

Nitrogen-related local vibrational modes in ZnO:N

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We study the influence of nitrogen, a potential acceptor in ZnO, on the lattice dynamics of ZnO. A series of samples grown by chemical vapor deposition (CVD) containing different nitrogen concentrations, as determined by secondary ion mass spectroscopy (SIMS), was investigated. The Raman spectra revealed vibrational modes at 275, 510, 582, 643, and 856 cm^{-1} in addition to the host phonons of ZnO. The intensity of these additional modes correlates linearly with the nitrogen concentration and can be used as a quantitative measure of nitrogen in ZnO. These modes are interpreted as local vibrational modes. Furthermore, SIMS showed a correlation between the concentration of incorporated nitrogen and unintentional hydrogen, similar to the incorporation of the *p*-dopant magnesium and hydrogen in GaN during metalorganic CVD. © 2002 American Institute of Physics. [DOI: 10.1063/1.1461903]

There is increasing interest in investigating the properties of ZnO epitaxial films with a direct gap of 3.37 eV at room temperature.¹ The material is a potential competitor for GaN-based light-emitting devices in the ultraviolet and blue spectral range. There are reports of superior ZnO properties such as a high exciton binding energy combined with a low lasing threshold density² and a good resistance to bombardment with high-energy particles.^{3,4} For other wide-band-gap semiconductors as GaN (Ref. 5) and ZnSe (Ref. 6) controlled *p*-type doping is problematic. As-grown ZnO typically has *n*-type conductivity with background concentrations between 10^{16} and 10^{17} cm^{-3} . However, there have been reports on the synthesis of *p*-conducting ZnO doped with As (Ref. 7) and a Ga/N codoping⁸ as well as the fabrication of a *p-n*-junction by excimer-laser doping.⁹ In this letter, we report on doping experiments with nitrogen as a potential acceptor and its influence on the lattice dynamics of ZnO.

The ZnO thin films under investigation were grown by chemical vapor deposition (CVD) using a home built epitaxy system which consists of a horizontal quartz reactor and a resistance heating with different temperature zones. Metallic zinc was kept in one zone at a temperature of 470 °C. The growth temperature was 650 °C. We used NO_2 as oxygen precursor and NH_3 as nitrogen source for the doping experiments. The epitaxial films were deposited on GaN/sapphire templates which offers the advantage of a lattice parameter similar to ZnO. We investigated samples containing different nitrogen concentrations. Secondary ion mass spectroscopy (SIMS) was applied to determine the concentration of nitrogen and unintentional dopants such as hydrogen. The primary ion species was cesium. Nitrogen was detected as $^{14}\text{N}^{16}\text{O}^-$ and hydrogen as $^{64}\text{Zn}^1\text{H}^-$ clusters. The given abso-

lute concentrations are accurate to within half an order of magnitude. Despite this accuracy the relative error is less than 10%. The Raman-scattering experiments were carried out in backscattering geometry with a triple-grating spectrometer equipped with a cooled charge-coupled device detector. The lines at 488 and 514.5 nm of an Ar^+/Kr^+ mixed-gas laser were used for excitation. The line positions were determined with an accuracy better than 1 cm^{-1} .

Wurtzite ZnO belongs to the C_{6v} symmetry group and, therefore, there are the Raman-active phonon modes E_2 (low), E_2 (high), A_1 (TO), A_1 (LO), E_1 (TO), and E_1 (LO). The B_1 modes are silent. According to the well-known selection rules we expect to observe the E_2 modes and the A_1 (LO) mode in unpolarized Raman spectra taken in backscattering geometry. Their respective frequencies are 101, 437, and 574 cm^{-1} .¹⁰

Figure 1 shows Raman spectra of nitrogen-doped ZnO. Beside the expected E_2 (low) and E_2 (high) mode of ZnO we find a variety of other modes, which need to be explained. At 569 cm^{-1} we find the E_2 (high) mode of the GaN template. The feature at 332 cm^{-1} is a second-order structure of ZnO, which was interpreted as $2E_2(M)$ by Calleja and Cardona.¹¹ There are five more modes with frequencies of 275, 510, 582, 643, and 856 cm^{-1} which do not belong to first- or second-order structures of ZnO or the GaN template material. The mode at 582 cm^{-1} was already found in ZnO:N by Wang *et al.* and interpreted as A_1 (LO) mode,¹² whereas they gave no explanation for the four remaining Raman modes, but suggested that these modes may be related to nitrogen doping. We also find a well-resolved 582 cm^{-1} mode with a high intensity (see Fig. 1), but because the A_1 (LO) mode is not allowed in backscattering configuration with crossed polarization we conclude that it is not the A_1 (LO) mode of ZnO. However, we agree that all of the additional modes are nitrogen related and will give experimental evidence for this assignment in the following.

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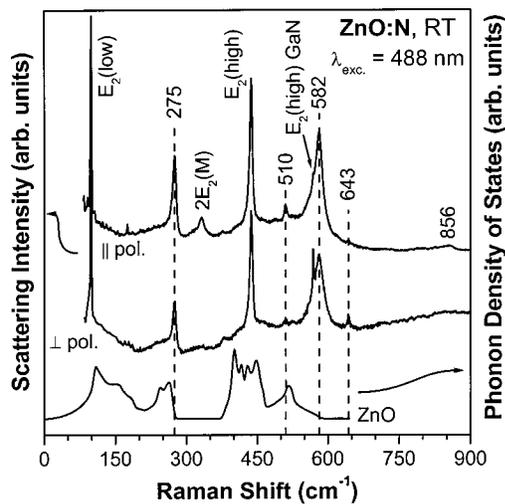


FIG. 1. Room temperature Raman spectra of nitrogen-doped ZnO in parallel and crossed polarization (upper two spectra) as well as a calculated PDOS of ZnO. The additional modes in ZnO:N are marked by their respective frequencies.

The lowest spectrum in Fig. 1 is a calculated phonon density of states (PDOS) for ZnO. The theoretical model applied for the determination of the PDOS is analog to that described in Ref. 13 with the respective parameters for ZnO. Comparing the energetic position of the five modes with the PDOS one notices that they are in regions with a relatively low density of states, except for the mode at 510 cm^{-1} , which is close to a local maximum of the PDOS. However, an interpretation of the Raman features as local vibrational modes (LVMs) is likely.

In total we investigated five samples with different nitrogen concentration as estimated from the growth parameters. Figure 2 exhibits spectra of the samples. Sample A is undoped ZnO, and the estimated nitrogen concentration increases from sample B to sample E. Neither of the additional modes are found in undoped material. Also in ZnO:Ga (not shown) none of these Raman modes was observed. The intensity of the five modes increases with nitrogen concentration. Furthermore, the intensity of the A_1 (LO) mode from

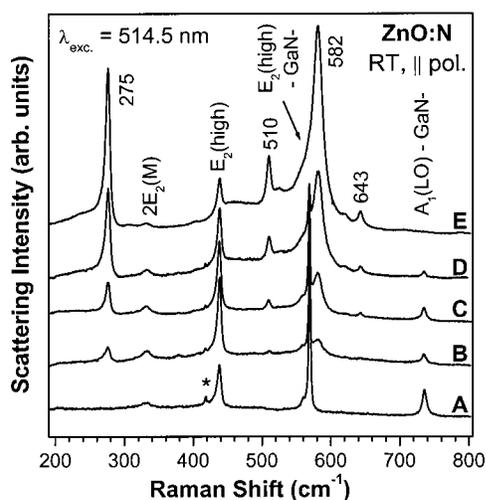


FIG. 2. Room temperature Raman spectra of five ZnO samples. The nitrogen concentration increases from sample A to E. The peak marked by an asterisk originates from the sapphire substrate.

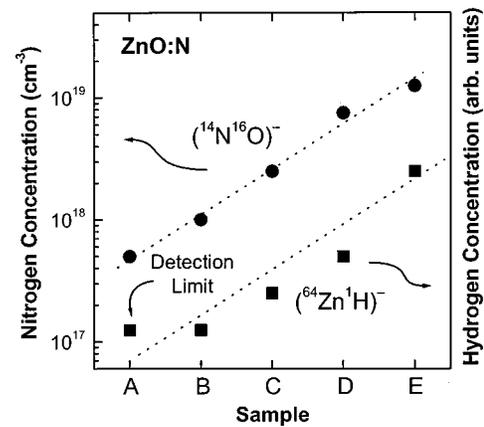


FIG. 3. Nitrogen and hydrogen concentration in the samples under investigation as determined from SIMS. The nitrogen concentration increases from sample A to E. The hydrogen concentration linearly correlates with the nitrogen concentration. Dashed lines are a guide to the eye only.

the GaN template subsequently decreases from A to E. This results from the higher absorption in the visible spectral range with increasing nitrogen concentration (see Fig. 6 in Ref. 12). The correlation of the mode intensities and the nitrogen concentration leads to the conclusion that all the additional modes are LVMs of nitrogen in ZnO. Another possible explanation could be that these modes originate from regions with a high density of states which can be observed in first-order Raman spectra of highly defective material.¹⁴ One argument against these assignments is the comparison with the calculated PDOS as shown above. Second, there are no signs of an inferior material quality of the doped material. For instance the full width at half maximum of the E_2 (high) mode in ZnO is $6\text{--}7\text{ cm}^{-1}$ independently of the doping level.

To obtain a quantitative correlation of the nitrogen concentration and the LVMs we performed SIMS measurements (Fig. 3). The nitrogen concentration was deduced from the signal intensity of the NO^- cluster consisting of ^{14}N and ^{16}O isotopes. The detection limit of this method is around 10^{17} cm^{-3} . As expected from the growth parameters the nitrogen concentration increases from sample A to E with a maximum concentration of about 10^{19} cm^{-3} . Simultaneously, the hydrogen concentration as detected by the $^{64}\text{Zn}^1\text{H}^-$ cluster linearly increases with the nitrogen content. Since we do not have a calibration standard for hydrogen, a quantitative scaling of the hydrogen concentration is unfortunately not possible. Nevertheless, a qualitative comparison of the samples can be given. A higher nitrogen concentration seems to drive the material to build in a higher concentration of compensating hydrogen (see Fig. 3). A similar mechanism as for GaN, where the concentration of magnesium acting as an acceptor and compensating hydrogen are linearly correlated,¹⁵ may be the reason for this behavior. This fact may have a strong impact on the compensation mechanism in ZnO, however, this is not the focus of this letter.

Figure 4 shows the intensity dependence of four of the nitrogen-related LVMs on nitrogen concentration. The data for the mode at 856 cm^{-1} are not shown, because its intensity is too weak for the low nitrogen containing samples. The LVMs with frequencies of $275, 510, 582,$ and 643 cm^{-1} have a linear dependence on the nitrogen concentration in the

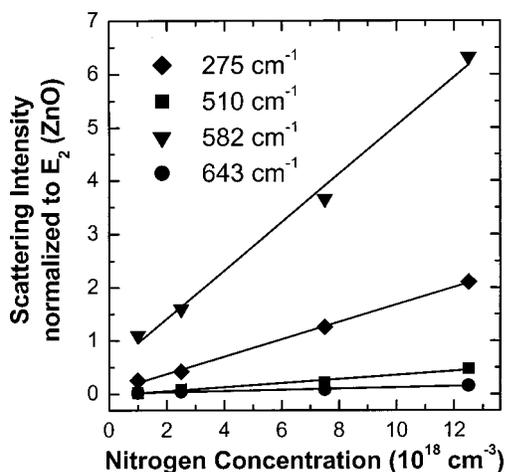


FIG. 4. Normalized intensity of the LVMs as function of the nitrogen concentration. The lines represent linear fits.

sample, which is the final evidence for their origin being local vibrations of nitrogen in ZnO. The different slopes may indicate different formation probabilities of the nitrogen-containing complexes. The exact configuration of the vibrating nitrogen-related complex cannot be deduced from these experiments and further studies are necessary. From calculations based on a modified valence-force model of Kane with a scaling factor of 0.3 (Ref. 16) we obtained values of 272 and 587 cm^{-1} for LVMs of nitrogen on a substitutional oxygen site in the ZnO lattice. First-principles calculations show that the formation of N_O and related complexes is very likely in ZnO.¹⁷ The vibrational properties and the correlation between the acceptor and hydrogen seems very similar in ZnO:N and GaN:Mg.¹⁸ Once calibrated (as in Fig. 4), it is now possible to determine nondestructively the nitrogen concentration in ZnO samples from their Raman spectra.

In summary, N-doped ZnO samples grown by CVD with different concentrations of nitrogen were investigated. The nitrogen and hydrogen concentrations were determined by secondary ion mass spectroscopy. In addition to the host phonons of ZnO we found modes at 275, 510, 582, 643, and 856 cm^{-1} in the Raman spectra of these samples. All five

modes scale in intensity with nitrogen content and are interpreted in terms of nitrogen-related local vibrational modes. The intensity of the LVMs can be used to nondestructively determine the nitrogen concentration in ZnO. Furthermore, a linear correlation between the nitrogen and hydrogen concentration in the samples was found. This could have a strong influence on the compensation mechanism in CVD-grown ZnO.

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