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Isotopic study of the nitrogen-related modes in N$^+$-implanted ZnO

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Micro-Raman measurements were performed to study the nitrogen-related modes in ZnO samples implanted with N$^+$. The two stable N isotopes, ^{14}N and ^{15}N, were implanted. Distinct peaks at 277 and 512 cm^{-1} are observed irrespective of the implanted isotope, both before and after rapid thermal annealing. The insensitivity of the mode frequencies to the implanted isotope rules out the explanation of these modes as local vibrational modes involving N motion. These modes were not detected in ZnO samples implanted with Zn$^+$, O$^+$, or P$^+$, which suggests that they may be associated with distortions/defects favored by the presence of N. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2734474]

In recent years there has been a growing interest in ZnO because of its advantageous physical properties—wide band gap and free exciton with 60 meV binding energy—for applications in integrated optoelectronic devices operating in the blue and ultraviolet spectral range.[1] However, as in other wide band gap semiconductors, *p*-type doping of ZnO is proving to be difficult. The demonstration of *p*-type doping in homoepitaxial N-doped ZnO grown by molecular beam epitaxy[2] paved the way to the realization of *p*-*n* junctions in ZnO based materials. Nevertheless, reproducible *p*-type doping is still a difficult issue and the yields of several approaches and different laboratories vary enormously.[3] Being nitrogen the primary acceptor candidate in ZnO, considerable effort has been devoted to characterize, by means of vibrational spectroscopy, the impurity incorporation and the formation of complexes that may reduce the doping efficiency of N in ZnO.[4–7] Kaschner *et al.*[5] reported the observation of several additional Raman peaks between 275 and 643 cm^{-1} in N-doped GaN epitaxial films grown by chemical vapor deposition. They were attributed to local vibrational modes (LVMs) of N in substitutional O site in the ZnO lattice. As the intensity of those peaks increased linearly with N concentration, it was further suggested that their intensity could be used to determine the N concentration in N-doped ZnO samples.[5] However, Bundesmann *et al.* disputed this interpretation, as they detected similar peaks in ZnO thin films doped with Fe, Sb, and Al, intentionally grown without N incorporation.[6] They attributed the additional Raman peaks to intrinsic host lattice defects. The controversy about the origin of these modes remains, as they have been observed in later works and have been assigned either to LVMs of N (Ref. 8) or to intrinsic host lattice defects.[9] Also, the correlation between N concentration and the intensity of the additional peaks has been confirmed by some works[8,10] and contradicted by others.[9] In a recent study,[10] on the basis of a local phonon density of states calculation, it was suggested that the additional mode observed at 275 cm^{-1} originates from localized vibration of the Zn atoms in a first-neighbor environment where part of the O atoms are replaced by N atoms. No experimental evidence of the participation of N atoms in the LVM observed in N-doped ZnO has been given so far.

In this work, we carry out an isotopic study of N$^+$-implanted ZnO to investigate the involvement of N vibration in the additional modes observed in N-doped ZnO. In order to check possible effects of the implantation damage inducing intrinsic host lattice defects, ZnO samples implanted with ions of the native species, Zn and O, were also studied. The specificity of the additional modes to N doping was further checked by studying a P$^+$-implanted sample.

The experiments were performed on ZnO single crystals obtained by the hydrothermal growth method. Growth details as well as x-ray and photoluminescence characterization of ZnO crystals obtained by this method have been published elsewhere.[11] The two stable isotopes of nitrogen, ^{14}N and ^{15}N, were implanted. For comparison purposes, further ZnO samples were implanted with P$^+$ and with the native species Zn and O. Multiple implantations at different energies were carried out to achieve a doping profile with a flat homogeneous region and doping densities around 5×10^{9} cm^{-3}. SRIM simulations[12] were performed to determine the corresponding implantation energies and doses for the selected ions. Both N$^+$ and O$^+$ implantations were carried out at 80, 130,

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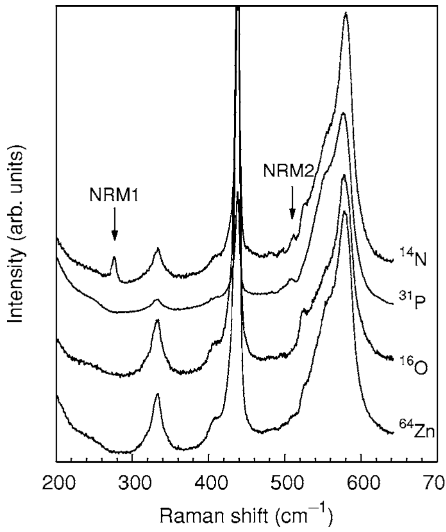

FIG. 1. Raman spectra of ZnO crystals implanted with two potential isoelectronic acceptor ions: N$^+$ and P$^+$, as well as with ions of the native species: O$^+$ and Zn$^+$.

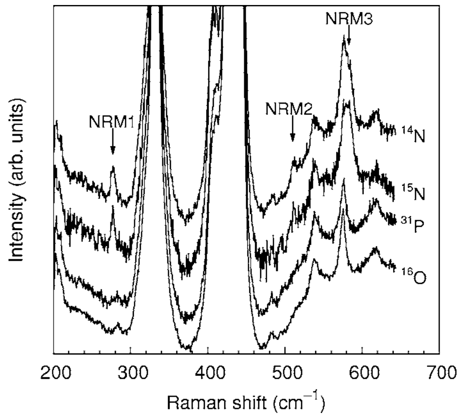

FIG. 2. Raman spectra of ZnO crystals implanted with O$^+$, P$^+$, and with ions of the two stable N isotopes: ^{14}N$^+$ and ^{15}N$^+$ after RTA.

and 185 keV, with respective doses of 3×10^{14}, 5.4×10^{14}, and 7.8×10^{14} cm^{-2}. A similar profile for the heavier P impurity was achieved by P$^+$ implantation at 100, 175, and (under double ionization) 300 keV, with doses of 2×10^{14}, 3.6×10^{14}, and 1.08×10^{15} cm^{-2}, respectively. In all cases, a nearly homogeneous depth doping profile extending for about 220 nm is obtained. For Zn$^+$, double ionization was not available and a narrower profile with a 50 nm flat region was obtained by implanting at 80 and 185 keV with respective doses of 9×10^{13} and 4.1×10^{14} cm^{-2}. Rapid thermal annealings (RTA) were carried out in an ADDAX-RM system with a SiC susceptor at 950 °C for 10 s under continuous O$_2$ flow.

Raman scattering spectra were recorded in backscattering configuration on a (0001) face using the 514.5 nm line of an Ar$^+$ laser as excitation source. The scattered light was collected with a confocal microscope with a lateral and depth resolution of about 1 μm and analyzed using a Jobin-Yvon T64000 spectrometer equipped with a LN$_2$ cooled charge coupled device detector.

Figure 1 shows Raman spectra of the ZnO samples ion implanted with different species. No postimplantation annealing treatment was performed on these samples. The band between 520 and 600 cm^{-1} is due to disorder-activated longitudinal optical (DALO) modes and reflects the lattice disorder in the implanted layer.[8] To facilitate the comparison between the spectra of the implanted layers, the spectra shown in Fig. 1 have been normalized so that all of them display a similar DALO intensity. Besides the DALO band, all spectra show a strong $E_2^{\rm high}$ peak at 438 cm^{-1} and a second-order difference mode at 333 cm^{-1},[13] which primarily arise from the undamaged crystal beyond the implantation profile. Clearly, two additional peaks appear in the spectrum of the N$^+$-implanted sample at 277 and 512 cm^{-1}. At these frequencies, the layers implanted with ions of the native species do not display any Raman feature and therefore the additional peaks cannot be attributed to intrinsic host lattice defects. As these modes appear to be related to the presence of N in the lattice, we shall refer to them as nitrogen-related modes (NRMs), NRM1 and NRM2, respectively. In the P$^+$-implanted layer, a weak broad band appears at 508 cm^{-1}, slightly below the NRM2 frequency. Despite their proximity in frequency, these bands have different origins, as they exhibit a different annealing behavior: whereas NRM2 is still detected after RTA, the 508 cm^{-1} mode vanishes in P$^+$-implanted samples after annealing. The N$^+$-implanted sample displays a weak feature at 524 cm^{-1}, which is also observed in the spectra of the samples ion implanted with the native species, and hence can be attributed to intrinsic host lattice defects produced by the implantation. The fact that this feature is most prominent in the O$^+$-implanted sample suggests that it might be related to interstitial O or O antisite defects.[14] This feature is not present in the spectrum of the P$^+$-implanted sample. Although this is not fully understood, it could be due to the higher degree of damage in the probed region of the P$^+$-implanted sample, as indicated by the broader DALO band and the higher intensity ratio between the DALO band and the second-order mode at 333 cm^{-1} observed in this sample.

An excellent lattice recovery of the implanted layers is achieved by RTA, as can be seen from the spectra displayed in Fig. 2. The DALO band has been completely removed by the annealing, and the second-order structures revealed by the spectra of the P$^+$- and O$^+$-implanted samples are virtually identical to those of the virgin ZnO.[13] In contrast, the samples implanted with N$^+$ display additional features at 277, 512, and 582 cm^{-1}, labeled as NRM1, NRM2, and NRM3 in Fig. 2. NRM1 and NRM2 correspond to the NRMs already observed in the N$^+$-implanted samples before annealing. Note that the weak feature displayed by P$^+$- and O$^+$-implanted samples at ≈284 cm^{-1}, although close to the NRM1 frequency, actually corresponds to a second-order mode previously assigned to $B_1^{\rm high}-B_1^{\rm low}$ in bulk ZnO.[13]

The NRMs show a substantial decrease in intensity after annealing, contrary to what one would expect for substitutional LVMs, and most notably, their frequencies do not change in the sample implanted with ^{15}N$^+$. For a substitutional LVM of N, a rough estimate of the expected isotopic shift can be obtained from the empirical diatomic model,[15]

$$\frac{\omega_{\rm LVM}(^{15}{\rm N})}{\omega_{\rm LVM}(^{14}{\rm N})} \approx \sqrt{\frac{\mu({\rm Zn}-{}^{14}{\rm N})}{\mu({\rm Zn}-{}^{15}{\rm N})}}, \tag{1}$$

where $\mu({\rm Zn{-}N})$ is the reduced mass of the Zn–N pair. Using Eq. (1) we obtain for the lowest frequency NRM an expected isotopic shift $\Delta\omega_{\rm NRM1}\approx 8$ cm^{-1}, which is not observed in the spectra of Fig. 2. Even higher shifts should be expected for

NRM2 and NRM3. However, all the NRMs observed in the sample implanted with $^{14}N^+$ lie at the same frequencies as those detected in the sample implanted with $^{15}N^+$. Our isotopic doping experiments indicate that whereas the NRM1, NRM2, and NRM3 modes are clearly related to the presence of N in the ZnO lattice, they cannot be attributed to LVMs of substitutional N in the O site. The insensitivity of the NRM1 frequency to the isotopic mass would be consistent with the attribution of this mode to a vibration of Zn atoms in a local environment, where part of their first-neighbor O atoms are replaced by N atoms in the ZnO lattice.[10] However, one would expect the number of substitutional N atoms to increase after RTA, and hence the intensity of such a mode should be greater in annealed samples, in contrast with the experimental observation. Therefore, our results suggest that these modes are probably due to localized vibrations associated with local distortions of the lattice caused by nonsubstitutional N or to a complex defect favored by the presence of N. It is worth noting that, in contrast with Ref. 6, we observe these additional modes *only* in the spectra of the ZnO samples implanted with N^+ and they are not present in samples implanted with P^+ or with the native species. Therefore, we conclude that, contrary to the suggestion made in Ref. 6, these modes cannot be attributed to intrinsic host lattice defects.

In summary, we have investigated ZnO samples ion implanted with several atomic species as well as with two nitrogen isotopes, ^{14}N and ^{15}N. The Raman spectra of the N^+-implanted samples exhibit additional modes at 277, 512, and 582 cm^{-1} which are not present in the spectra of the samples implanted with other species. The NRMs occur at the same frequencies in samples implanted with $^{14}N^+$ and with $^{15}N^+$. This is an experimental evidence that N motion is not involved in the NRMs of ZnO:N. These modes are not observed in ZnO samples ion implanted with the native species, which indicates that they are not due to intrinsic host lattice defects either. Alternatively, our results suggest that the presence of N in the ZnO lattice induces a local lattice distortion or the formation of a complex defect that does not occur for other potential acceptors such as P.

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