

Optical and structural properties of homoepitaxial ZnO

T. P. Bartel^a, M. R. Wagner ^{*a}, U. Habocek^a, A. Hoffmann^a
C. Neumann^b, S. Lautenschläger^b, J. Sann^b, B. K. Meyer^b

^aInstitut für Festkörperphysik, Technische Universität Berlin, Hardenbergstr. 36,
10623 Berlin, Germany;

^bI. Physikalisches Institut, Justus Liebig Universität Giessen, Heinrich-Buff-Ring 16,
35392 Gießen, Germany

ABSTRACT

Two dimensional homoepitaxial growth of high quality ZnO epilayers was achieved by chemical vapor deposition techniques without a buffer layer. We report on the optical and structural properties of these epilayers with particular focus on the polarity of the surface of the substrate. Photoluminescence spectra exhibit strong dependence of the bound exciton recombinations on the termination of the substrate. This is particularly pronounced in the large variety of transition lines in the O-face terminated sample with values for the full width at half maximum as low as 80 μ eV. Cross-sectional micro Raman spectroscopy and high resolution transmission electron microscopy reveal the presence of strain in the epilayer grown on O-face ZnO by a shift of the non-polar E₂(high) mode and a variation in the lattice constant ratio. Still, the crystal quality of the films is further increased compared to the substrate, which is shown by a half-width of 17" of the XRD rocking curve in both epilayers on Zn-face and O-face terminated ZnO substrate.

Keywords: ZnO, homoepitaxy, Raman scattering, high resolution TEM, surface polarity, strain, lattice constants

1. INTRODUCTION

ZnO is a wide bandgap II-VI semiconductor that currently experiences renewed interest in the scientific community due primarily to its excellent optical and electronic properties. It has a high exciton binding energy of 60meV which means that excitonic structures are stable well above room temperature and a bandgap of 3.37eV at 300K [1, 2]. Excitonic recombinations lie in the blue to UV spectral range which makes it a promising candidate for a high efficiency UV light source. In particular ZnO polariton lasers could offer coherent and monochromatic light source operating at room temperature [3, 4]. Because of its wide bandgap, ZnO is solar blind and is already used today as a transparent front electrode in solar cells. It is also radiation resistant making it an interesting candidate for space applications.

However, for the realization of electronic devices and sizable market impact it is essential to achieve reliable acceptor doping. Although some publications claim p-doping [5-9], the hole concentration and carrier mobility is still too low for efficient optoelectronic devices. Indeed, the binding energies of the shallowest acceptors in ZnO (150-250meV), as well as their self compensation and limited solubility make p-doping of ZnO a challenge for laboratories worldwide. In nominally undoped ZnO material, it is essential to avoid the incorporation of impurities which can act as additional donors and to achieve a high crystalline quality to minimize defect-induced free carriers.

Because high quality ZnO substrates were unavailable up to recently, ZnO was grown in heteroepitaxy on different substrates such as Sapphire and GaN where it suffers from large thermal expansion and lattice mismatches. Since the group III elements Al and Ga form shallow donors in ZnO, there is a severe contamination with donors in the layers due to diffusion processes. Therefore, the natural choice for high quality epilayers is the homoepitaxial growth on ZnO substrates. So far, there are only a few publications about the impact of homoepitaxial growth conditions on the ZnO epilayer quality [6, 10-15]. Still, ZnO substrates from different suppliers show large variation in structural and optical properties. As a result, monocrystalline ZnO can exhibit varying lattice parameters and c/a ratios. A better understanding of these structural issues and the defects involved with it may help solving the doping problem of ZnO.

*markus.wagner@physik.tu-berlin.de; phone 49 30 314-24440; fax 49 30 314-22064

This paper studies ZnO epilayers grown homoepitaxially on ZnO substrates with different surface polarity (Zn-face or O-face termination) by photoluminescence spectroscopy, cross section Raman scattering, x-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). If the substrate surface is prepared in a way adequate for 2D growth of the epilayer (epi-ready), no major differences between substrate and an undoped epilayer are expected. In the case of ZnO however, different optical properties, and strain states were observed which are affected by the surface polarity of the substrate.

2. EXPERIMENTAL RESULTS

Epitaxial nominally undoped ZnO layers of approximately 1 μm in thickness were grown by chemical vapor deposition on zinc and oxygen polar ZnO substrates. Before growth, the substrates were annealed at 1150°C in a flowing oxygen atmosphere. This procedure removes polishing damage and produces terrace like structures necessary for two-dimensional growth.

The optical characterization was performed by low temperature photoluminescence spectroscopy. The luminescence was excited by the 325nm line of a HeCd laser with 45mW output power and detected by a bi-alkali detector using a one meter Spex double spectrometer. Figure 1 shows the PL of homoepitaxial ZnO epilayers on ZnO substrate with Zn-face and O-face termination at a temperature of 2K. The displayed energy range between 3.358eV and 3.365eV covers the dominant bound exciton lines. Apparently, there is a significant difference in the bound exciton recombinations between these two samples. The ZnO layer on Zn-face substrates exhibits four recombination lines, labeled I_8 , I_{6a} , I_5 as well as an additional line, which has not been observed before. The full width at half maximum is as small as 80 μeV , indicating superior layer quality. The energetic positions of the known bound excitons in strain free ZnO single crystals are indicated by dashed vertical drop lines. So far, only the chemical identities of the I_6 and the I_8 lines in these spectra could be identified as Al and Ga donors, respectively [16]. Concerning the energetic positions of the I_8 , I_{6a} and I_5 recombinations of the Zn-face ZnO layer, there is an excellent agreement with exciton recombinations in strain free single crystals. Since it is well known that internal strain may shift the excitonic emission lines, the luminescence spectrum suggests no considerable strain in the Zn-face sample.

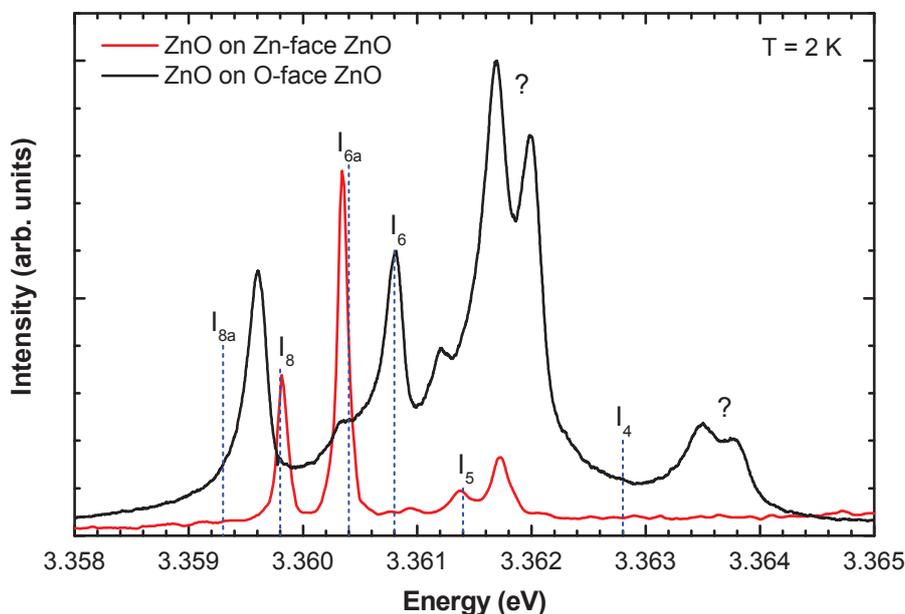


Fig. 1: PL spectra of CVD grown ZnO epilayers on Zn-face and O-face terminated ZnO substrate. Spectra were recorded at 2 Kelvin and show the range of the bound exciton recombinations

The luminescence of the ZnO layer on O-face ZnO substrate, however, shows up to eight excitonic recombinations. Interestingly, there is no conformance in the emission lines in the two samples. Aside from the two major and two minor lines between I_5 and I_{8a} , two double structures at higher energies appear (labeled with question marks). These lines are observed for the first time in homoepitaxial grown ZnO on O-face substrate and are extensively analyzed elsewhere [17]. The large amount of additional lines in the O-face sample further suggests that the variety of impurities in the layer is considerable larger in the ZnO layer on O-face substrate, possibly due to a more efficient diffusion process from the substrate. The missing agreement of the observed recombination lines with the exciton energies in single crystal ZnO could result from strain fields in the O-face sample due to the increased incorporation of impurities. This can lead to a small shift of the bound exciton lines compared to their fully relaxed positions. Additionally, the full width at half maximum of the narrowest I6 line is with a value of $120\mu\text{eV}$ around 50 percent larger than in the Zn-face sample and could also result from internal strain due to a greater defect density in O-face material. Nevertheless, the half-width in both samples suggest a superior structural quality of the ZnO epilayers compared to the substrate.

The structural properties were investigated by cross-sectional micro Raman, XRD and HRTEM. The Raman measurements were performed at room-temperature using a DILOR XY 800 triple-grating Raman spectrometer with 1800 lines/mm and a liquid nitrogen cooled CCD camera as detector. The samples were excited parallel to the surface by an $\text{Ar}^+ - \text{Kr}^+$ laser which was focused by micro optics to a radial symmetric spot of about 500nm diameter. The scattered light was detected in backscattering geometry. Since the crystal c-axis is perpendicular to the surface, the geometry corresponds to the $x(\dots)\underline{x}$ configuration for cross-sectional (in-plane) scattering in the Porto-notation. Raman selection rules show that the $A_1(\text{TO})$, $E_2(\text{low})$ and $E_2(\text{high})$ modes are the only Raman permitted modes for wurtzite ZnO in this scattering geometry [18].

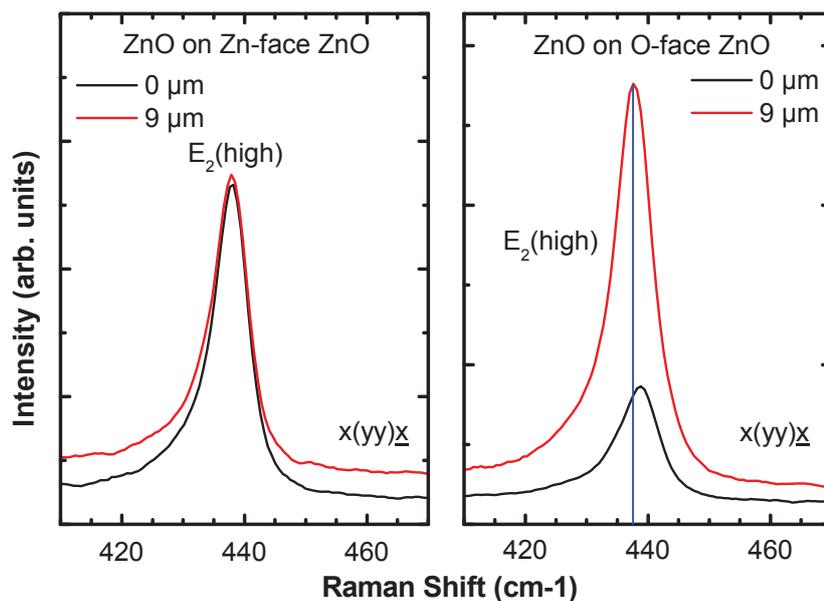


Fig. 2: Room-temperature Raman spectra of ZnO on Zn-face and O-face ZnO in the range of the $E_2(\text{high})$ mode. Spectra were recorded in cross-section geometry at the surface ($0\mu\text{m}$) and at a depth of $9\mu\text{m}$.

The Raman spectra at 300 Kelvin are displayed in Fig. 2. Only the spectral range of the $E_2(\text{high})$ mode is displayed. For both epilayers (ZnO on Zn-face substrate in the left graph, ZnO on O-face substrate in the right graph), two different spectra are shown. The $0\mu\text{m}$ spectrum was recorded at the surface, whereas the second spectrum originates from scattering at $9\mu\text{m}$ below the surface of the layer. Apparently, there is no difference in the spectral position and full width

at half maximum of the $E_2(\text{high})$ mode in the Zn-face sample as a function of depth. Both spectra show the $E_2(\text{high})$ mode at $437,6 \text{ cm}^{-1}$ which is very close to the value of 437 cm^{-1} for the $E_2(\text{high})$ in relaxed ZnO [18]. However, in the O-face sample, we observe a shift of the $E_2(\text{high})$ mode in the epilayer to $438,4 \text{ cm}^{-1}$. The full width at half maximum in the two samples is with values of $4,7 \text{ cm}^{-1}$ and $5,3 \text{ cm}^{-1}$ slightly larger in the ZnO epilayer grown on O-face compared to the one on Zn-face ZnO. The Raman results seem to indicate that the growth on the Zn-terminated surface of the ZnO template has produced a slightly better crystal quality than the growth on O-face. This result is in agreement with previously published data on micro Raman scattering in homoepitaxial grown ZnO [19]. Our finding of a depth independent and strain free position of the $E_2(\text{high})$ Raman mode in the Zn-face sample also corresponds with the non-shifted position and narrow half-width of the bound exciton lines in the PL spectra.

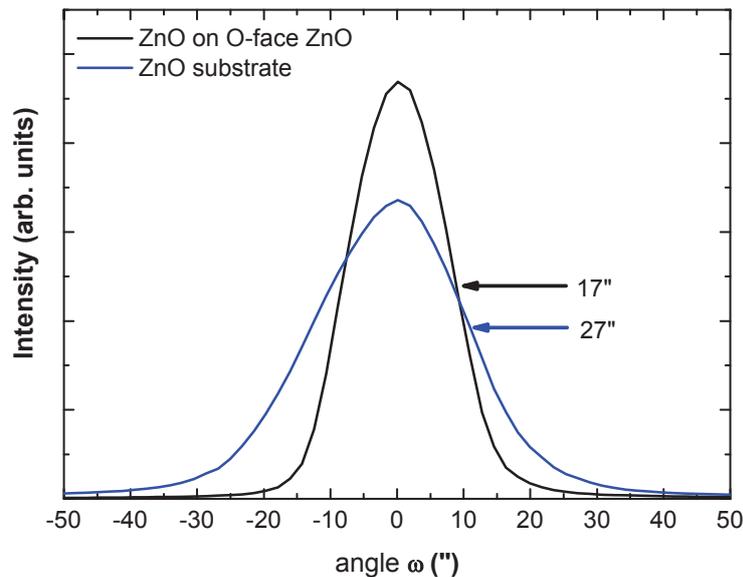


Fig. 3: XRD rocking curve on the (0002) reflection of ZnO substrate and ZnO epilayer on O-face ZnO

In order to compare the crystal quality of the epilayers with those of the substrate, X-ray diffraction was performed. The measurements of the rocking curve on the (0002) reflection are shown in Fig. 3 for the substrate and the O-face epilayer. The substrate has a full width at half maximum of 27° . Compared to the substrate, the half-width of the epilayer is even smaller and with 17° already at the limit of the instrumental resolution. The same half-width was also found for the Zn-face sample. The investigations of the out of plane properties further indicate coherent two-dimensionally grown films.

To gain insight into the microscopic structure of the samples, HRTEM micrographs and exit wave reconstructions were undertaken in the substrate and the epilayers for both polarities. The samples were prepared for HRTEM imaging by using standard cross sectional preparation procedure with mechanical thinning and ion milling. After ion milling, the samples were etched in a HF solution and a KOH solution for 2 minutes each. They were then rinsed in warm and room temperature Methanol for 1 minute each. The wet etching procedure produces steep wedges, particularly on the Zn-face oriented samples. Residual damage from mechanical grinding and ion milling is completely removed and the sample exhibit an atomically flat surface as has been observed in GaN etched with KOH [20]. This is ideal for high resolution imaging as the crystal orientation remains stable even at the very edge of the sample. Scherzer images and though focal series were recorded on a Philips CM300 FEG operated at 300 kV. Exit wave reconstructions extend the point resolution to the information limit of 0.8 \AA and were performed using the software package Trueimage [21].

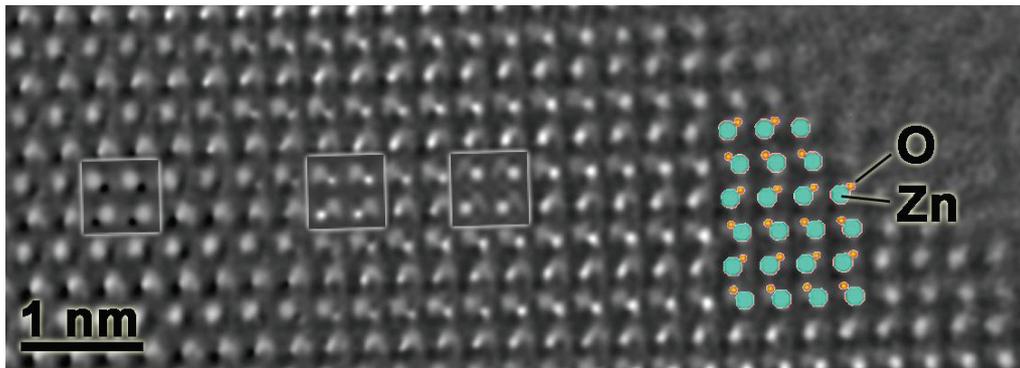


Fig. 4: Phase of the electron exit wave reconstructed by through focal series in the substrate in [11-20] zone axis. An atomic overlay illustrates the structure used for exit wave simulation compared with the experiment for three thicknesses (overlaid squares). The resolution is sufficient to determine the polarity of the material.

Fig. 4 shows the phase of a reconstructed exit wave of [11-20] zone axis zinc substrate. An atomic overlay sketches the zinc and oxygen columns in this orientation and from this model, exit waves were computed for three thicknesses (from right to left) of 3, 6, and 8 nm with the MacTempas software [22]. The results are overlaid to the image and are in excellent agreement with the experiment. The heavier zinc columns have a very localized state, while it is much wider in the lighter oxygen column. Zinc and oxide columns can thus be resolved in this orientation and allow a direct determination of the polarity of the material.

Exit wave reconstructions were undertaken in various locations of the samples in substrates and epilayers. In this way the polarity of the substrates could be confirmed. The epilayers showed the same polarity as the substrate, i.e., epilayers grown on the Zn-face remained zinc polar and O-face epilayers were grown on the O-face substrate. As a consequence, polarity is controlled by the substrate orientation no polarity changes were observed in the epilayers.

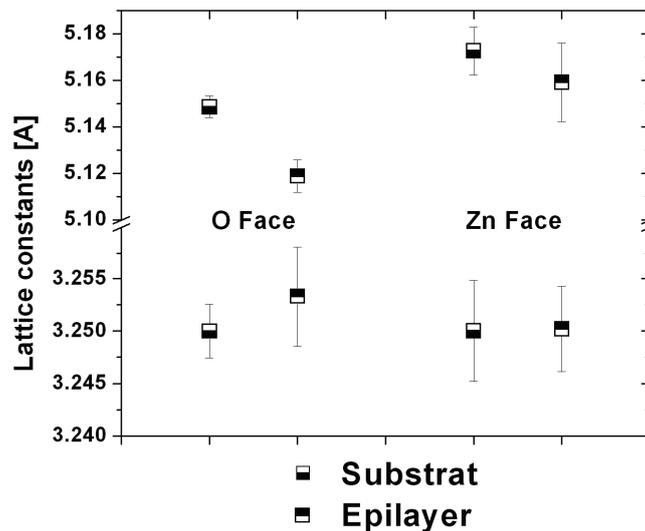


Fig. 5: Strain in the c and a lattice constants. The a lattice constant remains stable within the measuring error for substrate and epilayer for both polarities. However the c lattice constant of the O-face epilayer exhibits a compressive strain.

In a next step, the strain was evaluated both in reconstructed exit waves as well as images taken at Scherzer defocus. Because of instabilities in the imaging system over the course of several measurement days, the magnification of the microscope was adjusted such that the *a*-lattice parameter in the substrate ZnO material is equal to 3.25Å. Fig. 5 shows the lattice parameters *a* and *c* for the O-face and Zn-face substrate and epilayers, respectively. It is noted, that the *a*-lattice remains constant inside the measurement error of about 0.5 pm. For the *c*-lattice however, a compressive strain of about 0.5% is observed in the epilayer of the O-face material. The Zn-face material, however, only exhibits a small compressive strain in the epilayer, which lies within the measurement error. These results are in excellent agreement with the micro Raman measurements which only showed a shift of the E₂(high) Raman mode in the O-face sample whereas it remained constant in the Zn-face sample. Surprisingly, the *c*-lattice constants of the substrates are different when measured in O-face and Zn-face material. Because the images were recorded close to the epilayer (<5µm) from the substrate/epilayer interface), this effect is believed to be due to structural changes caused during the epilayer growth.

The results from the HRTEM measurements correlate well with the evaluation that the O-face epilayer is under strain. Indeed it is seen from Fig. 3 and Fig. 5, that the lattice is compressively strained in O face material, while the strain in Zn-face material is negligible. In earlier Raman experiments on homoepitaxial ZnO [19] the appearance of the E₂ mode that should have been forbidden was tentatively explained by a tilt of the *c*-axis or crystal perturbations. In the present samples, no misalignment of the *c*-axis could be observed in diffractive mode.

3. CONCLUSION

In conclusion, it has been shown, that homoepitaxially grown ZnO epilayer exhibits excellent optical properties. Excitonic line widths are as low as 80µeV for Zn-face material and 120µeV for O-face material. The bound exciton spectrum in O-face ZnO shows a wide variety of transition lines. XRD measurements demonstrate that the quality of the epilayers is improved for both polarities when compared to the substrate. Yet micro Raman and HRTEM studies of the samples show that the epilayers have a very different strain state. In the Zn-face sample, no significant strain could be observed. In addition, the exciton transition energies in the PL spectra match those in strain-free single crystals. On the other hand, micro-Raman and HRTEM measurements clearly show that the *c* lattice of the O-face epilayer is subject to compressive strain. Together with the appearance of new luminescent transitions it is argued that additional impurities or defects are included in epilayers grown on O-face substrates.

4. ACKNOWLEDGEMENT

M.R.W. would like to acknowledge an Ernst-von-Siemens scholarship. T.P.B acknowledges the German National Academic Foundation for support. Support by C. Kisielowski of the National Center for Electron Microscopy, Lawrence Berkeley Lab, which is supported by the U.S. Department of Energy under Contract # DE-AC02-05CH11231 is acknowledged. Parts of this work were supported by DFG within SFB 296.

REFERENCES

- ¹ W. Y. Liang and A. D. Yoffe "Transmission spectra of ZnO single crystals", Phys. Rev. Lett. 20, 59 (1968).
- ² D. C. Reynolds, D. C. Look, B. Jogai, C. W. Litton, G. Cantwell, and W. C. Harsch, "Valence-band ordering in ZnO", Phys. Rev. B 60, 2340 (1999).
- ³ S. F. Chichibu, A. Uedono, A. Tsukazaki, T. Onuma, M. Zamfirescu, A. Ohtomo, A. Kavokin, G. Cantwell, C. W. Litton, T. Sota, and M. Kawasaki, "Exciton-polariton spectra and limiting factors for room temperature photoluminescence efficiency in ZnO, Semicond. Sci. Technol. 20, S67-S77 (2005).
- ⁴ M. Zamfirescu, A. Kavokin, B. Gil, G. Malpuech, M. Kaliteevski, „ZnO as a material mostly adapted for the realization of room-temperature polariton lasers", Phys. Rev. B 65, 161205(R) (2002).
- ⁵ K. Minegishi, Y. Koiwai, and K. Kikuchi, „Growth of p-type zinc oxide films by chemical vapor deposition" Jpn. J. Appl. Phys. 36, L1453 (1997).

- ⁶ D. C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason, and G. Cantwell, "Characterization of homoepitaxial p-type ZnO grown by molecular beam epitaxy" *Appl. Phys. Lett.* 81, 1830 (2002).
- ⁷ Y. R. Ryu, T. S. Lee, and H. W. White, "Properties of arsenic-doped p-type ZnO grown by hybrid beam deposition" *Appl. Phys. Lett.* 83, 87 (2003).
- ⁸ K.-K. Kim, H.-S. Kim, D.-K. Hwang, J.-H. Lim, and S.-J. Park, "Realization of p-type ZnO thin films via phosphorus doping and thermal activation of the dopant" *Appl. Phys. Lett.* 83, 63 (2003).
- ⁹ D. C. Look, "Electrical and optical properties of p-type ZnO", *Sem. Semicond. Sci. Technol.* 20, S55–S61, (2005)
- ¹⁰ C. Neumann, S. Lautenschläger, S. Graubner, J. Sann, N. Volbers, B. K. Meyer, J. Bläsing, A. Krost, F. Bertram, and J. Christen, "Homoeptaxy of ZnO: from the substrates to doping", *phys. Stat. sol. (b)* 244, No. 5, 1451-1457 (2007)
- ¹¹ H. Matsui, H. Saeki, T. Kawai, A. Sasaki, M. Yoshimoto, M. Tsubaki, and H. Tabata, *J. Vac. Sci. Technol. B* 22, 2454 (2004).
- ¹² J. Nause, S. Ganesan, and B. Nemeth, *Proc. SPIE* 5359, 220 (2004).
- ¹³ A. Zeuner, H. Alves, D. M. Hofmann, B. K. Meyer, M. Heuken, J. Bläsing, and A. Krost, "Structural and optical properties of epitaxial and bulk ZnO", *Appl. Phys. Lett.* 80, 2078 (2002).
- ¹⁴ H. Kato, M. Sano, K. Miyamoto, and T. Yao, *Jpn. J. Appl. Phys.* 42, 1002 (2003).
- ¹⁵ M. W. Cho, C. Harada, H. Suzuki, T. Minegishi, T. Yao, H. Ko, K. Maeda, and I. Nikura, *Superlattices Microstruct.* 38, 349 (2005).
- ¹⁶ B. K. Meyer, H. Alves, D. M. Hofmann, W. Kriegseis, D. Forster, "Bound exciton and donor-acceptor pair recombinations in ZnO", *Phys. Stat. Sol. (b)* 241, 231 (2004).
- ¹⁷ S. Lautenschläger, J. Sann, N. Volbers, B.K. Meyer, A. Hoffmann, U. Haboeck, and M. R Wagner "Asymmetry in the excitonic recombinations and impurity incorporation of the two polar faces of homoepitaxially grown ZnO films, to be published in PRB (2008)
- ¹⁸ T. C. Damen, S. P. S. Porto, and B. Tell, "Raman effect in zinc oxide", *Phys. Rev.* 142, 2 (1966)
- ¹⁹ M. R. Wagner, U. Haboeck, P. Zimmer, A. Hoffmann, S. Lautenschläger, C. Neumann, J. Sann, B. K. Meyer, "Photonic properties of ZnO epilayers" *Proc. of SPIE* Vol. 6474, 64740X, (2007)
- ²⁰ Jinschek, J.R. and C. Kisielowski, Time, energy, and spatially resolved TEM investigations of defects in InGaN. *Physica B: Condensed Matter*, 2006. 376-377: p. 536-539.
- ²¹ Kübel, C. and A. Thust, Truelmage: A Software Package for Focal-Series Reconstruction in HRTEM in *Electron Crystallography: Novel Approaches for Structure Determination of Nanosized Materials*. 2006. p. 373-392.
- ²² Kilaas, R. MacTempas. 2007 [cited 2007 01.12.2007]; Available from: <http://www.totalresolution.com>.