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## Photoluminescence Properties of ZnO Nanowires Grown on Ni Substrate

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Photoluminescence studies of zinc oxide nanowires produced by a carbo-thermal method on a nickel foil substrate are reported. Two types of as-grown samples: the first — containing only buffer film, and the second — containing both zinc oxide nanowires and buffer film grown in the same technological process, were investigated by means of the temperature-dependent photoluminescence. X-ray diffraction measurements of buffer film show that it is polycrystalline and is composed from wurtzite-type ZnO (main phase) and includes minority phases: rock salt type (Ni,Zn)O and hexagonal C<sub>3</sub>N<sub>4</sub>. The shape of the apparently monocrystalline nanowires is characterized by hexagonal section matching with the expectations of the hexagonal ZnO structure. The presence of LO-phonon replicas in photoluminescence spectra for the second sample is used as an argument for confirmation that ZnO nanowires are single crystalline. The method of growth of ZnO nanowires on nickel oxide opens perspectives to produce Zn<sub>1-x</sub>Ni<sub>x</sub>O diluted magnetic semiconductor nanowires.

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### 1. Introduction

Zinc oxide (ZnO) exhibits a wide, direct band-gap (3.37 eV) and a large exciton binding energy of 60 meV. A key requirement for many applications involving ZnO is its doping with specific elements in order to engineer its electrical and optical properties. By doping of ZnO with transition metal ions such as Fe, Co, Ni, and Mn, one can produce a diluted magnetic semiconductor (DMS) which may be ferromagnetic at high temperature. Carrier induced stable room tem-

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perature (RT) ferromagnetism has been predicted for transition-metal doped ZnO DMSs [1]. This prediction gave a motivation to extensive investigations ZnO based solid solutions, in particular to Ni-doped ZnO films [2], polycrystalline powders [3], nanoparticles [4], and nanowires [5, 6]. In this paper we report on the growth of ZnO nanowires (NWs) on a nickel foil substrate covered with a nickel oxide (NiO) thin film by carbo-thermal method and on the studies of the properties of grown NWs with the use of scanning electron microscopy (SEM), X-ray diffractometry (XRD) measurements, and photoluminescence (PL) spectroscopy.

## 2. Experiments

The growth of ZnO pencil-shaped nanowires by carbo-thermal method was carried out in a horizontal tube furnace in open quartz tube under ambient air atmosphere. The growth temperature was 930°C. The nickel substrate was chosen because during technological process its surface gets oxidized to NiO, a material that is known to be a good catalyst for the growth of ZnO nanostructures [7, 8]. A mixture of ZnO and graphite powder (0.3 g) with the mass ratio 1:1 was transferred to the round alumina boat and covered by a nickel foil. The distance between the powder surface and the nickel substrate was equal to 2 mm. Then the open quartz tube with alumina boat was inserted into the hot furnace. The growth process lasted 20 min. Subsequently, the quartz tube with alumina boat was pulled out from the furnace. After cooling down to RT, gray colored products were visible on the part of nickel substrate. The circularly shaped area with NWs formed on the surface of nickel foil corresponding to the edge of alumina boat.

XRD measurements were used for crystallographic phase analysis and for determination of a preferred orientation of the grown nanocrystals. For this structural characterization a high-resolution PANalytical diffractometer (Cu  $K_{\alpha_1}$  radiation) was used. The morphology of as-grown NWs and buffer film was investigated by SEM. The PL was excited using a 325 nm He–Cd laser lines and detected by CCD camera coupled to a spectrometer. The PL measurements were performed in a continuous-flow cryostat at temperatures in the range from 10 K to 296 K. Two types of as-grown samples were investigated: the first containing both nanowires and polycrystalline buffer film grown in the same technological process (sample A), and the second one containing only the buffer film (sample B).

## 3. Results

Surface morphology of the samples and NWs dimensions were determined by SEM. Figure 1 shows a low-magnification SEM image (45° tilted view) which indicates that we obtained straight ZnO NWs with uniform diameter and with smooth surfaces. The NWs are randomly distributed on the substrate and do not grow perpendicularly to the substrate surface. The inset of Fig. 1 shows a high-magnification SEM image of a pencil-like shape single ZnO nanowire with characteristic hexagonal section, and a polycrystalline buffer film. The average

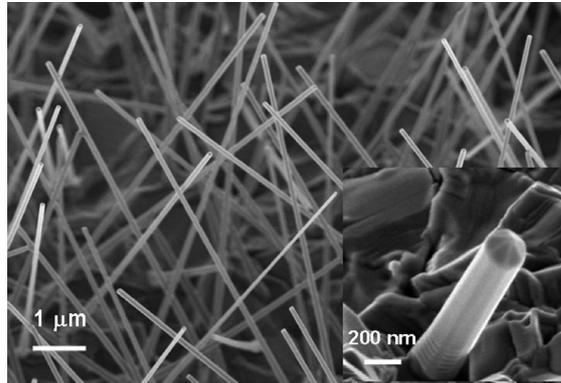


Fig. 1. SEM images ( $45^\circ$  tilted view) of the ZnO nanowires grown on nickel foil at  $930^\circ\text{C}$ . The inset shows magnification of a pencil-like shape single ZnO nanowire with characteristic hexagonal section and polycrystalline buffer film at the bottom.

lengths and diameters of NWs deduced from SEM images are in the range  $5\text{--}7\ \mu\text{m}$  and  $150\text{--}300\ \text{nm}$ , respectively.

Figures 2a and b illustrate typical XRD patterns of the buffer film measured on sample B for small and large scattering angles, respectively. The presence of 100, 002, 101 etc. reflections of ZnO (see Fig. 2a and b) confirms polycrystalline nature of the sample. Apart from reflections characteristic of wurtzite type ZnO, reflections from other phases are also visible. On the other hand, reflections at  $36.93^\circ$ ,  $42.92^\circ$ ,  $62.39^\circ$ ,  $74.81^\circ$ , and  $78.80^\circ$  (see Fig. 2a and b) were identified [9, 10] as corresponding to cubic  $\text{Ni}_{0.79}\text{Zn}_{0.21}\text{O}$  reflections 111, 200, 220, 311 and 222, respectively. The lattice parameter, and hence composition of cubic (Ni,Zn)O, was calculated from direct measurements of the scattering angle position for reflection 311. Additionally, the very weak reflection at  $36.93^\circ$  is probably related to NiO 200 reflection. In the pattern presented in Fig. 2a reflections at  $25.40^\circ$ ,  $26.41^\circ$ , and  $54.58^\circ$  were identified based on literature data [11] as corresponding to carbon nitride (hexagonal  $\text{C}_3\text{N}_4$ , space group  $P\bar{6}m2$ ) reflections 101, 002, and 200, respectively. Summarizing, XRD measurements confirm that the buffer film is polycrystalline, built from the wurtzite ZnO and rock salt (Ni,Zn)O structures. On the basis of XRD patterns we conclude that during our technological process the following phases were produced on Ni substrate and formed the buffer film:  $\text{Ni}_{0.79}\text{Zn}_{0.21}\text{O}$ , and ZnO, the first of them being an interface resulting from oxidation of Ni at presence of  $\text{ZnO}_x$  ( $x < 1$ ) vapor.

Figure 3a displays a low magnification SEM image of the as-grown ZnO NWs and buffer film, both grown in the same process at  $930^\circ\text{C}$ . For these two types of samples (sample A and B) the temperature dependence of the near band-gap PL was measured and analyzed. The strong near-band edge (NBE) emission observed both for the sample A and sample B confirms good optical quality of ZnO material. The samples A and B not only exhibit a strong and sharp PL signal in the UV

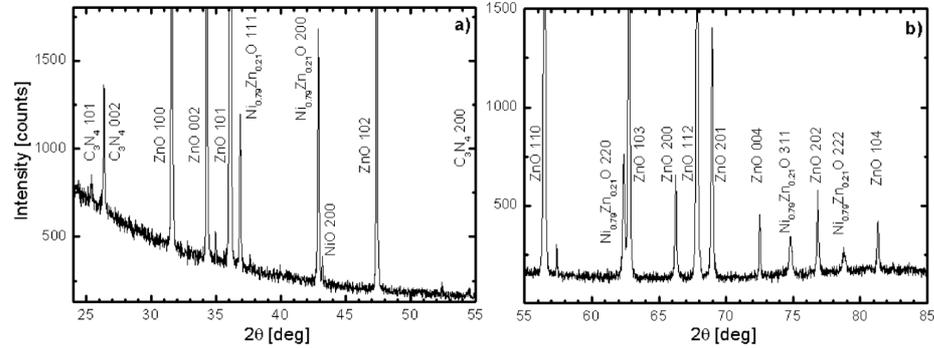


Fig. 2. X-ray diffraction patterns of the buffer film grown at temperature of  $930^{\circ}\text{C}$  on nickel foil substrate. The patterns were measured on sample B for small (a) and large (b) scattering angles.

but also a weak, green, defect related emission (with comparable intensities) in all collected PL spectra. The green band (at 2.34 eV) originates from the radiative recombination of photogenerated holes with singly ionized oxygen vacancies [12].

Low-temperature PL spectra shown in insets to Figs. 3b (3c) for sample A (B) are dominated by an emission peak centered at 3.361 eV (3.365 eV) originating from the radiative recombination of donor-bound excitons ( $\text{D}^0\text{X}$ ). This transition is inhomogeneously broadened due to the overlapping of several lines related to various donors. For both sample A and sample B, the spectra clearly show that the exciton emission is shifting to lower energy with increasing temperature. At temperatures 40–60 K, a small peak at 3.377 eV (3.375 eV) assigned to the free-exciton (FX) recombination starts to be sharply outlined, and simultaneously the intensity of the  $\text{D}^0\text{X}$  line, that was dominant at low  $T$ , distinctly increases. For sample A, as the temperature increases further, the FX emission becomes stronger and finally dominates the spectrum at RT. The NBE emission for sample B decreases relatively quickly with increasing temperature, and above 60 K disappears. At room temperature, only defect related emission is visible.

Additionally, at low temperature for sample A, we observe a peak at 3.328 eV which is most probably due to a two-electron satellite (TES) transitions of the donor-bound exciton recombination. In this process the donor electron of the  $\text{D}^0\text{X}$  is left in an excited ground state when the donor-bound exciton recombines. Next to the TES peak there are peaks at 3.307 eV (3.309 eV) which are attributed to the acceptor-bound excitons ( $\text{A}^0\text{X}$ ) and at 3.255 eV (3.245 eV) attributed to the donor-acceptor pair (DAP) emission.  $\text{A}^0\text{X}$  transition could be related to nitrogen acceptor and/or to complex that was formed due to the diffusion of Ni ions into ZnO [5]. The presence of atomic nitrogen during the growth process is confirmed by the XRD measurements where  $\text{C}_3\text{N}_4$  was formed in buffer film (see Fig. 2a).

As distinct from low-temperature spectra for sample B (inset in Fig. 3c), the spectra of sample A (inset in Fig. 3b) contain additionally phonon replicas of

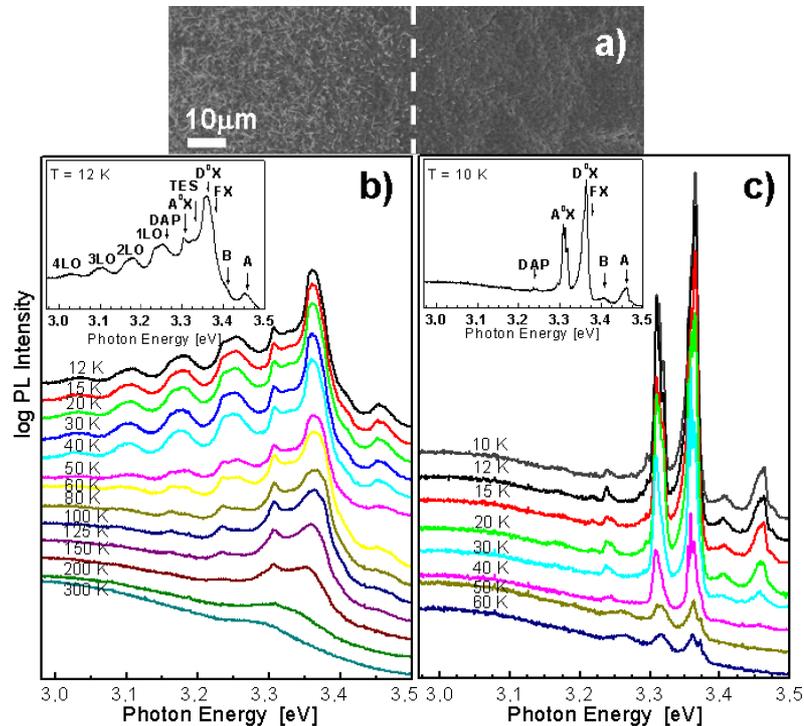


Fig. 3. (a) SEM image of the sample with ZnO nanowires (on the left — sample A) and polycrystalline buffer film (on the right — sample B) grown at temperature of 930°C. Temperature dependent PL spectra of sample A (b) and sample B (c). The insets show details of PL spectra obtained at the lowest temperature.

acceptor-bound excitons ( $A^0X$ ) and the DAP (up to fourth-order) which indicate a good crystallographic quality of this sample. The interpretation of these weak and broad peaks at about 72 meV below the energy of  $A^0X$  and DAP lines (see Fig. 3b) and next every 72 meV as attributed to the phonon replicas of  $A^0X$  and DAP (lines in Fig. 3b denoted as LO1 up to LO4) is based on a good agreement of the value of 72 meV with the longitudinal optical (LO) phonon energy in ZnO. The presence of LO-phonon replicas for sample A could be used as a proof that ZnO NWs are single crystalline, since no such LO-phonon replicas were observed for polycrystalline sample B.

Moreover, above the NBE emission of ZnO one can see (inset in Fig. 3a and b) two additional lines denoted as line A (3.46 eV) and line B (3.41 eV). Taking into account a possibility of Zn incorporation into cubic NiO the composition of  $Ni_{1-x}Zn_xO$  was calculated from energy position of line A. The obtained value of  $x = 0.23$  is in good agreement with XRD measurements ( $x = 0.21 \pm 0.01$ ). Hence, line A is interpreted as an excitonic recombination of  $Ni_{0.79}Zn_{0.21}O$  and line B as conduction band-to-acceptor level transition in this material.

The comparison of the intensities of particular PL lines, between two investigated samples, suggests that the obtained buffer film is Ni-rich and that as-grown ZnO NWs contain some Ni as well, although in a smaller concentration.

#### 4. Conclusions

ZnO NWs were grown by a carbo-thermal method on a nickel foil substrate. X-ray diffraction measurements show that buffer film is polycrystalline, has wurtzite hexagonal structure (ZnO), and includes minority phases: rock salt type ((Ni,Zn)O) and hexagonal ( $C_3N_4$ ). Both types of samples show strong near band edge emissions, a signature of good optical quality. The emission caused by radiative recombination of excitons bound to neutral donor ( $D^0X$ ) dominates the PL spectra at low temperatures. The comparison of PL spectra results suggests that buffer film is Ni-rich and that ZnO NWs grown on Ni substrate contain some nickel as well, although in a smaller concentration. This opens perspectives to produce  $Zn_{1-x}Ni_xO$  diluted magnetic semiconductor nanowires.

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