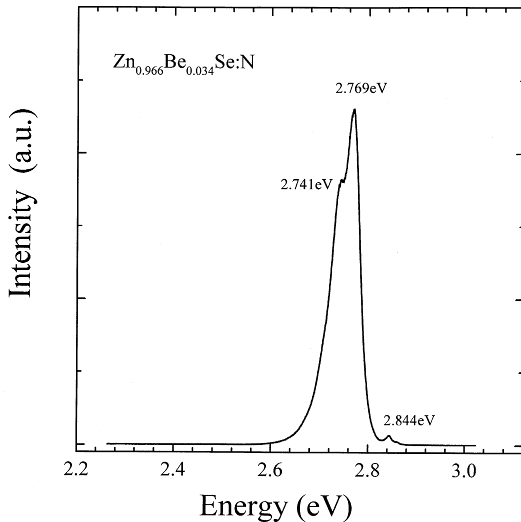

Fig. 3. Low-temperature (13 K) PL spectra of a nitrogen-doped ZnBeSe sample with 3.4% Be.

fitting to the exciton peaks to be more reliable. These are $E(0) = 2.803\,\text{eV}$, $\alpha = 38.5\,\text{meV}/\%$ and $\beta = -3.03\,\text{meV}/(\%)^2$. This behavior is different from the linear dependence assumed in Ref. [13]. It is important to recognize that the bandgap values are very sensitive to the Be composition, and its precise knowledge is thus necessary for device design optimization.

With the high-energy peaks assigned to free excitons, and thus giving the excitonic bandgap, it is apparent that the dominant peak is not far from this bandgap. Because of this proximity, its sharpness, as well as the fact that the position of this peak does not shift with excitation intensity, we attribute this peak to a bound exciton. We must emphasize that it is a deep bound exciton; note though, that from the temperature dependence of its peak position, we conclude that it has effective mass type characteristics [14]. However, its detailed origin remains to be investigated.

We have also examined several high-quality N-doped samples. All showed a dominant peak in the 2.76–2.80 eV region, depending mainly on Be content (Fig. 3 shows the spectra for our $Zn_{0.966}Be_{0.034}Se$ sample), and also, slightly, on excitation intensity. We believe that it is likely to be a DAP transition, based on the observed peak shift with intensity (a similar assignment was given in Ref. [11]). Assuming the DAP nature of this peak, one can conclude that, since the peak is relatively close to the band gap energy, it must be due to relatively shallow donors and acceptors; presumably the acceptor is substitutional N. Moreover, the bowing parameters obtained for this peak are similar to those of the excitonic peaks (see also above), which suggests that the activation energies of the impurities do not change appreciably with Be concentration in the range we have studied (below 6% Be).

Both N-doped and undoped samples of lesser quality (DCXRC FWHM > 300 arcsec) show a substantial deep PL. Interestingly, the presence of deep levels has also been reported in samples grown by the high-pressure Bridgman method [15], but our best samples as well as previously reported MBE grown samples (see, e.g. Ref. [11]), did not show such deep PL. We, thus, conclude that (in our samples) the deep PL relates to the structural quality of the samples rather than to the presence of "deep impurity" states. Note, however, that although this may be true in these samples, it is well known that deep impurity states may also produce deep level PL.

In summary, we have investigated a series of high quality – undoped and N-doped – ZnBeSe samples. The dominant PL feature of undoped samples is a deep bound excitonic transition, while doped samples exhibit impurity dominated PL. Our results, particularly on the undoped samples, show that the $Zn_{1-x}Be_xSe$ bandgap has bowing. We also suggest that deep PL can result from low structural quality of films.

Acknowledgements

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