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Heteroepitaxy of ZnO on GaN Templates

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We report on the growth of ZnO single crystal thin films on GaN templates by vapor phase deposition using Zn and NO_2 as precursors. The X-ray diffractogram showed the hexagonal crystal structure, and the half width of the rocking curve was 4 arcmin. The optical properties are investigated by temperature dependent photoluminescence. A series of neutral donor and acceptor bound exciton recombinations can be resolved at low temperatures with a linewidth as narrow as 0.7 meV. Free exciton emission is already dominating at 45 K proving the high quality of the epitaxial films.

Introduction II–VI semiconductor opto-electronic devices can well operate in the green and red spectral range but stable blue and ultraviolet emitters could not be realised up to now. ZnO and its ternary alloys ZnMgO and ZnCdO have the potential to compete with the III–V nitrides especially when considering the serious influence of structural defects on the device performance. ZnO bulk crystals for homoepitaxy are available; like GaN, ZnO is a direct band gap semiconductor with a room temperature energy gap at 3.3 eV (375 nm), it has comparable piezoelectric constants as GaN, and also crystallises in the wurtzite structure. Excitonic lasing at low thresholds at room temperature has been reported recently [1, 2]. Key issues before going to device realisation are (i) the ability to grow heterostructures and quantum wells [3], (ii) bipolar doping (p-doping is still an open question in ZnO despite first successful efforts), and (iii) to obtain films of high crystalline quality with low residual carrier densities and of low dislocation densities. The latter could be established by growing on ZnO substrates (homoepitaxy) or on substrates with close lattice matching such as GaN (heteroepitaxy).

Experimental Here we report on ZnO films grown on 1 μm thick GaN epitaxial films which were grown by MOCVD on (0001) sapphire substrates using the low temperature buffer concept.

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We used a home built epitaxy system which consists of a horizontal quartz reactor, and a resistance heating with different temperature zones. Metallic Zn with 6 N purity was kept in one zone at temperature of 470 °C, and was transported by a purified N_2 carrier gas with a flow rate of 200 sccm to the substrate. The growth temperature was varied between 600 and 850 °C and an optimum temperature of 650 °C was found in these investigations. As oxygen precursor we used NO_2 which was transported with a flow rate of 70 sccm in reverse flow towards the substrate. Typical growth rate was 2 μm/h. The ZnO films obtained were characterised by X-ray diffraction techniques (θ–2θ, reciprocal space contour mapping), atomic force microscopy, and temperature dependent photoluminescence (PL) using a HeCd laser (30 mW) as an excitation source.

Results and Discussion In Fig. 1 we compare two films both grown at 650 °C having different layer thickness. For the 1 μm ZnO film two diffraction peaks are visible, one from ZnO and one from the GaN template. For the 15 μm thick film there are two diffraction peaks from ZnO originating from different areas in the film. The one at lower angles is from part of the film above a thickness of approx. 7 μm (obtained by a simulation with the Bede program) whereas the other one comes from areas closer to the interface where the film is still under strain. The lattice spacing in the thin film are $c = 5.2019$ Å, $a = 3.2514$ Å, in the thick film the relaxed part has $c = 5.204$ Å, $a = 3.250$ Å, the strained part has $c = 5.200$ Å, $a = 3.253$ Å. In bulk ZnO (from Eagle Picher with a room temperature carrier density of 2×10^{17} cm^{-3}) we obtain for the lattice constants $c = 5.206$ Å and $a = 3.2493$ Å. The full width at half maximum (FWHM) of the rocking curve was 4 arcmin for the epitaxial films.

Next we discuss the optical properties of the ZnO films. Figure 2 shows the PL spectra of a 1 μm thick ZnO film (b) in comparison with a bulk ZnO crystal (a). A series of sharp excitonic lines comprising donor bound and acceptor bound excitons with a full width at half maximum (FWHM) of 0.7 meV can be resolved in both films. In the bulk ZnO (Fig. 2a) the prominent lines are I_4 and I_5 (D^0X), and I_6 and I_9 (A^0X) (line assignment according to Refs. [4, 5]). In the epitaxial film different neutral donor bound exciton recombinations appear (from 3.372 to 3.361 eV), the strongest recombination is from the neutral acceptor bound exciton I_6 as well as I_9. However, in contrast to the

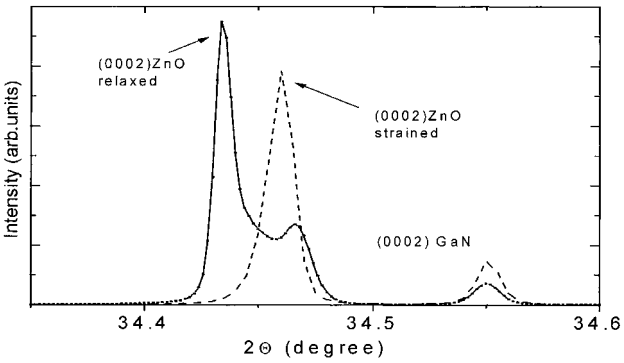

Fig. 1. X-ray diffraction of ZnO epilayers on (0002) GaN templates for a 1 μm thick film (dashed line) and for a film thickness of 15 μm (solid line)

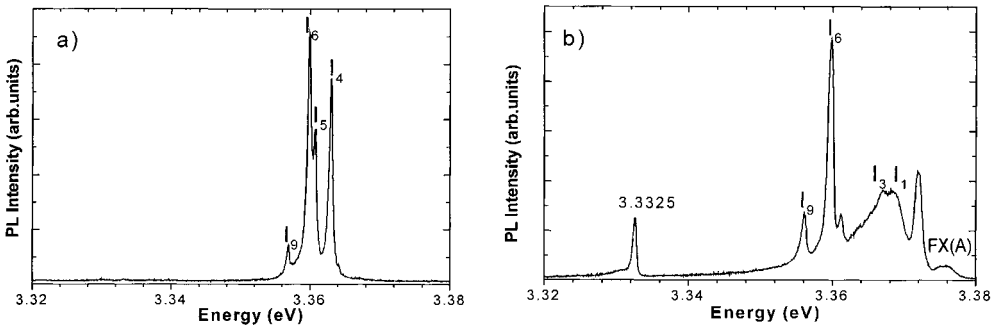

Fig. 2. Photoluminescence spectra (4.2 K) of a) bulk ZnO single crystal and b) ZnO epitaxial film (thickness 1 μm), for details see text

bulk crystal, free exciton recombination with the A-valence band FX(A) at 3.375 eV is already visible at 4 K.

In the epitaxial films there is hardly any emission detectable at lower energies. The green luminescence band at 2.43 eV is seen in the room temperature measurements but is a factor of 20 less intense than the band edge emission. From 45 K up to room temperature free exciton emission is the dominating radiative channel. Already at 30 K (see Fig. 3) the free exciton emission intensity is comparable to the bound exciton recombinations. The transitions at approx. 3.31 eV and 3.24 eV are longitudinal optical (LO) phonon replicas (1LO, 2LO) of the free exciton emission at 3.375 eV. The dominance of the free exciton emission together with the narrow linewidth is strong evidence for the high quality of the ZnO epitaxial films. In bulk ZnO of reasonably high quality ($n = 2 \times 10^{17}$ cm^{-3} and with a mobility of 220 cm^2/Vs at room temperature) free exciton emission becomes significant only at temperatures above 60 K.

The X-ray diffraction measurements showed for thin epitaxial ZnO layers on GaN templates that lattice constants c and a differ from those of bulk ZnO, i.e. the films are under strain. Since there is considerable lattice mismatch between GaN and ZnO no pseudomorphic growth is expected. The strain could thus arise from the difference between the thermal expansion coefficients. Spatially resolved cathodoluminescence and Raman measurements (the E_2-mode is sensitive to strain) investigating the role of strain are presented at this conference [6].

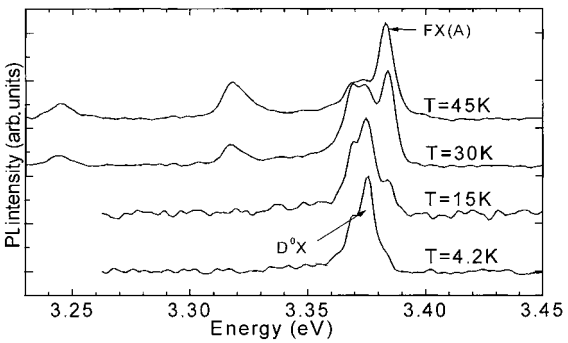

Fig. 3. Photoluminescence spectra measured with low resulution set-up for epitaxial ZnO at 4.2, 15, 30 and 45 K. The free and D^0X exciton transitions are indicated by arrows

The electrical properties of the ZnO films on GaN could not be judged by Hall-effect measurements since the GaN template controls the conduction. We observed no difference in the Hall-effect before and after deposition. However, judging from the optical investigations (free exciton emission, small half-width) the free carrier density in the films should be well below $10^{17}\,cm^{-3}$ making it possible to start with doping experiments.

There is further room for improvement taking into account that ZnO and GaN are by no means perfectly lattice matched although a lattice misfit as small as 0.7% has been reported for ZnO on GaN templates [7]. Dislocation densities are $2 \times 10^8\,cm^{-2}$, a number, which will still have a significant influence on the optical and electrical properties. Commercial ZnO substrates with reasonable quality and dislocation densities below $10^5\,cm^{-2}$ are now available, yet at a rather high price. It opens a route to homoepitaxy, and our approach using GaN templates was necessary to establish the optimum growth conditions in the vapour phase epitaxy of ZnO using metallic Zn and NO_2 as precursors. Details of the homoepitaxial films will be reported elsewhere [8].

Conclusions We fabricated high quality ZnO epitaxial films with vapour phase epitaxy on GaN templates. With optimal growth conditions the X-ray investigations showed single crystalline, wurtzite structure with a FWHM of the rocking curve of 4 arcmin. The free exciton emission with a linewidth of 0.7 meV dominates already at low temperatures (>30 K). Further improvements will be possible by growing on lattice matched ZnO substrates.

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