

High-energy vibrational modes in nitrogen-doped ZnO

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We present results of Raman-scattering experiments on a series of nitrogen-doped ZnO epilayers grown by chemical vapor deposition. Nitrogen, a potential acceptor in ZnO, was introduced by the thermal decomposition of ammonia (NH₃). We found a structure consisting of at least four lines with frequencies of 2253, 2277, 2291, and 2304 cm⁻¹. They in-

crease in intensity simultaneously with additional modes in the energy range of the host phonons: both scale with the nitrogen concentration in the samples. The origin of the high-energy structure is tentatively assigned to vibrations of lattice-bound nitrogen or complexes, composed of the constituents of the dopant NH₃.

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The superior properties of ZnO such as a high exciton binding energy combined with a low lasing threshold density [1] and a good resistance to electron [2] and proton [3] irradiation makes it a potential competitor for GaN-based light-emitting devices in the ultraviolet and blue spectral range. To avoid problems like lattice and thermal mismatch homojunctions of n- and p-type ZnO are required. Despite efforts of several groups it is still a problem to obtain p-type ZnO with pronounced high conductivity. Potential candidates for acceptors and thus p-type doping are As [4], P [5], as well as a codoping with Ga and N [6], and primarily N [7].

In previous work we found five additional lines in the low-energy region of the vibrational spectrum of ZnO:N [8], which we assigned to be nitrogen-related local vibrational modes (LVMs). Recently Reuss et al. [9] agreed with this interpretation in their Raman data of N-implanted ZnO samples while Bundesmann et al. [10] denied the relation to nitrogen incorporation and suggested host lattice defects as their origin instead. In our nitrogen-doped samples signs of an inferior material quality were not visible rendering the latter interpretation unlikely. Considering that these lines scale in intensity with the nitrogen content we adhere to our assignment of these modes to nitrogen-related LVMs.

In this Letter we show that in the high-energy region of the Raman spectrum there are additional modes with an in-

tensity also proportional to the nitrogen content in the sample. These vibrations occur around 2300 cm⁻¹, near but below the frequency of the free N₂ molecule [11]. We discuss these new modes in terms of nitrogen incorporation in ZnO.

We focus on ZnO layers grown by chemical vapor deposition (CVD). Nitrogen was introduced by the thermal decomposition of ammonia (NH₃). The films were deposited on GaN/sapphire templates and contain different amounts of nitrogen determined by secondary ion mass spectroscopy (SIMS). The full growth procedure and SIMS details are described elsewhere [8]. The Raman experiments were carried out in backscattering geometry with a triple-grating Dilor XY 800 spectrometer using a charge-coupled device (CCD) for detection. The 488 nm line of an Ar⁺/Kr⁺ mixed-gas laser was used for excitation.

Figure 1 presents spectra of three N-doped ZnO films with increasing nitrogen concentration. In the vicinity of the Raman allowed host phonons the well-known additional lines appear (Fig. 1, left, marked with dashed lines) and grow in intensity proportional to the nitrogen incorporation. Simultaneously the intensity of the lines originating of the GaN substrate decreases due to the higher absorption of the ZnO film in the visible spectral range with increasing nitrogen concentration [12]. Table 1 summarizes all occurring modes and their assignment.

On the right in Fig. 1 the Raman spectra around 2300 cm⁻¹ of the same samples are shown. Aside from the

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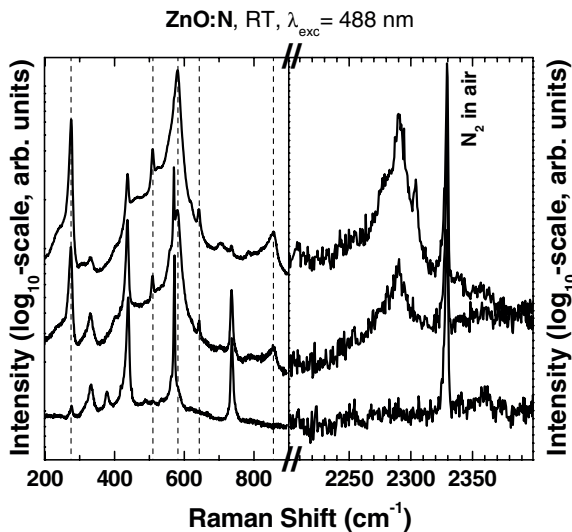


Figure 1 Room temperature Raman spectra of ZnO:N films with increasing nitrogen concentration from bottom to top in the energy range of the host phonons (left) and around 2300 cm^{-1} (right). The dashed lines on the left indicate the positions of the nitrogen-related LVMs. The spectra were normalized to the E_2 (high) mode of ZnO (left) and the N_2 vibration in air (right), respectively. They were offset vertically for clarity.

N_2 vibration in air with a frequency of 2329 cm^{-1} [11] a band close to this line but much broader grows in intensity similar to the LVMs among the host phonons in the low-energy region. We observed this band in different ZnO:N samples independently of the excitation energy.

The frequency range and shape of this structure reminds of Mg-doped GaN, where the incorporation of hydrogen leads to a compensation effect. Raman spectra of p-type GaN:Mg exhibit five lines [16] around 2200 cm^{-1} . Four of these modes found by Brandt et al. [17] were assigned to vibrational modes of Mg–H complexes and the presence of diatomic molecules such as N_2 or H_2 , alternatively to a H-decorated native defect. Harima et al. [18] showed the correlation of hydrogen incorporation during different growth conditions. Their results support an interpretation in terms of a reorientation of initial Mg_{Ga} –N–H complexes and the formation of new complexes with electrical inactive hydrogen [19].

Table 1 Vibrational modes in the low-energy region of ZnO:N samples.

Frequency (cm^{-1})	Origin	Assignment	Reference
275	ZnO:N	nitrogen-related	[8]
332	ZnO	$2E_2$ (M)	[13]
437	ZnO	E_2 (high)	[14]
510	ZnO:N	nitrogen-related	[8]
567	GaN	E_2 (high)	[15]
582	ZnO:N	nitrogen-related	[8]
643	ZnO:N	nitrogen-related	[8]
735	GaN	A_1 (LO)	[15]
856	ZnO:N	nitrogen-related	[8]

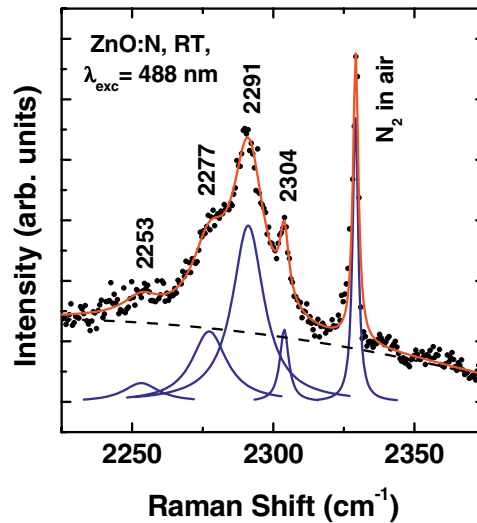


Figure 2 (online colour at: www.pss-rapid.com) Raman spectrum (black dots) of a highly doped ZnO:N sample in the vicinity of 2300 cm^{-1} . The red curve represents a fit consisting of five Lorentzians (blue lines) and a parabolic background (dashed curve).

Returning to ZnO:N, the nitrogen-related band in our films consists of at least four lines differing in intensity. Figure 2 displays the spectrum of the highest doped sample with a nitrogen concentration of approximately 10^{19} cm^{-3} . The experimental data (black dots) are well described by a fit (red line) consisting of five Lorentzians (blue curves), and a slightly parabolic background (dashed line).

The nitrogen-related vibrations occur at 2253, 2277, 2291, and 2304 cm^{-1} . Due to the scaling with the LVMs or rather the nitrogen concentration and the appearance close to the vibration of N_2 in air we tentatively assign this structure to vibrations of lattice-bound nitrogen or complexes. They may consist of pure nitrogen or hydrogen and nitrogen, namely the constituents of the initial dopant NH_3 .

In the range up to 4000 cm^{-1} we did not find more new features in our Raman spectra, in particular not between 3300 and 3700 cm^{-1} . McCluskey et al. [20] performed infrared spectroscopy on an undoped single crystal ZnO sample and observed an oxygen–hydrogen stretch mode at 3326.3 cm^{-1} , in good agreement with the theoretical predictions for hydrogen in an antibonding configuration by van de Walle [21]. Considering again the similarity to GaN:Mg, where in infrared absorption spectra [22] and in Raman spectra [18] of semi-insulating samples a mode at 3125 cm^{-1} and 3123 cm^{-1} , respectively, was observed, the absence of any line above 3000 cm^{-1} in our Raman spectra of ZnO:N might indicate a binding mechanism of the incorporated nitrogen and hydrogen similar to that in p-type GaN.

In summary, N-doped ZnO films grown by CVD with different nitrogen concentrations were investigated. Besides five additional peaks in the energy region of the host phonons we observed a structure around 2300 cm^{-1} , both

scaling in intensity with the nitrogen incorporation in the samples. The high-energy feature consists of four lines at 2253, 2277, 2291, and 2304 cm^{-1} close to the N_2 vibration in air at 2329 cm^{-1} . We suggest an interpretation as vibrational modes of nitrogen or complexes involving nitrogen and hydrogen. Further experimental and theoretical work is necessary to specify the detailed origin of these lines.

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