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Microscopic Analysis of High Quality Thick ZnO CVD Layers: Imaging of Growth Domains, Strain Relaxation, and Impurity Incorporation

T. Riemann (a), J. Christen (a), G. Kaczmarczyk (b), A. Kaschner (b), A. Hoffmann[1]) (b), A. Zeuner (c), D. Hofmann (c), and B.K. Meyer (c)

(a) Otto-von-Guericke Universität Magdeburg, Fakultät für Naturwissenschaften IEP, Abt. Festkörperphysik, Universitätsplatz 2, D-39106 Magdeburg, Germany

(b) Technische Universität Berlin, Institut für Festkörperphysik, Hardenbergstraße 36, D-10623 Berlin, Germany

(c) I. Physikalisches Institut, Justus-Liebig-University Giessen, Heinrich-Buff-Ring 16, D-35392 Giessen, Germany

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We report on spatially-resolved low-temperature luminescence and Raman experiments on ZnO epilayers grown on GaN templates by vapor phase deposition. Our investigations reveal that the peak luminescence position of the free and bound exciton lines of ZnO depends on the distance from the substrate. Different acceptor and donor species become locally dominant. Furthermore, a strong red shift occurs directly at the interface, indicating strong local internal electric fields. From Raman experiments we determined the spatial evolution of the compressive strain in the ZnO epilayer and the induced tensile strain in the GaN templates.

Introduction A major problem in growing ZnO epitaxially is the mismatch of the lattice constants and thermal expansion coefficients between the layer and common substrates, e.g. sapphire [1] and GaN [2]. Consequently, most ZnO layers and also their substrates are highly strained. The unfavorable growth condition results in defect concentrations in the layers which are not homogeneously distributed. To study the influence of the spatially varying (in particular, the thickness-dependent) strain and defects on the optical properties in heteroepitaxial ZnO, we performed highly spatially and spectrally resolved cathodoluminescence (CL) microscopy. This technique allowed us to map the vertical luminescence distribution in the layer, thus extracting the dependence of the optical properties on the layer thickness. In order to independently determine the strain and the doping we carried out micro-Raman spectroscopy on the same regions investigated by CL [3].

Experimental The sample under study is an undoped, thick ZnO layer grown on a GaN/sapphire template using chemical vapor deposition (CVD) at an optimum temperature of 650 °C. Details of the growth procedure were described in [4]. While lower growth rates lead to a closed layer terminated by a surface consisting of hexagonal mesas with an average size of 6 μm, the higher growth rates result in similarly wide, but irregularly shaped columnar domains of different heights clearly isolated from each

[1]) Corresponding author; Tel.: +49-30-31422001; Fax: +49-30-31422064; e-mail: hoffmann@physik.tu-berlin.de

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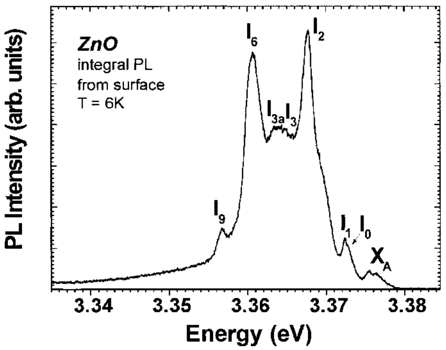

Fig. 1. Luminescence spectrum of the ZnO epilayer grown on a GaN template

other. In contrast to this unsatisfactory morphology, perfect optical quality is found in low-temperature CL measurements. CL microscopy was performed in a fully computer-controlled, modified scanning electron microscope (spatial resolution better than 100 nm) yielding CL spectrum linescan and CL wavelength images (CLWI). Micro-Raman measurements were carried out using a triple-grating Dilor spectrometer and the 515.4 nm line of an Ar^+ laser for excitation.

Results and Discussion The high optical quality of the investigated ZnO epilayer manifests itself by a series of sharp excitonic lines comprising free X_A and impurity bound excitons I_1–I_{11} (line assignment according to [5]) of FWHM <0.9 meV (spectral resolution) (see Fig. 1). In Fig. 2 (bottom) the frequency shift of the E_2-Raman line is plotted as a function of the local z-position in ZnO in c-(growth-)direction. A strong compressive strain is observed at the ZnO/GaN interface while the ZnO is almost fully relaxed at the surface. In the upper part of Fig. 2, two local Raman spectra are compared. Spectrum (1) was detected in the vicinity of the interface, while (2) was recorded adjacent to the surface. This directly evidences a compressive strain in the ZnO and a tensile strain in the underlying GaN layers. Spectrally resolved cross-sectional CL yields further insight into the growth evolution (see Fig. 3). The free and bound exciton line of the GaN template is red

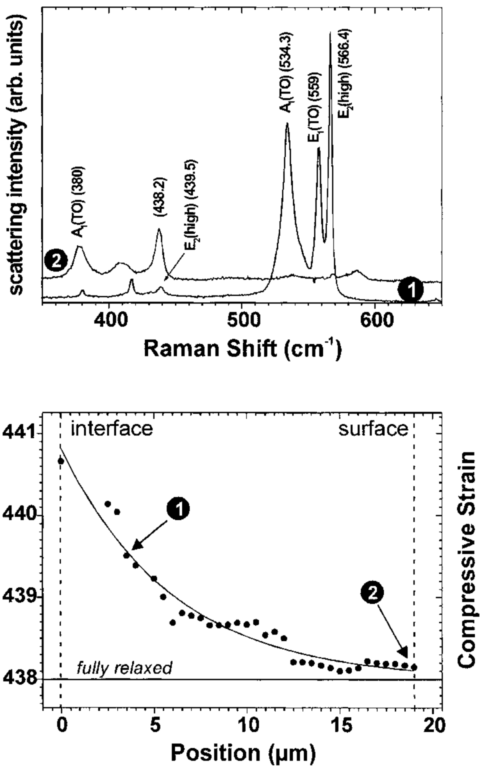

Fig. 2. Top: Room temperature Raman spectra measured near the ZnO/GaN interface (1) and near the ZnO surface (2). Bottom: Shift of the E_2-Raman mode as function of the z-postion in growth direction

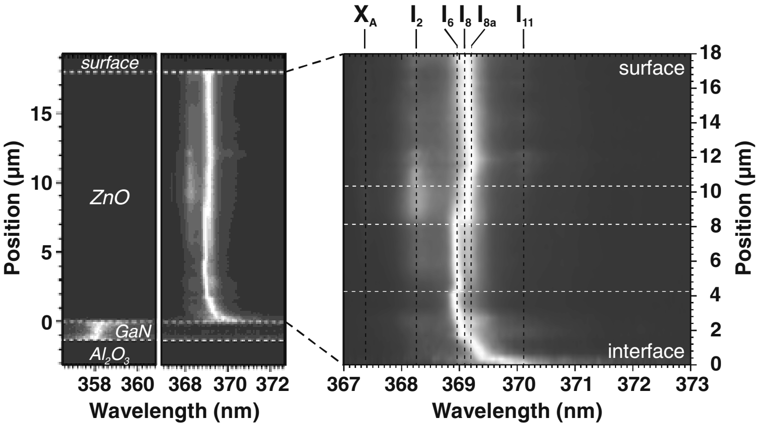

Fig. 3. CL linescan taken at 4.2 K along the growth direction (z) through the ZnO and the GaN cross section

shifted, which is in agreement with the tensile strain observed in Raman. The ZnO luminescence spectra at the ZnO/GaN interface are completely governed by a red shifted, weak and unstructured broad luminescence band (FWHM = 12 meV) around 3.349 eV, indicating a high defect density and strong impurity incorporation. However,

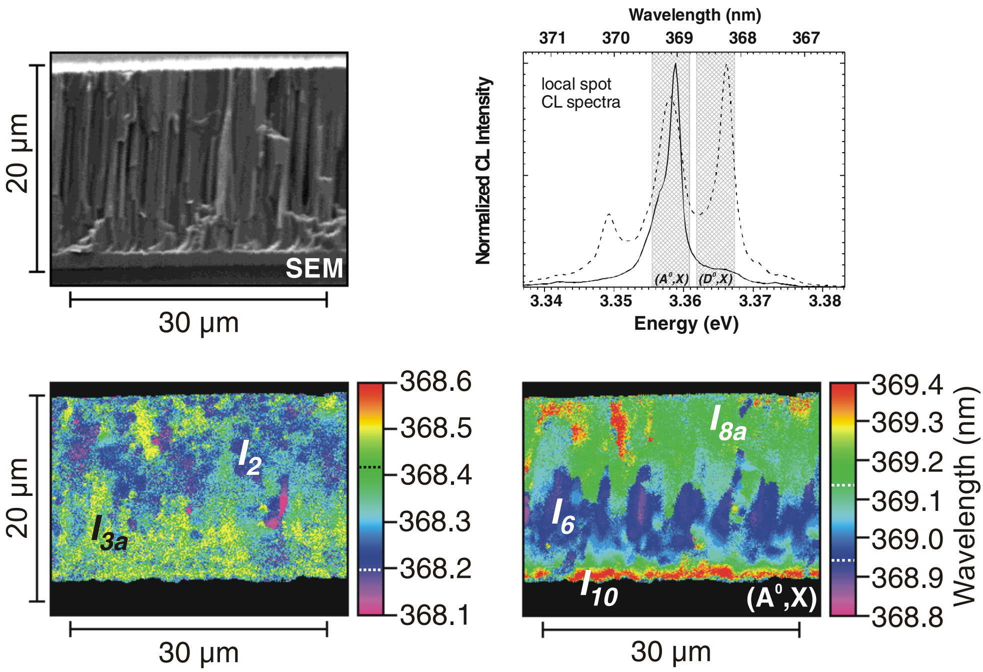

Fig. 4. Cross sectional SEM and CL wavelength mappings (T = 5 K) parallel to the sample c-axis

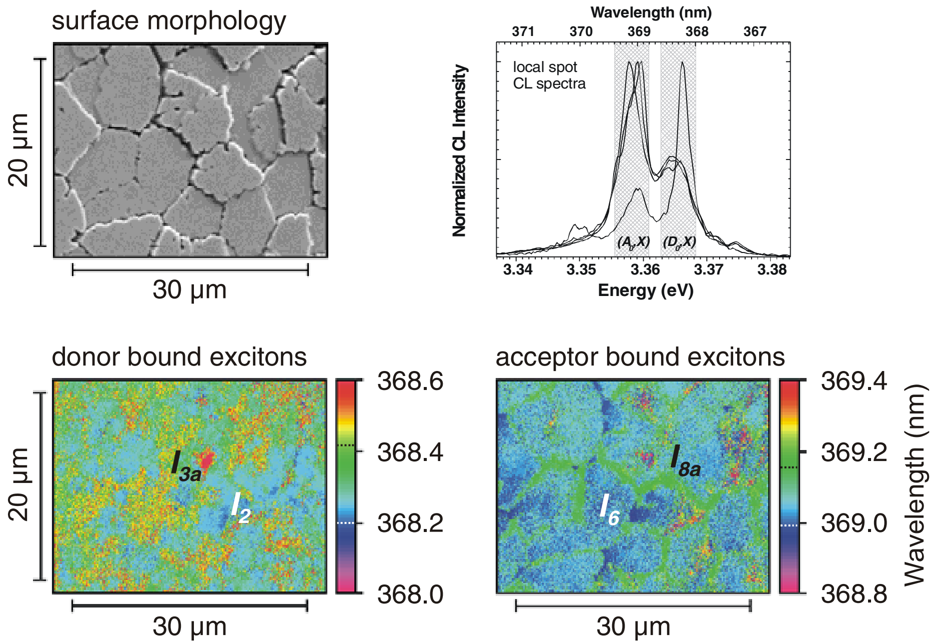

Fig. 5. Plan view SEM and CL wavelength mappings (T = 5 K) of the ZnO epilayer

in this area in the Raman spectra no coupled phonon–plasmon mode could be detected. With advancing growth a relaxation of this red shift by more than 12 meV is accompanied by a dramatic increase in CL intensity by two orders of magnitude. The red shift indicates strong local internal electrical fields in the vicinity of the interface and may be explained by the Franz-Keldysh effect. After this first few μm of ZnO growth, a dramatic change in the luminescence spectra is observed. A splitting into a series of sharp excitonic lines occurs and the free exciton X_A (3.374 eV), donor bound (D^0,X), i.e. I_1–I_5 (3.371–3.360 eV), and acceptor bound excitons (A^0,X), i.e. I_6–I_{11} (3.360–3.349 eV) can be clearly resolved. While the various (D^0,X) lines dominated by I_2 and I_{3a} are continuously present up to the surface (see the CLWI, lower left of Fig. 4), different acceptors dominate in the initial and final stage of growth. Originally, I_6 and I_{10} dominate the luminescence while I_{8a} takes over advancing towards the surface (see CLWI lower right of Fig. 4).

An analogous behavior is found in plan view on the surface of the layer (see Fig. 5). While the donor bound excitons are randomly distributed on a microscopic lateral scale, a clear correlation between the different acceptor complexes and the surface morphology is evident and directly imaged by CL microscopy. Both the *c*-plane domain facets and the hexagonal mesa *c*-planes are dominated by I_6 and I_7 luminescence, whereas I_{8a} and the Na correlated [6] I_9 are only emitted by the morphological boundaries. In addition donor–acceptor pair recombination [6] is spectrally and spatially resolved, showing spot luminescence strongly vertically and laterally localized.

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