

# Asymmetry in the excitonic recombinations and impurity incorporation of the two polar faces of homoepitaxially grown ZnO films

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Homoepitaxial ZnO layers were grown on O-polar and Zn-polar surfaces of ZnO single crystal substrates by chemical vapor deposition. While the structural properties (surface roughness and rocking curve half width) were identical within experimental error, the optical properties as monitored by photoluminescence (PL) were strikingly different. Four excitonic recombination lines are exclusively found on the O-polar surface. In order to understand the defects involved, secondary ion mass spectrometry was employed which clearly demonstrated that the impurity incorporation is substantially higher on the O-polar surface. Temperature and power dependent PL measurements provide further insight into the initial-final state recombinations. The observed recombinations are caused by excitons bound to a neutral defect complex. In order to account for the thermalization behavior found in the temperature dependent measurements, splittings in the excited as well as in the ground state must be present. Possible defect models are discussed.

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Surface polarity plays an important role in device properties of wurtzite semiconductors as demonstrated by the influence of piezoelectric and spontaneous polarization on optical recombinations in light emitting devices, the formation of two-dimensional electron gases in high speed and high power field effect transistors, barrier heights in the Schottky diodes, and sensor properties of the III-V nitrides. Since the two polar faces have different surface configuration, chemistry and composition distinct differences in defect incorporation of the two polar surfaces are likely to occur.<sup>1-4</sup> As a specific example, higher residual impurity concentration on the N-polar faces of GaN is found.<sup>3,4</sup> However, more important, the incorporation of acceptors is substantially different leading to *p*-type conduction for GaN:Mg on the Ga-polar face, but resulting in highly resistive or semi-insulating properties on the N-polar face.<sup>3</sup> ZnO has many properties in common with the III nitrides (wurtzite structure, piezoelectric coupling constants, and pyroelectricity), but the current understanding of polarity on defect incorporation and acceptor doping has not yet been established. While the growth of III nitrides is more or less restricted to heteroepitaxy, this is not the case for ZnO. The issue of substrates for ZnO epitaxy is an ongoing important topic, in spite of the recent progress in growth technology of ZnO-based materials and heterostructures. Alternatives to the widely used sapphire substrates in terms of lattice and thermal expansion matching are ScAlMgO<sub>4</sub> and—the obvious natural choice—ZnO substrates. However, bulk ZnO substrates are still on a developing stage in terms of perfect crystallinity and surface preparation for epitaxial growth. A high temperature annealing step was necessary to remove the subsurface damage from polishing and produce “epiready” surfaces with terracelike structures.<sup>5</sup> Two-dimensional growth could be achieved on both polar surfaces of bulk ZnO substrates, and now provide the unique opportunity to explore the role of the surface polarity on the structural and optical properties of the thin films.<sup>6</sup>

In this paper, we compare the photoluminescence (PL) properties of ZnO epilayers grown on Zn- and O-polar surfaces. We use temperature and power dependent measurements to establish the excitonic character of recombinations exclusively present on the O-polar termination of the layers. Secondary ion mass spectrometry (SIMS) documents that the impurity incorporation is substantially higher on the O face of the ZnO layers. The fine structure splittings of the excitonic recombinations provide evidence on the defect responsible for the observed recombinations.

The ZnO epilayers were grown by chemical vapor deposition on Zn- and O-polar substrates provided by CrysTec. Prior to growth, the substrates were annealed at 1150 °C in a flowing oxygen atmosphere to remove polishing damage and provide terracelike structures as nucleation for the two-dimensional growth. Epitaxial films of approximately 2 μm thickness were grown in the same run on two substrates with a different polarity. The luminescence spectra were measured in the temperature range between 4.2 and 30 K, exciting the luminescence with a HeCd laser at 325 nm. The luminescence was detected in combination with a 1 m Jobin Yvon monochromator and a UV enhanced photomultiplier tube. For power dependent measurements, neutral density filters were used. SIMS measurements were performed with a Cameca/Riber MIQ256 with a Cs<sup>+</sup> source for negative secondary ions and a MIQ56 with an O<sup>2+</sup> source for positive secondary ions.

X-ray diffraction and atomic force microscopy measurements showed, within statistical fluctuations, identical properties of the films in terms of rocking curve half width and surface roughness. Both samples clearly revealed two-dimensional growth mode, which is an important fact.

Figure 1 shows the 4.2 K photoluminescence spectrum of the O-polar epilayer. The lines *I*<sub>8</sub> (3.3598 eV), *I*<sub>6a</sub> (3.3604 eV), *I*<sub>6</sub> (3.361 eV), and *I*<sub>5</sub> (3.3614 eV) are known from previous investigations on bulk ZnO crystals<sup>7</sup> and thin

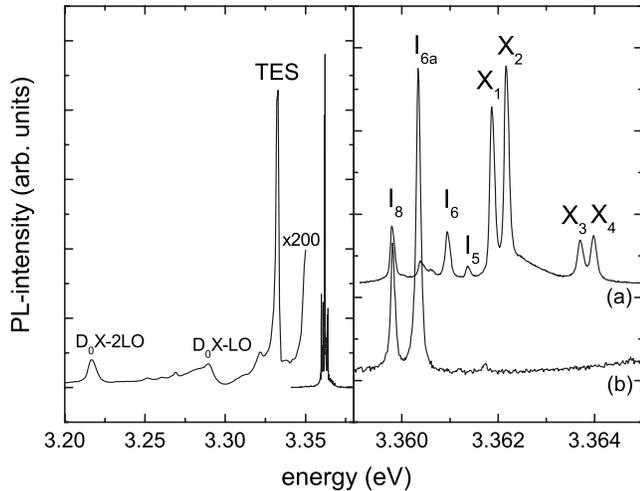


FIG. 1. Right-hand side photoluminescence spectra of ZnO epilayer with (a) O-face polarity and (b) Zn-face polarity; the observed recombination lines are marked X<sub>1</sub> to X<sub>4</sub> ( $T=4.2$  K, HeCd excitation). Left-hand side PL spectrum of the O-polar film extended to lower energies.

films and are also the recombinations found on the Zn-polar face (not shown). The lines at 3.3619 (X<sub>1</sub>), 3.3622 (X<sub>2</sub>), 3.3637 (X<sub>3</sub>), and 3.3640 eV (X<sub>4</sub>) are only present on our homoepitaxial ZnO thin films grown on the O polar face of the ZnO substrate. Remarkable is the line splitting and line separation: X<sub>1</sub> to X<sub>3</sub> and X<sub>2</sub> to X<sub>4</sub> are separated by 1.8 meV, whereas the splitting between X<sub>1</sub> and X<sub>2</sub> and the splitting between X<sub>3</sub> and X<sub>4</sub> are 0.3 meV each. In order to gain further insight into the radiative transitions, we employed temperature dependent measurements. From 7 to 30 K, the intensity of X<sub>1</sub> to X<sub>4</sub> as well as the other bound exciton recombinations decrease in intensity in agreement with the small localization energies of the bound exciton complexes (see Fig. 2). The peak intensity ratio between X<sub>1</sub> and X<sub>2</sub> is temperature independent (see Fig. 3). However, the peak intensity ratios between X<sub>3</sub> and X<sub>1</sub> as well as X<sub>4</sub> and X<sub>1</sub> change upon temperature increase (see Fig. 3), indicating a thermally acti-

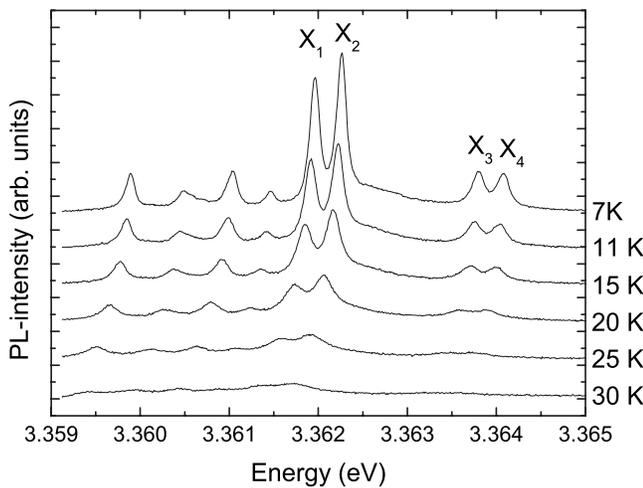


FIG. 2. Temperature dependent photoluminescence measurements of the O-polar film from 7 to 30 K (HeCd excitation).

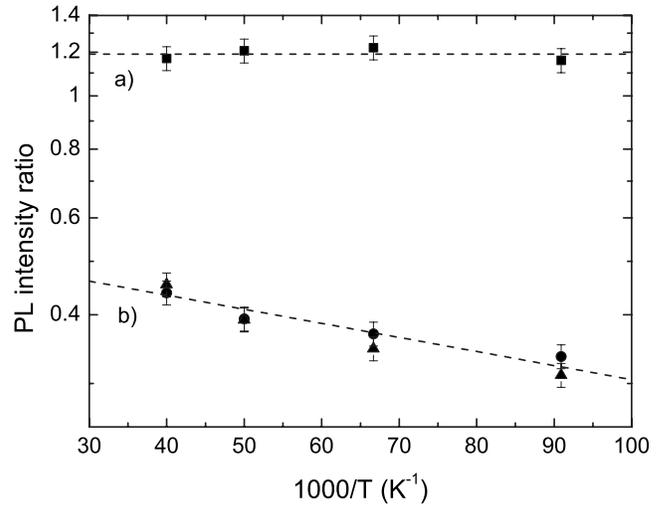


FIG. 3. (a) Intensity ratios of the X<sub>2</sub> to X<sub>1</sub> lines (squares) as a function of the inverse temperature. (b) Intensity ratio of the X<sub>3</sub> to X<sub>1</sub> (circles) and X<sub>4</sub> to X<sub>1</sub> (triangles) lines as a function of inverse temperature. The drawn line is a fit with an activation energy of  $0.6 \pm 0.1$  meV.

vated population in the emitting states. The change in the intensity ratio X<sub>3</sub>/X<sub>1</sub> is activated by  $0.6 \pm 0.1$  meV which is of the order of the larger splitting of 1.8 meV—the separation between X<sub>1</sub> (X<sub>2</sub>) and X<sub>3</sub> (X<sub>4</sub>). It is not consistent with the splitting between X<sub>1</sub>(X<sub>3</sub>) and X<sub>2</sub>(X<sub>4</sub>) of 0.3 meV. This information will be used to construct a level scheme for the observed recombinations (see below).

Power dependent measurements are shown in Fig. 4. Reducing the excitation power by a factor of 10–100 reduces the intensity of all lines in the same way. As a comparison, the behavior of the two lines at 3.361 eV (I<sub>6</sub>) and at 3.3622 eV (X<sub>2</sub>) is shown in the inset of Fig. 4. Both lines exhibit the same slope, i.e., are caused by bound exciton recombinations.

Is the impurity incorporation on both polar surfaces of ZnO different/ In the case of GaN, it was found that the

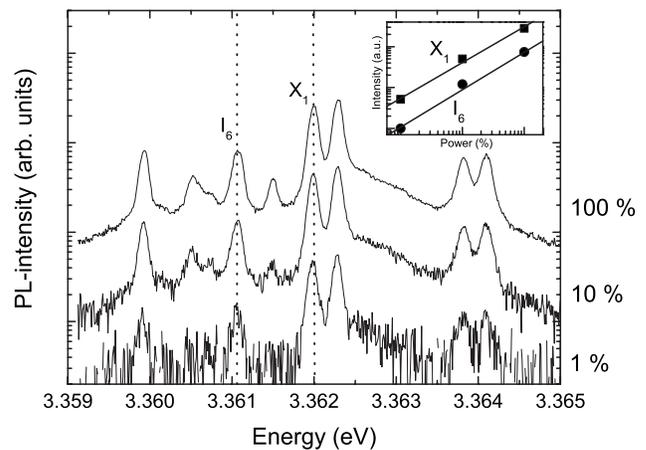


FIG. 4. Excitation power dependent photoluminescence spectra reducing the power from 100% to 1%. The inset shows as a comparison of the behavior of the I<sub>6</sub> (circles) and X<sub>2</sub> (squares) recombination lines.

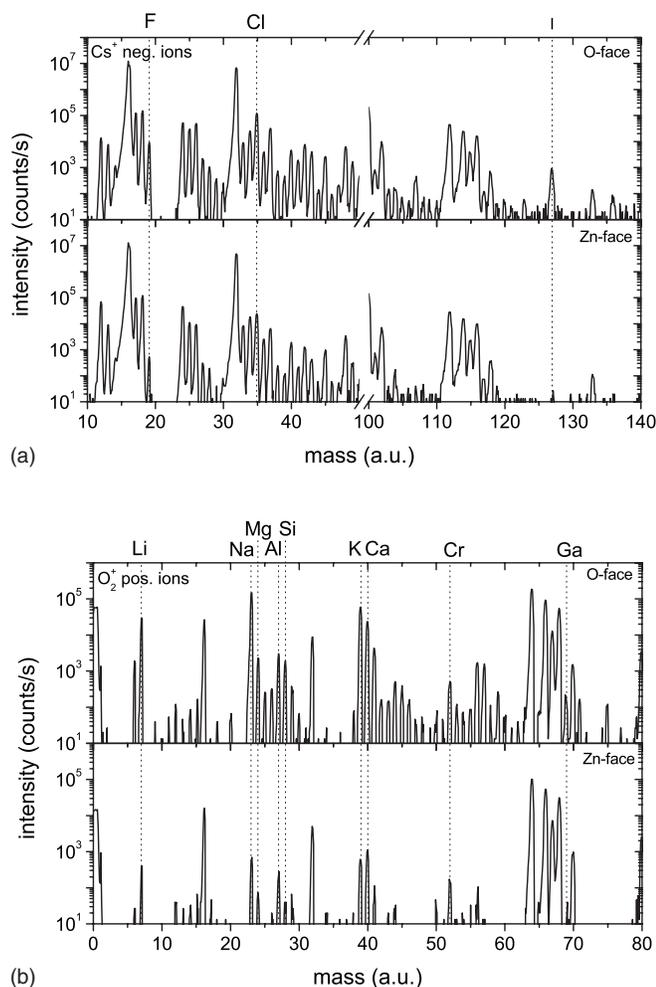


FIG. 5. Secondary ion mass spectra of Zn- and O-polar epitaxial films (a) for negative secondary ions and (b) for positive secondary ions.

polarity influences the impurity incorporation; the N-face films have a 2 orders of magnitude higher incorporation rate for C, O and Al, while Si was more easily incorporated into the Ga-polar films.<sup>4</sup> In Fig. 5, we compare the mass spectra for negative and positive secondary ions of the Zn- and O-polar films. The relative content of the impurities can be evaluated by normalizing to the matrix. In the case of negative secondary ions, it is the ZnO signal; for positive secondary ions, it is the Zn signal. For better comparison, Fig. 6 shows the impurity concentrations of the O-polar film normalized to those of the Zn-polar film. The O-polar film has a substantial higher amount of the group-VII elements F, Cl, and I [see Figs. 5 and 6] and of Si. The mass numbers 60 and 76 can be attributed to  $\text{SiO}_2$  and  $\text{SiO}_3$ , respectively. The mass number 56 could originate from  $\text{CaO}$ , for 57 we have no good guess. An even more pronounced difference in the impurity incorporation shows up for the detection of the positive secondary ions. Li, Na, K, and Ca are almost 2 orders of magnitude more in O-polar; ZnO, Mg, Al, and Si concentrations are higher by 1 order of magnitude [Figs. 5 and 6]. Since we employ a hot wall epitaxial process, one part of the impurities can originate from the hot quartz reactor tubes, and the other part can originate from the ZnO substrate. The

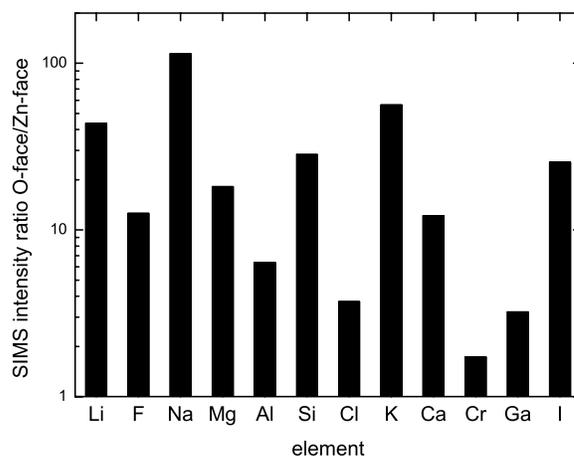


FIG. 6. Intensity ratio of the normalized secondary ion intensities of the O-polar epitaxial film to the Zn-polar film.

samples are typically exhibited to a temperature of  $650^\circ\text{C}$  for at least 4 h. The residual impurities in the substrate are Li with  $\text{mid-}10^{17}\text{ cm}^{-3}$ , Na and K around  $10^{16}\text{ cm}^{-3}$ , Mg and Al around  $10^{17}\text{ cm}^{-3}$ , Ga with  $\text{mid-}10^{16}\text{ cm}^{-3}$ , and Fe and Cu with  $(1-2)\times 10^{18}\text{ cm}^{-3}$  (averaged concentrations for several bulk ZnO substrates). Li and Na on Zn sites act as deep acceptors, Al and Ga are shallow donors, and Fe and Cu are deep recombination centers. The group-VII elements, which are expected to be shallow donors, have so far not been identified in bound exciton recombinations.

Let us set our data in the context of published work on ZnO. We are only aware of two reports on the photoluminescence properties of Zn- and O-polar surfaces both on bulk ZnO crystals.<sup>8,9</sup> Apart from intensity differences, the two polar surfaces showed almost the same bound exciton (BX) recombinations. Sherriff *et al.*<sup>9</sup> noticed differences in BX-1LO recombination lines being more significant in O-polar ZnO, but there were no recombinations exclusively present on one of the polar surfaces (SIMS data were not provided). It is in line with Raman measurements taken along the cleavage plane of a bulk substrate from the O-polar to the Zn-polar surface. Within statistical fluctuations, they showed unchanged line positions of the  $E_2$  (high) mode and unchanged line width of  $6.2 \pm 0.2\text{ cm}^{-1}$ , which is the value also found on the Zn-polar epilayer. The linewidth increased to  $7.5\text{ cm}^{-1}$  on the O-polar surface in line with the higher impurity incorporation (for the epilayers, excitation was parallel to the plane of the film perpendicular to the  $c$  axis; surface excitation parallel to the  $c$  axis always gives averaged information of film and substrate).<sup>10</sup>

In 1984, Dean *et al.*<sup>11</sup> reported on the observation of a new isoelectronic trap luminescence in GaP which gives rise to a multiple line spectrum. Strong polarity effects were found for these centers and they were only observed on the (111B) P-terminated crystal face. The complex was tentatively identified as an exciton bound at a uniaxial center composed of a  $\text{B}_{\text{Ga}}\text{-N}_{\text{P}}$  associate and nearby  $\text{N}_{\text{P}}$ . The GaP crystals were contaminated by B and N through the BN liner tube.

A decisive microscopic identification of the defect causing the four line spectrum in ZnO ( $X_1$  to  $X_4$ ) is not possible.

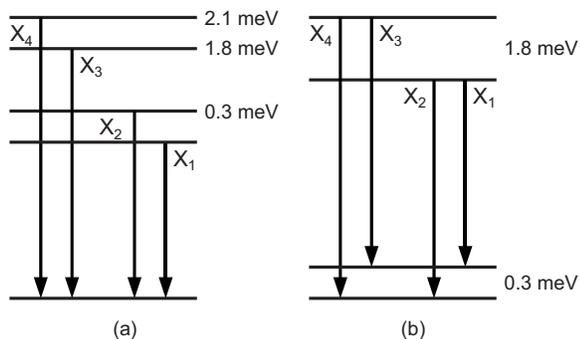


FIG. 7. Level scheme for the  $X_1$  to  $X_4$  transitions (a) for the splitting in the excited state only and (b) the respective splitting in the excited and ground state.

There is, however, enough spectroscopic information available which allows to construct a defect level scheme and draw conclusions on the defect involved. It is unlikely that we are dealing with four individual, independent bound exciton recombinations which would imply four additionally incorporated impurities. The intensity ratios of  $X_1$  to  $X_2$ ,  $X_3$  and  $X_4$  were always the same in different growth runs on O-polar surfaces. This is a clear manifestation that they belong together and to one specific defect. The lines can be caused by excited states of the bound exciton [see Fig. 7(a)]—a situation described in the work of Rühle and Klingenstein<sup>12</sup> for a neutral donor bound exciton in InP—or from a more complex defect with splittings in the excited and ground state [see Fig. 7(b)]. Within the framework of the model of excited states, we should expect thermally activated behavior for the lines  $X_2$ ,  $X_3$ , and  $X_4$ , with activation energies of 0.3, 1.8, and 2.1 meV, respectively. As seen in the temperature dependent measurements, the intensity ratio of  $X_1$  to  $X_2$  does not change, but  $X_3$  and  $X_4$  increase in intensity with respect to  $X_1$  having, within experimental error, identical activation energies (see Fig. 3). Hence, the initial state has two emitting levels separated by 1.8 meV; in the ground state, there is an additional splitting into two levels separated by 0.3 meV, and model (b) is the appropriate one.

The photoluminescence studies clearly indicated bound exciton recombination properties. We exclude in the following the binding of excitons to charged defects,<sup>13</sup> i.e., we only consider neutral defects or defect complexes. The observation of discrete emission lines reminds of the defect models such as distant donor-acceptor pair and exciton bound to complex defect recombinations. The excitons can bind to isoelectronic traps (nitrogen pairs in GaP) or to donor-acceptor pairs (Cd-O, Zn-O in GaP).<sup>14</sup> The isoelectronic complex is certainly not an appropriate description for  $X_1$  to  $X_4$  in ZnO, since the isoelectronic element Mg is found in very low concentrations; there is no indication for the incorporation of other isoelectronic elements (e.g., S and Se). In the following, we discuss the possibility of constructing a defect model from the pairing of donors and acceptors (eventually double donors and/or acceptors) as a neutral complex to which excitons can bind. Only certain elements can be involved based on the SIMS results. Donors are quite abundant—the group-III as well as the group-VII donors. Acceptors in ZnO are uncommon, and in the undoped films,

we find no traces of N and small contaminations of As (as a memory effect in the reactor from previous doping studies). Only Li and Na are present in truly significant concentrations. Yet, the group-I elements on Zn site in their neutral charge states are deep; distorted acceptors<sup>15,16</sup> and that will not change upon pairing with a substitutional donor. Anyhow, a singly charged donor-acceptor pair ( $D^+A^-$ ) is not able to explain the splitting in the ground state. Neither donor ( $D^+$ ) nor acceptor ( $A^-$ ) has orbital degeneracy which could give rise to a splitting. This situation does not change when the model is extended to double donor-acceptor pairs as documented in CdS,<sup>17</sup> where the double donor was explained by a sulfur vacancy. The oxygen vacancy in ZnO is a deep donor and a negative  $U$ -center stable in the  $2+$  charge state. Can intrinsic defects be involved in the complex?

The films were grown under oxygen-rich conditions, thus oxygen interstitials and zinc vacancies will be the defects accommodating the nonstoichiometry. Zinc vacancies are the most abundant intrinsic defects in  $n$ -type ZnO according to positron annihilation experiments<sup>18</sup> and theoretical calculations.<sup>19</sup> Pairing of zinc vacancies with substitutional donors (A centers) is a well documented fact in most of the II-VI compound semiconductors.<sup>20</sup> Furthermore, excitonic recombination at neutral double acceptor-donor complexes has been observed in ZnSe (Ref. 21) and CdS (Ref. 22). Pohl *et al.*<sup>21</sup> reported on the optical properties of the  $I_{1d}$  recombination center in ZnSe and explained the findings by an associate formed by  $V_{Zn}$  and an interstitial lithium, while the pairing with an  $Al_{Zn}$  donor could not be excluded. In GaN, Tuomisto *et al.*<sup>23</sup> showed that the growth polarity had a crucial impact on the formation of metal vacancies and vacancy clusters, which were more abundant on the N-polar face. Theoretical calculations show that Zn vacancies and oxygen interstitials act as deep centers with strong electron-phonon coupling. Pairing with a nearest or next nearest impurity will probably not change this picture. In the wide band gap II-VI compound semiconductors, ZnS and ZnSe, the defect complexes consisting of a Zn vacancy associated with a group-III or group-VII donor give rise to broad emission bands in the visible spectral range (see, e.g., Ref. 24). Exciton binding at such defects has not been observed.

The localization energies of  $X_1$  to  $X_4$  indicate binding at a donor type complex with a binding energy slightly smaller than for the hydrogen (44 meV) and the Al donor (55 meV) (see Ref. 7). Look *et al.*<sup>25</sup> provided evidence for the existence of a shallow donor complex with 30 meV binding energy comprised of a Zn interstitial paired with a nitrogen acceptor (N substitutes for O in ZnO). They pointed out that other combinations of Zn interstitial-acceptor pairs could exist producing a bound state and behave as shallow donors<sup>25</sup>—the acceptor could be Li on Zn site.<sup>26</sup> This suggestion is indeed appealing considering the fact that the concentration of Li is substantial higher on the O-face compared to the Zn-face ZnO layers (see Fig. 6). Magneto-optical experiments are needed to gain further insight into the electronic properties of the states involved in the transitions.

In conclusion, ZnO films deposited by chemical vapor deposition on ZnO substrates show a clear asymmetry with

respect to the polar surfaces on defect incorporation and optical properties. We used the experimental data to construct a defect model capable to explain the experimental findings. The clearly demonstrated asymmetry should motivate ex-

perimental and theoretical investigations on how concepts, such as the use of surfactants in combination with nonstoichiometry, will allow for a controlled incorporation of dopants and hence open a way toward *p*-type doping in ZnO.

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