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Nitrogen incorporation in homoepitaxial ZnO CVD epilayers

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ZnO:N thin films have been deposited on oxygen and zinc terminated polar surfaces of ZnO. The nitrogen incorporation in the epilayers, using NH_3 as doping source, was investigated as a function of the growth temperature in the range between 380 °C and 580 °C. We used Raman spectroscopy and low temperature photoluminescence to investigate the doping properties. It turned out that the nitrogen incorporation strongly depends on both, the surface polarity of the epitaxial films and the applied growth temperatures. In our CVD process low growth temperatures and Zn-terminated substrate surfaces clearly favour the nitrogen incorporation in the ZnO thin films.

1 Introduction The dependency of the incorporation of dopants on the surface polarity is a well known phenomenon of compound semiconductors. For example the Ga-polar surface of GaN clearly favours the incorporation of Mg_{Ga} [1] while in GaAs the incorporation of Si leads, depending on the polarity, to either n-type or p-type conduction [2, 3]. In ZnO the polarity as well seems to favour different impurity incorporations into the ZnO matrix [4]. In addition, the growth temperature has a tremendeous influence on the incorporation of dopants in some semiconductors. An example for this behaviour is the II−VI semiconductor ZnSe [5]. For the PLD growth of ZnO:N, Sumiya et al. reported a temperature dependent incorporation of nitrogen [6].

Nitrogen is considered to be a suitable candidate to form shallow acceptors [6–8], and has been used as dopant in one of the first ZnO homojunctiuon diode devices [9]. So far these results were based on a heteroepitaxial growth approach, either on GaN templates [7], on sapphire [10] or on scandium−aluminium−magnesium oxide (SCAM) substrates [6, 9]. Nevertheless the availability of high quality ZnO single crystal substrates and the superior properties of thin films grown on ZnO substrates [11] make it necessary to investigate if there is a difference in the nitrogen incorporation on the different polar faces of ZnO and how it depends on the growth temperature. For a large scale production of optoelectronic devices based on ZnO an easy to handle homoepitaxial CVD process will be the preferable choice. Investigations on the polarity and temperature dependent incorporation of nitrogen in such a process have yet not been conducted. In this Rapid Research Letter we investigate the nitrogen incorporation in homoepitaxial ZnO epilayers depending on the polarity and the growth temperature.
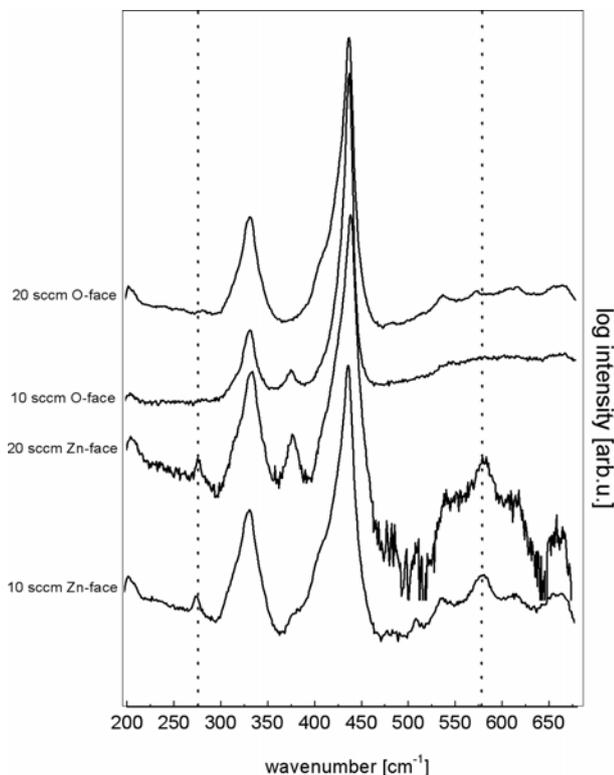
2 Experimental details We used a homebuilt CVD system to grow our ZnO thin films homoepitaxially on ZnO single crystal substrates, either obtained from Crystec or SWI. The single crystal substrates have been pretreated by annealing at 1150 °C under oxygen atmosphere to improve their morphological features. The CVD method used is similar to the one described by Neumann et al. [11]. The thin films were approximately 500 nm thick and were grown for both polarities with the same growth parameters. For the supplement of nitrogen we introduced an ammonia flow during the deposition process. Both, O-$(000\bar{1})$ and Zn-(0001) polar single crystals have been used to investigate the different nitrogen incorporation into the ZnO matrix.

To investigate the doping success we used low temperature (4 K) photoluminescence (PL) spectroscopy under

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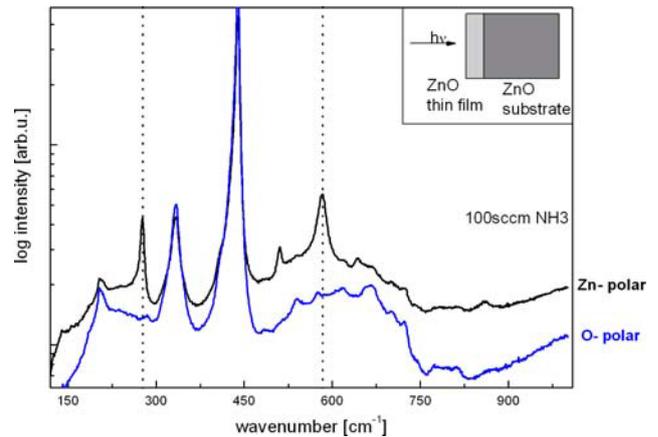Phys. Status Solidi RRL **3**, No. 1 (2009)

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excitation of a 325 nm HeCd laser, and Raman measurements (Renishaw, 633 nm laser line).

Different samples with ammonia flows of 10 sccm, 20 sccm and 100 sccm were grown on the two polar ZnO surfaces. The growth temperature was varied between 380 °C and 580 °C.

3 Experimental results and discussion On the zinc polar (0001) surface the Raman modes, especially at 275 cm^{-1} and 582 cm^{-1}, that have been assigned to nitrogen related modes by Kaschner et al. [12], appeared and increased in intensity with increasing flow of ammonia during the growth process. This behaviour can clearly be seen in Fig. 1. In contrast, the films grown on the oxygen polar surface do not reveal these nitrogen related modes. The Zn-polar thin film grown with the highest ammonia flow (100 sccm), clearly revealed the two characteristic nitrogen Raman modes at 275 cm^{-1} and 582 cm^{-1} (Fig. 2). Yet, even at this high amount of ammonia flow no nitrogen-related Raman modes show up on the oxygen polar epilayer (see Fig. 2). This doping asymmetry is also found in the low temperature PL investigations. On the Zn-polar thin film the well known nitrogen induced donor–acceptor pair (DAP) transition [7] with its zero phonon line at 3.244 eV and its 1LO phonon replica at 3.172 eV (Fig. 3) is observed. The 3.31 eV line is attributed to a band–acceptor (e, A$_0$) transition caused by stacking faults as described by

Figure 2 (online colour at: www.pss-rapid.com) Raman shift of ZnO thin films grown on oxygen-polar and zinc-polar ZnO single crystals at a substrate temperature of 400 °C (excitation with a 633 nm laser line). The ammonia flow was 100 sccm for both samples. The excitation geometry is shown in the inset.

Schirra et al. [13]. Its absence on the O-polar layer is obviously correlated with the very low incorporation of nitrogen on this polar surface and the fact that we detect no DAP transition caused by the nitrogen acceptor (see Fig. 3). The feature at 3.329 eV in the O-polar face is most likely the Y-line, which is an excitonic transition at dislocations [7]. Both lines (3.31 eV and 3.329 eV) are absent in high quality undoped ZnO thin films [11]. At the low growth temperatures one cannot expect a pure 2D growth mode, so the appearance of stacking faults or dislocations can in part be expected. The optical and vibrational data of the undoped epilayers can be found elsewhere [4, 11, 14].

So far our findings on the strongly surface-polarity-dependent nitrogen incorporation are supported, with respect to the better suitability of the Zn-polar surface, by the findings of Maki et al. [15]. They reported on the different
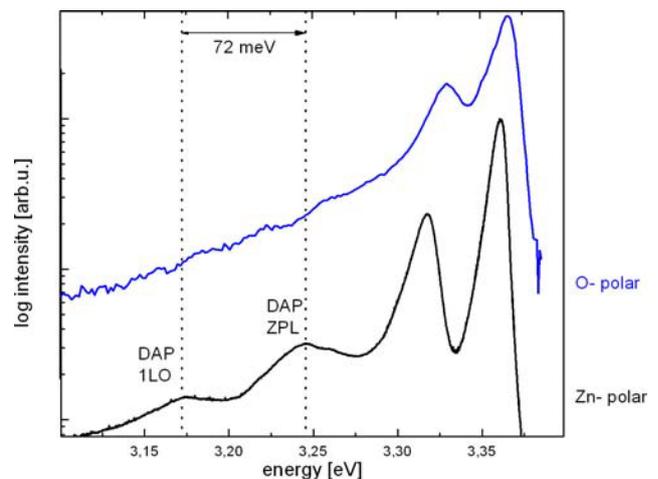

Figure 1 Measurements of the Raman shift of different ZnO thin films. Backscattering geometry has been used and excitation was with a 633 nm laser line. All films were grown at 380 °C.
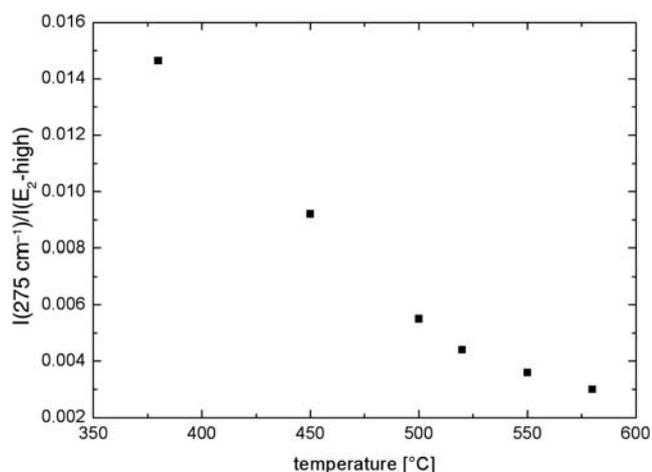

Figure 3 (online colour at: www.pss-rapid.com) PL spectra of two thin films with different polarity grown with 10 sccm NH$_3$ flow. The spectrum was taken at under excitation of a 325 nm HeCd laser line.

Figure 4 Ratio of intensities of the local nitrogen Raman mode at 275 cm^{-1} and the E$_2$-high Raman mode of ZnO. With increasing temperature the intensity of the 275 cm^{-1} mode decreases.

sticking of nitrogen radicals on the different polar surfaces of ZnO single crystals. The Zn-polar surface incorporates nitrogen more efficiently [15]. However one has to have in mind that the irradiation of nitrogen radicals with an ECR gun, and in common, an UHV process like i.e. MBE, are very different approaches compared to the CVD process where surface chemistry plays an important role. This asymmetric behaviour in the dopant incorporation is well known from other compound semiconductors. In GaN for example the p-type doping with Mg depends strongly on whether the surface exhibits Ga or N polarity [1]. Li et al. propose a rather simple model for the better incorporation of Mg on the Ga-face side of GaN [1]. Nevertheless the incorporation of nitrogen preferentially on Zn-polar ZnO seems to be another story. The chemical sensing properties of ZnO for NH$_3$ are known for some time [16]. For the chemisorption Casarin et al. proposed a model in wich the ammonia chemisorbs on the ZnO (0001) face quite well due to its basic character and the acidic character of the conjunct Zn atom [17]. Charge is transferred from the NH$_3$ molecule to the Zn atom. This sticking of ammonia on the zinc-polar face of ZnO could be an additional reason for the better nitrogen incorporation on this polar face. The thermal decomposition of NH$_3$ without a catalyst should be negble at growth temperatures around 400 °C. Eventually in addition to the better sticking of NH$_3$ the decomposition of it is also enhanced on the zinc terminated face. This would explain the linear dependence of nitrogen and hydrogen found by SIMS measurements by Kaschner et al. [12]. The next step was to investigate the influence of the growth temperature on the nitrogen incorporation. We produced a series of samples with an ammonia flow of 10 sccm, the growth temperature was varied between 380 °C and 580 °C while all the other growth parameters remained the same. To measure the amount of nitrogen we took the ratio of the 275 cm^{-1} local nitrogen Raman mode in ZnO and the E$_2$-high mode of ZnO. The total nitrogen

concentration in the films which are still transparent, ranges between $2-7 \times 10^{19}$ cm^{-3} according to SIMS. With increasing temperature a lower amount of nitrogen is incorporated into the thin films. This behaviour is similar to other II−VI semiconductors. In ZnSe, for example, the nitrogen incorporation is clearly favoured at lower growth temperatures as well [5].

In conclusion the nitrogen incorporation in CVD grown ZnO thin films, with ammonia as doping gas, has been investigated. The Zn-polar face clearly favours the nitrogen incorporation. We confirmed that low growth temperatures and Zn-polar single crystal substrates are essential for the incorporation of nitrogen in a homoepitaxial CVD process.

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