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Effects of N implantation on defect formation in ZnO nanowires

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Abstract

One-dimensional ZnO nanowires are a promising material system for a wide range of optoelectronic and photonic applications. Utilization of ZnO, however, requires high-quality ZnO with reliable n-type and p-type conductivity, with the latter remaining elusive, so far. In this work we report on effects of N doping via ion implantation on defect formation in ZnO nanowires studied by optically detected paramagnetic resonance (ODMR) spectroscopy complemented by photoluminescence spectroscopy. After N implantation, zinc interstitial shallow donors, which are formed as a result of ion implantation, are observed in addition to effective mass type shallow donors. Additionally, ODMR signals related to oxygen vacancies can be observed. Implantation also causes formation of a new nitrogen related defect center, which acts as an acceptor. The present findings are of importance for understanding impacts of different defects and impurities on electronic properties of nanostructured ZnO and achieving p-type conductivity via nitrogen doping.

Keywords: Zinc oxide, Optically detected magnetic resonance, Photoluminescence, Defects, Nitrogen

1. Introduction

One-dimensional ZnO nanowire (NW) structures have recently attracted a substantial scientific and technological interest as building blocks for a wide range of optoelectronic and photonic applications, such as ultraviolet light emitting diodes, solar cells, photo detectors, as well as gas sensors and photocatalysts[1–8]. These structures have the advantage of combining the material properties of ZnO, namely its wide and direct band gap (~ 3.3 eV at room temperature) and a large exciton binding energy (60 meV at room temperature), with those of nanoscale objects including a high surface-to-volume ratio, the freedom to design axial and lateral heterostructures, light trapping and reduced material consumption. In addition, ZnO is nontoxic, sustainable and cheap. Due to these properties ZnO has emerged as one of the leading candidates in the field of photocatalysis as an efficient material for photocatalytic water splitting[8] and photocatalytic waste water purification[7]. It was demonstrated that incorporation of dopants, especially anionic dopants, e.g. acceptors, into ZnO can further increase the photocatalytic efficiency as well as lower the excitation energy from the ultraviolet into the visible spectral range[7,9,10]. Especially nitrogen-doped ZnO is a very promising material for increased photocatalytic efficiency[11–15]. Achieving p-type ZnO via acceptor doping is also required for applications in optoelectronic devices, as the basic structure of such devices relies on p-n junctions. But like many wide band-gap semiconductors ZnO suffers from the asymmetric doping problem[16–18], i.e. n-type doping can be achieved easily while p-type doping remains elusive. Thus, optoelectronic applications requiring pn-junctions as well as photocatalytic applications benefitting from acceptor doping are hindered by the lack of an efficient p-type doping method. To address this issue and to achieve efficient and reliable p-type doping in ZnO, dopants like group-V elements, e.g. N[19–21],

P[22,23] , Sb[24,25], As[26,27], etc as well as group-I elements[28] were introduced as acceptors.

N is considered to be a promising candidate among those acceptor elements, since it has a similar atomic radius and electronegativity as O[29]. Subsequently, N-doping was used by many groups in order to fabricate p-type ZnO films. However, only a small number of groups were successful with the fabrication of p-type ZnO. The difficulty stems mostly from both compensating effects of the donor-type defects and the low solubility of p-type dopants[30]. Later it was demonstrated by theoretical and experimental studies that nitrogen substituting for oxygen (N_O) cannot form a shallow acceptor state[31–33]. Up to now, there is still an ongoing discussion how N-doping leads to the formation of shallow acceptors in ZnO. It is important to keep in mind that the doping processes can be largely affected by growth conditions, as well as the type and concentration of dopants. For instance, it was reported that the p-type conductivity could be promoted in nanostructured ZnO[21,28,34,35]. So far, the exact physical mechanism responsible for this effect remains unknown. But the formation of complexes with residual defects and impurities surely has to be considered, since it is known that the energy level of the N acceptor can be affected by its local surrounding[36], complexing with residual group III impurities[37] and intrinsic defects forming e.g. N_O-V_{Zn} or $N_{Zn}-2V_{Zn}$ [38–40], as well as by the formation of N-N molecules[35,41]. Moreover, due to the large surface-to-volume ratio of NWs, defects located at the surface or in its close vicinity become more and more important. Indeed, it was reported that N-related defects near the surface can have different formation energies as well as optical properties[42–44].

Ion implantation has in the past been proven to be a reliable method to introduce dopants in a controlled manner. In this work we employ optically detected magnetic resonance (ODMR)

spectroscopy complemented by photoluminescence (PL) experiments to study the effects of N implantation on the defect formation in ZnO NWs in order to gain information on the chemical environment of N atoms in ZnO NWs, which can open up new routes for efficient and reliable p-type doping in ZnO NWs.

2. Experimental details

The ZnO NWs investigated in this study were grown by spin coating a 0.1 M methanol solution of zinc acetate ($\text{Zn}(\text{CH}_3\text{COOH})_2$) on fluorine doped Tin oxide (FTO) glasses and subsequently annealing them at 350 °C for 30 min. Afterwards, the obtained ZnO seeded FTO glass was put into a mixed aqueous solution of zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (0.05 M) and hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) (0.05 M) for 24 h at a temperature of 90 °C. The ZnO NWs were then acquired after annealing at 450 °C for 60 min. The ion implantation was carried out at room temperature with an accelerator voltage of 30 kV and a nominal N implantation dose of 5×10^{15} ions/cm². The N implanted ZnO samples were subsequently annealed at 450 °C for 60 min. For a more detailed description of the growth process see Ref.[45].

The morphology of the NWs was investigated with a LEO 1550 Gemini scanning electron microscope (SEM), operated with an extraction voltage in the range of 2 - 4 kV. PL and ODMR measurements were performed using the 351 nm line of an Ar^+ ion laser as an excitation source. The PL signals were detected at 5K by a photomultiplier tube assembled with a grating monochromator. The ODMR experiments were performed using a Q-band spectrometer operating at 34 GHz microwave frequency at a temperature of 4.2 K. ODMR signals were measured as a change of the integrated PL intensity detected within the visible spectral range of 420 - 1000 nm under magnetic resonance conditions by a Si detector. In order to avoid

contributions of laser leakage in the detected PL signal, appropriate long-pass and short-pass optical filters were inserted in the detection and excitation path, respectively. The ODMR spectra were modelled by using the Easyspin software package[46].

3. Results and discussion

Representative SEM images of the as-grown and N-implanted NWs are shown in Figure 1 (a) and (b). The NWs form a dense array and have diameters ranging from 60 to 200 nm and a length of around 3 μm [45]. The as-grown and N-implanted NWs are mostly vertically oriented along the crystallographic c-axis ([0001]-axis) and have a hexagonal cross-section. The orientation of the NWs was confirmed by x-ray diffraction experiments published in an earlier work [45] which also show that the NWs crystalize in the wurtzite structure along the crystallographic c-axis. However, some of the NWs in both as-grown and N-implanted samples are found to be randomly tilted with angles up to 15°.

A typical PL spectrum of the as grown ZnO NWs measured at 5 K is depicted in Figure 2. In the near-band-edge (NBE) spectral range it is dominated by transitions stemming from neutral donor bound excitons (D^0X), free excitons (FX) and their longitudinal optical (LO) phonon replicas (FX-LO) – see the inset in Fig. 2 for a close-up of the PL spectrum within the NBE spectral region. In addition, the spectrum contains a broad PL band that peaks at around 1.95 eV. This red emission in bulk ZnO was shown to be partly related to the presence of intrinsic defects, such as zinc vacancies[47]. After N implantation one can see that the maximum position of the dominant broad emission shifts to 1.89 eV, indicating that different defects are now involved in the recombination process. In addition, a weak PL band within the 2.1-2.5 eV spectral range appears, which could be related to the presence of oxygen vacancies, as shown by previous studies of

ZnO bulk crystals [48,49]. In the NBE spectral range, N-implantation leads to the appearance of a sharp PL peak at a slightly lower energy than the D^0X transition. The similar peak was observed by Ton-That et al. in ZnO NWs annealed in nitrogen plasma and assigned to a neutral acceptor bound (A^0X) exciton related to nitrogen[35]. In addition to these additional PL bands, the overall PL intensity was lower by a factor of 15 in the N-implanted ZnO NWs as compared to the as-grown ZnO NWs, which was likely caused by the formation of non-radiative recombination centers due to the implantation damage.

To investigate the formation of point defects related to N implantation we employed the ODMR technique, which is known to be among the most powerful and versatile experimental methods for defect identification[50]. The ODMR spectra were analyzed using the following spin-Hamiltonian that includes an electron Zeeman term and a term describing the central hyperfine interaction:

$$\mathcal{H} = \mu_B \mathbf{B} \mathbf{g} \mathbf{S} + \mathbf{S} \mathbf{A} \mathbf{I} \quad (1)$$

Here, $\mathbf{S}$ denotes an effective electron spin, $\mathbf{I}$ the nuclear spin and $\mathbf{B}$ is an external magnetic field. $\mathbf{g}$ and $\mathbf{A}$ are the electron g-tensor and the hyperfine interaction tensor, respectively and μ_B is the Bohr magneton. The spin-Hamiltonian parameters obtained from fitting the experimental data are summarized in Table I. The modeling was done considering a random tilt of the NWs by up to 15° from the vertical direction (Fig. 1), which was simulated by introducing a broadening of the ODMR lines as compared to that measured from a reference bulk ZnO. As can be seen from the SEM images, the NWs do not all have the same in-plane orientation. Therefore, we investigated if the individual NWs constituting the ensemble have a preferential or a random orientation of the crystallographic a- and b-axes. This was carried out by performing a statistical analysis of the orientation of the crystallographic a-axis from the SEM images. The top-view

SEM images of the NWs are along the c-axis, which means that the a-axis is pointing from the center of the hexagonal cross-section to one of the edges (see Fig. 3). Subsequently, we determine the angle by which the NW is rotated in-plane (around the c-axis) away from the reference position. The analysis yields, that the majority of the NW (around 80%) have random orientations (see Fig. 3). This was taken into account for the modelling of ODMR signals of non-axial defects.

Figure 4 shows ODMR spectra of as grown ZnO NWs (a) and N-implanted ZnO:N NWs (b). The experimental spectra are marked as “exp”, while the total simulated spectra beneath them are marked as “sim”. Simulated spectra of different defects using equation (1) are shown by the dashed lines. Both, as-grown and N-implanted ZnO NWs have an unidentified background signal. The ODMR spectra of the as grown ZnO NWs consist of four signals. From the low field side to the high field side of the spectrum those are: (i) The ODMR signal that contains two peaks centered at around 1205 mT. It corresponds to an acceptor center with a g-value larger than 2 and can be best fitted assuming that it is related to a negatively charged Zn vacancy, V_{Zn}^- [51,52]. Zinc vacancies have the lowest formation energies in n-type ZnO among all native point defects and are, therefore, expected to be present with a sufficiently high concentration in bulk ZnO[53]. Our results show that V_{Zn} is also abundant in ZnO nanostructures such as NWs and can, therefore, be considered as a common native defect in this material. The ODMR signal (ii), labeled as D1, consists of a single line that peaks around 1200 mT, has g-factor of ~ 1.98 and is not identified so far. The ODMR signal (iii) peaking around 1225 mT can be reasonably simulated by a spin triplet center composed of V_{Zn}^- and EM. Such spin triplet systems consisting of exchange coupled pairs of a donors and acceptors are quite common in ZnO[52,54]. The ODMR signal (iv) contains a single line ($S=1/2$) with a g factor of ~ 1.96 . Such a signal is

characteristic for shallow donors in ZnO[50]. An analysis of the slight anisotropy of the g-factor suggests that ODMR signal (i) stems from an effective mass (EM)-type donor[50]. Additionally, there is a broad unidentified background signal.

After N-implantation several new ODMR signals can be observed, in addition to the ODMR signals observed in the as-grown ZnO NWs. The signals are ordered from high-field side of the spectrum to the low field side of the spectrum. Firstly, the N implanted ZnO NWs exhibit a second shallow donor signal. The origin of this additional shallow donor signal is most likely zinc interstitials (Zn_i), which were observed in ZnO nanostructures before[54,55] and can easily be created after ion implantation[39]. Secondly, there is an ODMR signal consisting of a single line with a g-factor of ~ 1.996 (peaking around 1215 mT) which can be attributed to oxygen vacancies (V_O)[49,56,57]. The appearance of the V_O ODMR signal is consistent with the PL results, which also indicate the formation of V_O 's after N implantation. Thirdly, there is a new ODMR signal with a g-factor larger than 2 peaking at 1209 mT, which indicates that it originates from an acceptor-type defect. A defect with the very similar spin-Hamiltonian parameters was observed by electron paramagnetic resonance experiments in the same samples and was labeled as the N-center[58]. The N-center can be described by assuming a resolved hyperfine interaction with a nuclear spin ($I=1$) with almost 100 % natural abundance. Nitrogen is the only element that fulfills these criteria, since the ^{14}N isotope has $I = 1$ and 99.6 % natural abundance. It is interesting to note that the spin-Hamiltonian parameters of the N-center are quite different from the known parameters of N_O [33,59] and the N_2 -molecule[60,61], which are commonly observed in N-doped ZnO bulk and thin-films. Therefore, the N-center must have a different structure than the two N-related acceptors so far observed in ZnO.

To elucidate the role of the revealed defects in carrier recombination, we performed ODMR experiments with different spectral detection windows for the ZnO:N NWs, which are shown in Fig. 5. From fitting the ODMR spectra in Fig. 5 we extracted the ODMR intensities of different centers in certain spectral ranges (see Fig. 6, the horizontal bars). The intensity of the V_{Zn} ODMR signal peaks in the spectral window ranging from 780 to 950 nm, which is in the same range as it was determined in earlier EPR and ODMR studies of bulk ZnO by Wang et al.[47]. This implies the same origin of the red emission in bulk and nanostructured ZnO. The intensity of the N-center ODMR signal gradually increases with increasing the detection wavelength, which indicates that the N-center acts as a deep center. This is in agreement with the photo-EPR experiments performed earlier, which also identify the N-center as a deep acceptor with the energy level of $E_v+1.1$ eV[58]. The ODMR signal intensities of the EM and Zn_i shallow donors, as well as the V_{Zn} /EM triplet centers are also increasing with increasing detection wavelength, indicating that the recombination processes observed in ODMR are most likely involve radiative transitions between the shallow donors and deep acceptors.

4. Conclusion

In conclusion, we have investigated the effects of N implantation on defect formation in ZnO NWs by ODMR and PL spectroscopies. After N-implantation three new PL radiative recombination processes are detected. The first one is related to an A^0X transition related to nitrogen, the second one to the presence of oxygen vacancies and the third one to deep acceptors N-related acceptors. The formation of these defects is further confirmed by the ODMR measurements, based on the observation of the ODMR signals related to an oxygen vacancy and the nitrogen related N-center, which acts as a deep acceptor. The spin Hamiltonian parameters of

the N-center differs from the known N-related EPR signals from the isolated nitrogen atom substituting for oxygen (N_O) and the nitrogen molecule (N₂), which were so far observed in bulk and thin-film ZnO. This proves that N can be incorporated in a different configuration in ZnO NWs as compared to ZnO bulk and thin films. The present findings are of importance for understanding impacts of different defects and impurities on electronic properties of nanostructured ZnO and achieving p-type conductivity via nitrogen doping.

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Figures:

Figure 1:

Figure 2:

Figure 3:

Figure 4:

Figure 5:

Figure 6:

Figure captions:

Figure 1: SEM images of the as-grown (a) and N-implanted (b) ZnO NWs.

Figure 2: Typical PL spectra measured at 5 K from as-grown and N-implanted ZnO NWs. The spectra are displayed in the linear scale and vertically offset for clarity. The inset depicts a close-up of the PL spectra within the NBE spectral region, shown in a semi-logarithmic scale.

Figure 3: Statistical distribution of the orientation of the NWs crystallographic a-axis.

Figure 4: Experimental ODMR spectra (labelled as “exp”) of the as-grown and N-implanted ZnO NWs measured at 4 K under the orientation of an applied magnetic field perpendicular to the crystallographic c-axis. The simulated ODMR spectra of the defects using the spin Hamiltonian parameters from Table 1 are shown by the dashed lines, whereas the total simulated spectra (labeled as “sim”) are displayed by the thick solid lines.

Figure 5: Experimental ODMR spectra (labelled as “exp”) of the N-implanted ZnO NWs with the orientation of an applied magnetic field perpendicular to the crystallographic c-axis measured at 4 K in different spectral ranges for detection. The simulated ODMR spectra of the defects using the spin Hamiltonian parameters from Table 1 are shown by the dashed lines, whereas the total simulated spectra (labeled as “sim”) are displayed by the thick solid lines.

Figure 6: Spectral dependences of the ODMR signals of V_{Zn} , N-center, V_{Zn}/EM , Zn_i and EM. The spectral detection windows are marked by the colored bars.

Table 1: Summary of the spin-Hamiltonian parameters of the defects discussed in this work. The axial components of the electron $\mathbf{g}$ -tensor are denoted as $g_{\perp}$ and $g_{\parallel}$. The perpendicular and parallel components $A_{\perp}$ and $A_{\parallel}$ of the hyperfine interaction tensor $\mathbf{A}$, as well as the axially symmetric part D and asymmetry parameter E of the fine structure tensor $\mathbf{D}$ are given in MHz. The parallel and perpendicular directions are with respect to the c -axis. For the non-axial centers, φ is the angle between the z and c axis.

Center	S	I	g_x	g_y	$g_{\perp}$	$g_{\parallel}$	$ A_{\perp} $	$ A_{\parallel} $	φ (deg)
V_{Zn^-} (axial)	1/2				2.0193	2.0028			
V_{Zn^-} (non-axial)	1/2		2.0173	2.0183		2.0028			110.75
N-center	1/2	1			2.0069	2.0054	35	52	
V_{Zn}/EM	1		1.9816	1.9866		1.9799			110.75
D1	1/2				1.987	1.985			
V_O^+	1/2				1.9960	1.9945			
EM	1/2				1.955	1.957			
Zn_i	1/2				1.9595	1.9605			