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Defect Properties of ZnO Nanowires

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Abstract. In this work we examined optical and defect properties of as-grown and Ni-coated ZnO nanowires (NWs) grown by rapid thermal chemical vapor deposition by means of optically detected magnetic resonance (ODMR). Several grown-in defects are revealed by monitoring visible photoluminescence (PL) emissions and are attributed to Zn vacancies, O vacancies, a shallow (but not effective mass) donor and exchange-coupled pairs of a Zn vacancy and a Zn interstitial. It is also found that the same ODMR signals are detected in the as-grown and Ni-coated NWs, indicating that metal coatings does not significantly affect formation of the aforementioned defects and that the observed defects are located in the bulk of the NWs.

Keywords: ZnO, defects, Nanowires, ODMR

PACS: 76.70.Hb, 78.55.Et, 78.67.Qa

INTRODUCTION

ZnO is a wide band gap semiconductor (~3.3 eV at room temperature) with a large exciton binding energy of around ~60 meV. It is currently attracting an increasing interest as a promising material for applications in a wide variety of electronic and optoelectronic devices, such as UV light emitting diodes (LEDs), solar cells, gas sensors and spintronics [1, 2]. Furthermore, ZnO can be easily synthesized in various nano-scale forms, which could further enhance device functionality [3]. However, to realize the full potential of ZnO in device applications it is necessary to overcome difficulties in controlling its electrical conductivity, especially in achieving a p-type conductive material. In order to solve this problem one needs to have an in-depth understanding of defect physics in ZnO, since intrinsic defects and/or their complexes with impurities that are introduced during the growth often act as donors and compensate acceptor dopants.

By employing magnetic resonance (MR) spectroscopy, which is known to be a powerful technique to investigate chemical identity and local structure of defects, it was possible to obtain a substantial amount of information on defects in ZnO. MR signatures and, in a number of cases, energy level positions of the main intrinsic defects including oxygen and zinc vacancies (V_O and V_{Zn}) and zinc interstitials (Zn_i), as well as impurities [4,5] could be provided. So far, the majority of the MR studies were focused on bulk ZnO that is either as-grown [6-10] or subjected to irradiation [11-13] or ion implantation [14,15]. V_{Zn} is concluded to be the dominant intrinsic defect in as-grown bulk ZnO [8], whereas other intrinsic defects and their complexes were detected in irradiated/implanted structures. MR studies were also extended [16,17] to epitaxial films, which were grown under non-equilibrium conditions by molecular beam epitaxy (MBE). MR studies of defects in nano-crystalline ZnO were so far mainly devoted to shallow donors [18,19]. This was partly related to a limited sensitivity of traditional MR methods, such as electron spin resonance (ESR), which are often found to be inadequate for investigations of nanostructures due to their small volume and, therefore, a low total number of defects. This problem was overcome most recently by using the optically detected magnetic resonance (ODMR) technique [20]. Several grown-in defects were observed in ZnO nanowires (NWs) and were attributed to Zn vacancies, a shallow (but not effective mass) donor and exchange-coupled pairs of a Zn vacancy and a Zn interstitial [21]. In this work, we further investigate defect formation and related recombination processes in as-grown ZnO NWs by ODMR. In addition, effects of Ni coating on defect formation are examined. Metal coating is often a compulsory step during device fabrication required either for fabrication of electrical contacts or for enhancing device functionality.

EXPERIMENTAL DETAILS

The ZnO NWs studied in this work were grown by rapid thermal chemical vapor deposition (RTCVD) on gold coated c-plane sapphire substrates. The gold catalyst was deposited by electron beam evaporation with a thickness of ~ 3 nm. The growth of the ZnO NWs was performed at 950 °C with a pressure of 20 Torr under Ar and O₂ flow of 100 and 2 sccm, respectively. Then ZnO NWs were capped by a Ni film with a thickness of 10 nm deposited by electron beam evaporation at room temperature (RT). A more detailed description of the growth procedure and structural analysis of the NWs can be found in Ref. 22. ODMR measurements were performed using the 364 nm line of an Ar⁺ ion laser as an excitation source at a temperature of 3 K with a microwave (MW) frequency of 9.25 GHz (X-band) and adjustable MW powers between 1 and 200 mW. ODMR signals were monitored in the visible spectral region with a Si detector as MW-induced changes of PL intensity. Angular dependent ODMR measurements were performed by varying an angle Θ between the direction of an applied magnetic field **B** and the direction (Z) normal to the substrate surface (which coincides with the c-axis for the majority of the NWs).

RESULTS AND DISCUSSION

Morphology of the ZnO NWs was examined earlier by SEM measurements [22]. The NWs are vertically aligned along the [0001] direction, and have a uniform size distribution with an average length of 30 μ m and an average diameter of 100 nm. Some of them are, however, randomly tilted by up to 20°. The implications of the tilting on spin resonance signals will be discussed below.

PL of the ZnO NWs at 5 K within the near band edge (NBE) range is dominated by several excitonic lines due to recombination of donor bound excitons (BXs) and surface excitons (SXs) [21, 22]. PL spectra of the Ni-coated NWs show the same emissions without additional features, implying that the coating does not lead to unintentional doping of impurities such as H in ZnO. At 5 K, however, the PL intensity decreases after Ni coating. In the visible spectral range, PL consists of a band that peaks at around 2.45 eV and exhibits a fine structure which can be attributed to copper impurities in ZnO [21]. This emission is relatively weak in the investigated NWs. This fact and the presence of the strong and well-structured excitonic emissions imply that the studied NWs have a superior optical quality.

Figure 1 (a) displays a comparison between ODMR spectra measured from the as-grown and Ni-coated NWs with the direction of an applied magnetic field at angles of 60°, 30° and 0° with respect to the z-axis. All ODMR spectra are composed of several rather broad and overlapping peaks that range from 324 to 338 mT. In order to identify the defects giving rise to the detected signals, the measured data were compared with spectra simulated using spin-Hamiltonian parameters of defects previously reported in bulk and nano-structured ZnO. The simulations were performed using EasySpin [23] with the following spin Hamiltonian:

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

Here μ_B is the Bohr magneton, **B** is the external magnetic field, and **S** and **g** denote the electron spin and the electron g-tensor, respectively. The modeling was done in the same way as described in Ref. [21], taking into account a random tilt of the NWs by up to 20° from the z-direction and also random orientations of the crystallographic a- and b-axes among individual NWs constituting the ensemble. The thick solid curves (red online) display the results of the simulations, representing the best fit to the experimental data assuming a minimal number of the involved defects. The individual contributions of the chosen defects are shown by the dashed (red online) curves. The corresponding spin-Hamiltonian parameters are summarized in Table 1).

TABLE 1). Summary of spin-Hamiltonian parameters of the defects discussed in this work. ϕ is the angle between the *z* and *c* axis for the non-axial defects.

Center	S	Axial		Non-axial			ϕ (deg)
		$g_{\parallel}$	$g_{\perp}$	g_{xx}	g_{yy}	g_{zz}	
V _{Zn} ⁻	½	2.0193	2.0024	2.0173	2.0183	2.0028	110.75
V _{Zn} /Zn _i	1			1.9888	1.9893	1.9816	110.75
V _O ⁺	½	1.9960	1.9945				0
Zn _i ⁺	½	1.9595	1.9605				0
D*	½	1.9565	1.9605				0

From the low-field side to the high-field side of the spectrum the revealed defects could be identified as negatively charged zinc vacancies V_{Zn}^- , exchange-coupled V_{Zn}/Zn_i pairs and a donor D^* center [21]. Though D^* is believed to be a rather shallow donor, it is not the known effective-mass donor judging from its slightly larger g-factor as compared with that of the effective-mass donor. From Fig. 1(a), the most pronounced ODMR signal in the investigated sample originates from the exchange-coupled V_{Zn}/Zn_i pairs. Previously it was shown that such a spin-triplet system which consists of an exchange coupled pair of a donor (D) and an acceptor (A) is quite common in ZnO and often contains relatively distant D-A pairs. The latter conclusion was based on the observed suppression of the related signals at high MW modulation frequencies due to a slow recombination rate of these distant pairs [12]. To shed light on the distance between the D and A centers (i.e. V_{Zn} and Zn_i) within the revealed complexes, the ODMR spectra were measured at different microwave modulation frequencies. The results of these measurements are shown in Figure 1 (b). Apparently increasing MW modulation frequency does not affect the intensity of the ODMR signal from the exchange-coupled V_{Zn}/Zn_i pairs. This suggests that the DA pairs of the complex in our ZnO NWs are located in close proximity to each other. Furthermore, the intensity of the ODMR signal at 330 mT, which is attributed to the axial V_{Zn} center, increases with increasing MW modulation frequency. This may indicate either a shorter spin-relaxation time or a higher recombination rate of these centers as compared with their non-axial counterparts. Alternatively, another ODMR signal with the same g-values as that for the axial component of V_{Zn} can be activated with increasing MW modulation frequency. In order to clearly distinguish between these two possibilities further studies are necessary and are currently in progress.

FIGURE 1. ODMR spectra of the as grown ZnO NWs (the thin solid lines, black) and the Ni-coated ZnO NWs (the dotted line, blue) taken at 3 K (a) at different orientations of an applied magnetic field, (b) under different microwave modulation frequencies, and (c) different spectral ranges for detection. The ODMR spectra of the paramagnetic V_{Zn} , D^* and V_{Zn}/Zn_i centers simulated by using the spin-Hamiltonian parameters from table 1) are shown by the thin dashed lines (red), whereas the total simulated spectra are displayed by the thick solid lines (red).

To gain further insight into the defect recombination processes we studied the dependence of the ODMR signal on the spectral range of the detected PL (Fig. 1 (c)). From Fig 1 (c), the signals related to V_{Zn} , V_{Zn}/Zn_i pairs and D^* centers are the most pronounced within the 715-1000 nm spectral range, consistent with our previous result from bulk ZnO [8]. In the spectral range of 590-710 nm, an additional ODMR signal can be observed at a magnetic field of 331 mT. From its g-value, this signal can be attributed to positively charged oxygen vacancies V_O^+ which were shown [24] to contribute to the yellow (i.e. centered around 600 nm) emission in electron irradiated ZnO. We would like to point out that the ODMR signals related to V_O^+ were so far only reported in the e-irradiated ZnO. The present work proves that these defects are also formed in as-grown ZnO NWs and establishes the spectral range of the PL emission involving this defect as being of 590-710 nm.

Let us now discuss effects of Ni coating on the revealed defects. From Fig. 1(a), the same ODMR spectra are detected from the as-grown and Ni-coated ZnO NWs, which implies that the coating does not significantly affect the revealed defects. This in turn means that the defects observed in the as-grown and Ni-coated ZnO NWs must be located in the bulk of the NW, since Ni coating should certainly affect surface states [22].

CONCLUSIONS

In conclusion, we have employed the ODMR technique to examine optical and defect properties of the as-grown and Ni-coated ZnO NWs grown by RTCVD. Several grown-in defects are revealed by monitoring visible PL emissions and are attributed to zinc vacancies, a shallow (but not effective mass) donor, exchange-coupled pairs of zinc vacancies and zinc interstitials, as well as oxygen vacancies. The latter can only be detected within the spectral range of 590-710 nm. It is also found that the same ODMR signals are observed in both as-grown and Ni-coated NWs, indicating that the observed defects are located in the bulk regions of the NWs.

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