Proceedings of the XXXV International School of Semiconducting Compounds, Jaszowiec 2006

Microscopic Luminescence Properties of ZnO and ZnO Based Heterostructures

F. BERTRAM* AND J. CHRISTEN

Institute of Experimental Physics, Otto-von-Guericke-University Magdeburg
Postbox 4120, 39106 Magdeburg, Germany

The optical properties of excitonic recombinations in ZnO are investigated by spatially and spectrally resolved cathodoluminescence measurements. The relevance of cathodoluminescence microscopy as a spatially resolved luminescence technique as a simple but very powerful characterization method is stressed out in discussions of a wide variety of appropriate examples. A thorough discussion of the various features of the cathodoluminescence of an undoped ZnO bulk crystal, epitaxially grown ZnO and MgZnO/ZnO/MgZnO quantum well structure is given. Particular attention is devoted to the impact of the internal electrical fields, e.g. the Franz-Keldysh effect in ZnO. Furthermore, this study focuses on the spectral variations as a function of depth to the interface in ZnO homo- and heterostructures. Our aim is to establish the nature of the optical transitions influenced by internal fields, defects and impurity doping in ZnO/GaN and ZnO/ZnO interfaces. This review covers also the vertical transport, diffusion and capture of carriers in a MgZnO/ZnO/MgZnO quantum well structure.

PACS numbers: 78.60.Hk, 78.66.Hf, 81.05.Dz, 81.15.Gh

1. Introduction

ZnO has re-emerged into the center of international attention. With its wide direct band gap and featuring the largest exciton binding energy (62 meV) of all practical semiconductors ZnO is the most promising candidate for future high quantum efficiency light emitting/detecting devices. Although known for many years, there is still a lack of information on its microstructure and in particular its microscopic electronic and optical properties.

2. Experimental setup

The low temperature cathodoluminescence microscopy was performed in a home-built system based on a modified JEOL 6400 scanning electron microscope.

*corresponding author; e-mail: Frank.Bertram@physik.uni-magdeburg.de

Here, the focused electron beam is digitally scanned over the surface (256×200 pixels) while the emitted light is collected by an elliptical mirror and focused onto the entrance slit of a 27 cm focal-length grating monochromator. The light is detected by a diode array giving a complete cathodoluminescence (CL) spectrum at each pixel. Subsequently, the data are stored in a computer. The resulting data set $I_{CL}(x, y, \lambda)$ is evaluated *ex situ* to produce local spot-mode spectra, sets of pan- and/or monochromatic CL mappings, spectrum line scans etc. A specific feature is the compilation of CL wavelength images (CLWI), which map the local peak wavelength at each sampling point [1].

In our experiments the kinetic energy of the incident electron beam was set between 3 and 5 keV in order to achieve high spatial resolution. The beam current was varied between 6 and 300 pA. The samples were studied at a temperature of 4.2 K.

3. Discussion

3.1. Impact of internal electric fields, hetero- and homointerfaces

3.1.1. Bulk crystals

The optical spectra of ZnO bulk material is characterized by a rich structure of excitonic lines. Up to 20 emission lines are known [2]. An appreciated spectrum ($T = 4.2$ K) of a bulk crystal is depicted in Fig. 1. Here, the vertical lines give the energetic position of the free exciton (X) and bound excitons (BE) known in ZnO. The assignment occurs after [2]. In the sample under study the spatially averaged CL spectrum is dominated by the bound exciton emission of I_{6a} . In addition, the

Fig. 1. Spatially averaged CL spectrum (near band gap region) of ZnO bulk crystal ($T = 5$ K). The vertical lines mark the spectral positions of all known excitons in ZnO.

line of the free exciton (X), the bound excitons I_1 , and I_3 , as well the two-electron satellite (TES[†]) recombination line of the exciton I_{6a} can be easily identified.

The nominal unstrained crystal has been studied by means of scanning cathodoluminescence microscopy. Figure 2 depicts a CL spectrum line scan vi-

Fig. 2. (a) Local spectra and (b) CL spectrum line scan. The local spectra and the line scan were taken over a crack of a freshly cleaved surface of a ZnO bulk crystal. Towards the crack, I_1 and I_3 shift to higher energies, whereas I_5 , I_{6a} , and I_9 remain constant.

sualizing local spectra taken at equidistant sample positions along a line over a crack of a freshly cleaved cross-section. The local spectra exhibit a sharper line width of the excitonic lines than the spatially integrated spectrum in Fig. 1. More astonishing, the local spectra reveal distinct differences in their spectral features with their sample position: the intensity relation changes between I_{6a} and I_1/I_3 . From a dominating I_{6a} emission far away from the crack the CL spectrum is taking over by I_1 and I_3 in the vicinity of the crack. Simultaneously, I_1 and I_3 shift to higher energies ($\Delta E = 8.3$ meV), whereas the spectral positions of I_5 – I_9 remain constant. Hence, not the whole band shifts to higher energies, only single ionized bound exciton lines are affected. The blue shift of these excitonic lines may be explained by strong local internal electric fields (the Franz–Keldysh effect) in the vicinity of the crack. This is supported by the strong decreases in quantum efficiency.

[†]During the recombination of an exciton bound to a donor the donor final state can be the $1s$ state (normal D^0X line) or the excited state, the $2s$ or $2p$ state (TES-line).

3.1.2. Homo/heterointerfaces

Even more complex to bulk crystals is the luminescence of epitaxially grown ZnO. Chemical mismatch (III/V–II/VI oxide interface), lattice mismatch (different lattice constant, different thermal constant), and electrostatic fields (different spontaneous polarization, piezoelectrical polarization) influence the interface. The main difficulty in growing ZnO heteroepitaxially on foreign substrates is the mismatch of the lattice constants and thermal expansion coefficients between layer and common substrates, e.g. sapphire [3] and GaN [4]. The unfavorable growth condition results in unsatisfactory defects in the layers, which are not homogeneously distributed. The formation of defects within this material are poorly understood, for instance, the nature of the residual donor and acceptor and the identification of various emissions related to defects. The states localized at the interface of ZnO/GaN and ZnO/ZnO can be of significant concern for certain device applications. In particular, degenerate doping and high conductance can occur near this interface with GaN, potentially affecting lateral transport in the overgrown device. Hence, impurity diffusion, interface reaction and related defect formation are important to understand and control. Until now the physical origin of the impurities in ZnO has been unclear since it may involve: impurities substrate in/out-diffusion, native defects, morphological structural effects, and gas phase impurities.

This study focuses on the spectral variations of luminescence as a function of depth to the interface. Our aim is to establish the nature of the optical transitions due to defects and impurity doping in ZnO/GaN and ZnO/ZnO interfaces.

The ZnO epilayer under study was grown by metal organic chemical vapor phase epitaxy (MOVPE) on a GaN/sapphire template using a two-step process: first, a 0.44 μm thick low-temperature (LT) ZnO buffer was deposited at 450°C with tertiary-butanol as O-precursor and dimethyl-zinc (DMZn), respectively and subsequently *in situ* annealed for 4 min at 900°C inside the MOVPE reactor. The final nominally 2 μm thick ZnO layer is then grown in a second step at high temperature (900°C) using N₂O as O-precursor. Details of this optimized growth procedure are given elsewhere [5].

A cross-sectional CL spectrum line scan, i.e., a set of normalized CL spectra recorded while scanning in the growth direction along the samples freshly cleaved cross-section is depicted in Fig. 3. The layer sequence is directly visualized: the weak and broad (FWHM = 10 meV) emission from the GaN template appears slightly red shifted at $E = 3.468$ eV. Without the ZnO on top, the GaN would be compressively strained on sapphire.

The ZnO luminescence of the following 0.44 μm thick LT buffer is completely governed by a weak and unstructured broad luminescence band (FWHM = 11 meV) indicating a high defect density and strong impurity incorporation. Starting at around 3.357 eV at the LT-ZnO/GaN interface, a strong red shift accompanied by a further broadening of the ZnO luminescence occurs with advancing

Fig. 3. Cross-sectional CL spectrum line scan (left) directly visualizing the layer sequence of the ZnO sample. The sample consists of a GaN layer on sapphire followed by a $0.44 \mu\text{m}$ thick LT-ZnO buffer and the final $2.3 \mu\text{m}$ thick HT-ZnO layer (schematic drawing in the middle). Local spectra (right) are taken at different position from the cross-section of the sample (positions are marked).

growth. This red shift reaches its maximum (6 meV) at the homointerface between the LT-ZnO buffer and the final high-temperature (HT) ZnO epilayer. The red shift of the ZnO emission may be explained by strong local impurity incorporation and/or local internal electrical fields (the Franz-Keldysh effect) in the vicinity of the homointerface.

A complete relaxation of this red shift is achieved within the first micrometer of the HT-ZnO layer accompanied by a dramatic line narrowing. The final sharp excitonic line I_8 (FWHM < 2 meV) can be clearly observed up to the sample surface (at $2.7 \mu\text{m}$) at $E = 3.358$ eV and no further energy shift is observed. However, at the HT-ZnO surface, an abrupt minor red shift by 2 meV occurs. This indicates a residual minor tensile strain of the ZnO layers, as the samples cross-section is partially relaxed with respect to the layer's surface. The bound exciton line I_8 is related to Ga incorporation [6], which could be incorporated from the underlying GaN template.

3.2. Hetero and quantum structures, ternary systems

3.2.1. MgZnO: transport, diffusion and capture in single quantum wells

An important step in order to design ZnO-based optoelectronic devices is the realization of band gap engineering to create barrier layers and quantum wells in device heterostructures. On the one hand, a narrowing of the band gap can be achieved by the incorporation of cadmium into ZnO layers. On the other hand, the

incorporation of magnesium has been shown to increase the band gap of the resulting alloy [7]. Therefore MgZnO is an appropriate candidate as barrier material for ZnO quantum wells and seems well-suited for more sophisticated structures such as waveguides or distributed Bragg reflectors. ZnO–MgZnO multiple quantum well structures were already successfully grown and the quantization effects and an enhancement of the exciton binding energy in the ZnO quantum wells could be confirmed [7].

The ZnO–MgZnO samples were grown by MOVPE. The sample was grown on GaN/sapphire template at a growth temperature of 600°C. A ZnO buffer was included to improve the quality of the structure. Diethylzinc (DEZn), bis(methylcyclopentadienyl) magnesium (MeCp₂Mg), and nitrous oxide were used as the zinc, magnesium (Mg), and oxygen precursors, respectively. First, a 300 nm thick Mg_{0.06}Zn_{0.94}O epilayer was grown as barrier material. Then, a ZnO–MgZnO quantum well structure was grown. The width L of the ZnO quantum well, which was introduced 50 nm below the surface, was 2 nm [8].

Fig. 4. Integrated CL spectra at $T = 4.2$ K of the MgZnO/ZnO/MgZnO single quantum well structure.

In Fig. 4 there is the laterally integrated CL spectrum of the sample depicted. The spectrum is dominated by three spectral bands originating from the ZnO buffer ($E = 3.356$ eV), the 2 nm thick MgZnO/ZnO/MgZnO single quantum well (SQW) ($E = 3.383$ eV) and the Mg_{0.06}Zn_{0.94}O barrier ($E = 3.450$ eV). The position of the MgZnO barrier peak is known from thick MgZnO sample with [Mg] = 6%. In contrast, in the spectrum of quantum structure an additional band appears clearly assignable to the 2 nm thick single quantum well. In particular, the spectral band from the quantum structure, as well as from the barrier, exhibits two high energy shoulders or peaks, respectively.

Figure 5a shows a cross-sectional CL spectrum line scan of the sample structure. The ZnO, SQW and MgZnO emission are labeled. The scan begins with the ZnO buffer emission which increases very fast. An additionally depicted intensity line scan (Fig. 5b) gives the exact intensity relation of the three spectral parts versus vertical position. The rise in ZnO CL intensity provides a spatial

Fig. 5. (a) Cross-sectional CL spectrum line scan (logarithmic intensity scale) and (b) intensity line scan (linear intensity scale) from a cross-section of the MgZnO/ZnO/MgZnO single quantum well structure. The luminescence of the ZnO buffer, the MgZnO barrier, and the ZnO single quantum well is labeled.

resolution of the scan of 44 nm. In contrast, the intensity slop of ZnO into the barrier is significantly shallow. In the following, the MgZnO luminescence starts and crosses the SQW emission after about 300 nm. The SQW is burrowed 50 nm under the sample surface. The rise in the quantum well intensity gives excess to the ambipolar diffusion length of excitons recombining in the SQW $L_{\text{diff}} = 140\text{ nm}$.

4. Conclusion

We studied the spatial variation of excitons in ZnO material. From measurements of the cathodoluminescence of a bulk crystal we derived the strong impact of internal electrical fields in ZnO. The same relevance of internal fields was found in ZnO hetero- and homointerfaces. We showed that the optical properties of homo- and heteroepitaxially grown ZnO strongly depend on the distance to the interface. We explain the observed shifts in CL by the influence of both a vertical strain gradient and internal fields. The cross-sectional variation of luminescence in a MgZnO/ZnO/MgZnO single quantum well structure was studied with highly

spatially resolved cathodoluminescence microscopy. The transfer and capture of carriers into the well was analysed.

Acknowledgments

The authors would like to thank A. Dadgar and A. Krost from the University in Magdeburg, and Th. Gruber, C. Kirchner, R. Kling, A. Waag from Ulm University for supplying the ZnO samples.

References

- [1] J. Christen, M. Grundmann, D. Bimberg, *J. Vac. Sci. Technol. B* **9**, 2358 (1991); F. Bertram, T. Riemann, J. Christen, A. Kaschner, A. Hoffmann, C. Thomsen, K. Hiramatsu, T. Shibata, N. Sawaki, *Appl. Phys. Lett.* **74**, 359 (1999).
- [2] N. Presser, J. Gutowski, I. Broser, *Phys. Rev. B* **38**, 9746 (1988).
- [3] Y.F. Chen, D.M. Bagnell, H.J. Ko, K.T. Park, K. Hiraga, Z. Zhu, T. Yao, *J. Appl. Phys.* **84**, 3912 (1998).
- [4] R.D. Vispute, V. Talyansky, S. Choopun, R.P. Sharma, T. Venkatesan, M. He, X. Tang, J.B. Halpern, M.G. Spencer, Y.X. Li, L.G. Salamanca-Riba, A.A. Iliadis, K.A. Jones, *Appl. Phys. Lett.* **73**, 348 (1998).
- [5] A. Dadgar, N. Oleynik, D. Forster, S. Deiter, H. Witek, J. Bläsing, F. Bertram, A. Krtischil, A. Diez, J. Christen, A. Krost, *J. Crystal Growth* **267**, 140 (2004).
- [6] B.K. Meyer, H. Alves, D.M. Hofmann, W. Kriegseis, D. Forster, F. Bertram, J. Christen, A. Hoffmann, M. Straßburg, M. Dworzak, U. Haboeck, A.V. Rodina, *Phys. Status Solidi B* **241**, 231 (2004).
- [7] A. Ohtomo, M. Kawasaki, T. Koida, K. Masubuchi, H. Koinuma, *Appl. Phys. Lett.* **72**, 2466 (1998); S. Choopun, R.D. Vispute, W. Yang, R.P. Sharma, T. Venkatesan, H. Shen, *Appl. Phys. Lett.* **80**, 1529 (2002).
- [8] Th. Gruber, C. Kirchner, R. Kling, F. Reuss, A. Waag, *Appl. Phys. Lett.* **84**, 5359 (2004).