Vol. **112** (2007) *ACTA PHYSICA POLONICA A* No. 2

Proceedings of the XXXVI International School of Semiconducting Compounds, Jaszowiec 2007

Photoluminescence Properties of ZnO and ZnCdO Nanowires

W. Zaleszczyk*, K. Fronc, M. Aleszkiewicz, W. Paszkowicz, J. Wróbel, P. Dłużewski, S. Kret, M. Klepka, Ł. Kłopotowski, G. Karczewski and T. Wojtowicz

Institute of Physics, Polish Academy of Sciences
al. Lotników 32/46, 02-668 Warsaw, Poland

We report on the photoluminescence studies of ZnO and ZnCdO nanowires grown on SiO_2/Si substrates by low-pressure vapor phase synthesis. X-ray diffraction and transmission electron microscopy measurements show that the crystallographic structure of these ZnO and ZnCdO nanowires is of wurtzite-type with a high crystal perfection. Surface morphology of samples was determined by scanning electron microscopy and atomic force microscopy. The photoluminescence spectra of as-grown nanowires, nanowires extracted from the substrate and deposited onto Si wafer, and nanowires dispersed in ethanol by sonication were investigated at room temperature and compared to each other. The temperature dependence of the near band-gap photoluminescence emitted by the as-grown nanowires was also measured and analyzed.

PACS numbers: 78.55.Et, 78.67.Bf, 81.05.Dz, 81.07.Bc

1. Introduction

Zinc oxide (ZnO) is a wurtzite-type II–VI compound semiconductor with a wide, direct band-gap (3.37 eV at room temperature (RT)) and has an exciton binding energy of 60 meV, larger than thermal energy at RT of $k_{\mathrm{B}}T \approx 25$ meV. By alloying with CdO, which has a cubic NaCl-type structure and a narrower direct band gap of 2.4 eV [1], the band gap of resulting ZnCdO can be redshifted to a blue or even a green spectral range. Nanowires made of these oxides are promising "building blocks" for nanometer-scale optoelectronic devices operating in the green to UV spectral region and therefore, photoluminescence (PL) properties of ZnO [2–4] and ZnCdO [4, 5] nanowires (NWs) have attracted significant attention recently.

*corresponding author; e-mail: wzal@ifpan.edu.pl

2. Experiments

The fabrication of ZnO and $Zn_{1-x}Cd_xO$ ($x \approx 0.02$–0.05) tetrapod-like nanowires via a low-pressure vapor phase synthesis was performed at various temperatures (435, 535, and 570°C) at a pressure in the order of 1×10^{-2} Torr. A silicon wafer with 500 nm SiO_2 cap was used as a substrate. The growth was performed in a horizontal quartz tube furnace using metallic zinc (and cadmium) powder and oxygen gas. In the growth process, 3 g of high purity (5N) metallic zinc and in the case of ZnCdO NWs, also 0.6 g of cadmium powder was placed in quartz ampoule with a small 0.5 mm^2 hole. The ampoule was located inside the quartz tube in the vicinity of the substrates. The reaction lasted for 60 min. After cooling the furnace down to RT, grey colored products were seen on the Si substrate and on the quartz tube walls. Apart from the as-grown samples also NWs extracted from the substrate and deposited onto Si wafer and NWs dispersed in ethanol by sonication were studied. X-ray diffraction (XRD) measurements were used to determine the crystal phase of NWs and their preferred orientation. The presence of Cd was confirmed by electron probe microanalysis (EPMA). The general morphologies of as-grown NWs and NWs extracted from the original substrate and deposited onto the Si wafer were investigated by scanning electron microscope (SEM) and atomic force microscope (AFM), respectively. Detailed structural properties of NWs removed from SiO_2/Si and deposited on carbon mesh were examined by transmission electron microscope (TEM) equipped with selected area electron diffraction (SAED). The PL excited using 325 nm (He–Cd) or 351 nm (Ar^+) laser lines was measured at RT for all NWs and for as grown samples also as a function of temperature in the range of 13–296 K.

3. Results

The typical lengths and diameters of NWs obtained by the above described method are in the range of 0.1–10 μm and 10–100 nm, respectively. Figures 1a–f show high-magnification SEM images, which indicate that the density of NWs depends on the growth temperature. With increasing growth temperature the density of the NWs decreases. Figures 1h and i illustrate the typical XRD patterns for the ZnO and ZnCdO NW, respectively. A low magnification TEM image of the single ZnO NW can be seen in Fig. 1g. The corresponding SAED pattern (inset in Fig. 1g) and XRD patterns confirm that the NWs are single crystalline with the wurtzite structure.

The strong near-band edge (NBE) emission is observed from the as-grown ZnO and ZnCdO NWs. This additionally confirms the results of structural studies that the NWs have a very good crystallographic quality. The ZnO NWs exhibit not only a strong and sharp PL signal in the UV but also a weak, green band. As distinct from ZnO NWs, ZnCdO NWs show a stronger green, defect related emission. The green band in the PL spectra originates from the radiative recombination of photogenerated holes with singly ionized oxygen vacancies [6].

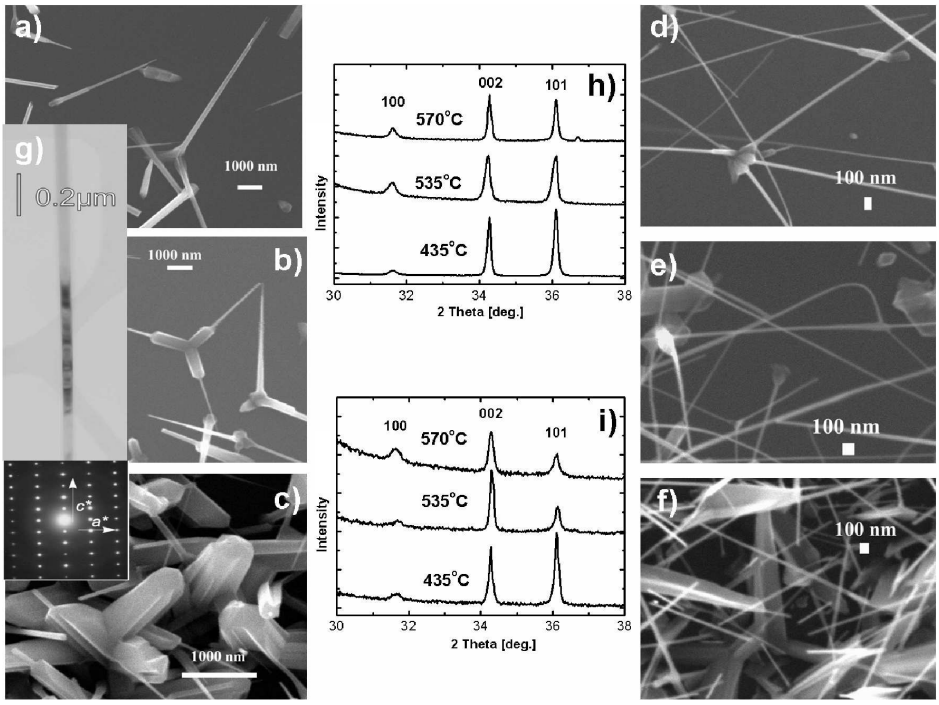

Fig. 1. (a)–(c) SEM images of the ZnO nanowires grown at various temperatures on SiO_2/Si substrate (T_g = 570, 535, 435°C for (a), (b), and (c), respectively); (d)–(f) SEM images of ZnCdO nanowires also grown on Si substrate at temperatures of 570, 535, 435°C ((d), (e), and (f), respectively); (g) low-magnification TEM image of ZnO nanowire grown at $T_g = 535$°C and corresponding SAED pattern. XRD patterns of the as-grown ZnO and ZnCdO nanowires are shown in parts (h) and (i), respectively.

Figure 2a and b displays, respectively, the low magnification SEM images of the as-grown ZnO and ZnCdO NWs, both grown at 435°C. For these two samples the temperature dependence of the near band-gap PL was measured and analyzed. The low-temperature PL spectra shown in Fig. 2c (d) for ZnO (ZnCdO) NWs are dominated by the emission peak at 3.359 eV (3.361 eV) originating from the radiative recombination of acceptor-bound excitons (A^0X). This line is inhomogeneously broadened due to the overlapping of several lines related to various acceptors. For both ZnO and ZnCdO NWs, the spectra clearly show that the exciton emission is shifting to lower energy with increasing temperature. At temperatures 50–80 K, a small peak at 3.369 eV (3.370 eV) assigned to the free-exciton (FX) recombination starts to appear, and simultaneously A^0X line, that was predominant at low T, disappears. This is interpreted as the unbinding of exciton with increasing thermal energy. As the temperature increases further, the donor–acceptor pair (DAP) emission becomes stronger than the FX emission and finally the transitions related to DAP dominate the spectrum at RT.

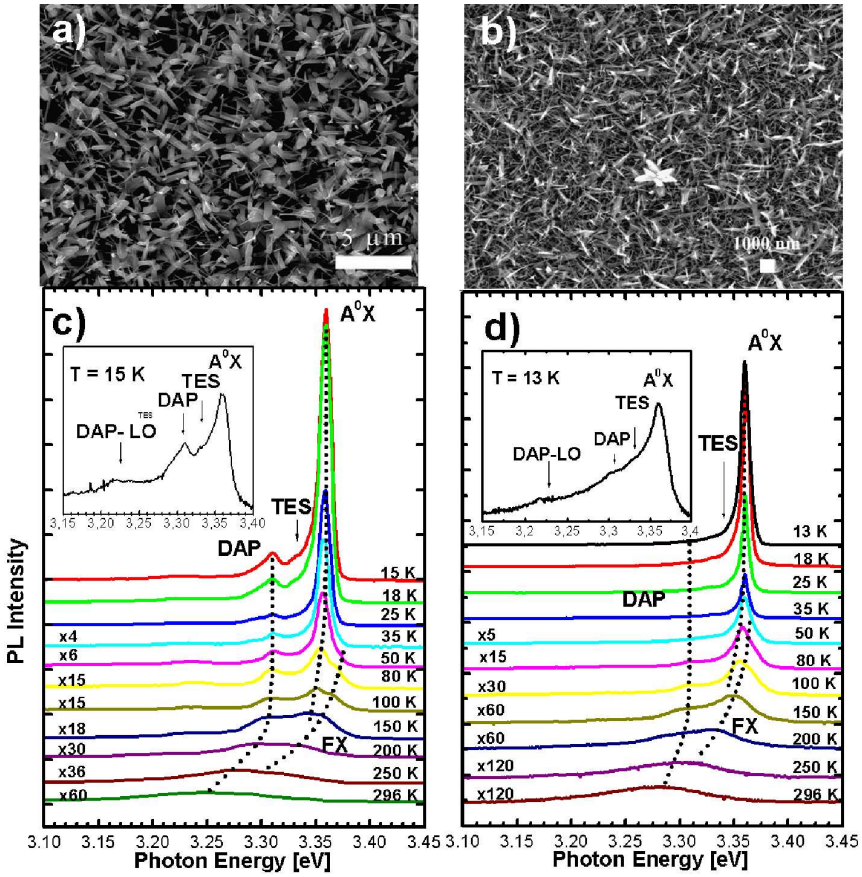

Fig. 2. SEM images of the ZnO and ZnCdO nanowires on substrate SiO_2/Si grown at temperature of 435°C ((a) and (b), respectively) and corresponding temperature--dependent PL spectra ((c) and (d), respectively). Both samples were excited with the use of 325 nm laser line. The insets show details of PL spectra obtained at the lowest temperature.

Additionally, at low temperature, we observe a peak at 3.329 eV (3.330 eV), which most probably is due to the two-electron satellite (TES) transition. Next to the TES peak there is a peak at 3.311 eV (3.306 eV), which is attributed to the DAP emission. Additionally, a weak and broad peak at energies around 3.235 eV (3.234 eV), that is 76 meV (72 meV) below the energy of DAP photoluminescence, is also visible. Since the energetic difference between peaks is almost identical to the longitudinal optical phonon energy, this additional peak is attributed to the phonon replica of DAP and denoted as DAP–LO. In spite of the narrowing of band gap in ZnCdO, a blueshift (of about 2 meV) of the NBE emission was observed in the PL spectra. This might be caused by a spinodal decomposition of ZnCdO into ZnO and CdO rich regions.

In order to study the PL from a small number of individual NWs we either dispersed them in ethanol by sonication or extracted them mechanically from the substrate and deposited onto Si wafer. The comparison of the room-temperature μ-PL measurements performed on several (≈ 10) ZnCdO NWs resting on Si wafer with the macro-PL of as-grown nanowires shows also a blueshift of the NBE emission (see Fig. 3a). This effect is probably a consequence of quantum confinement effect in nanowires having smaller diameters that were selectively transferred onto the silicon substrate.

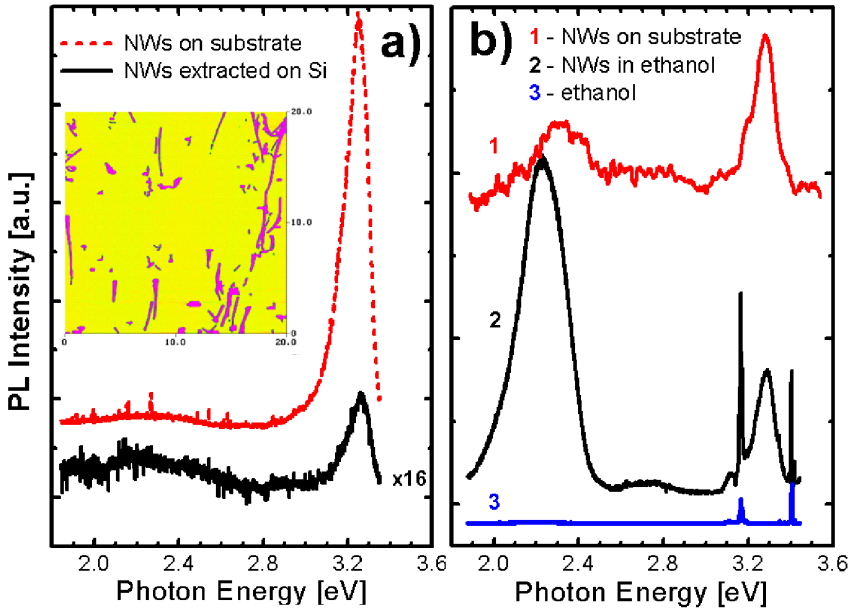

Fig. 3. (a) Comparison of RT photoluminescence spectra of ZnCdO nanowires grown at temperature of 570°C: as-grown (dashed line) and dry-extracted onto new Si wafer (solid line); (b) comparison of RT photoluminescence spectra of ZnCdO nanowires grown at temperature of 535°C: as-grown (line 1), dispersed in ethanol (line 2) and pure ethanol (line 3). All samples were excited with 351 nm laser line. Inset in part (a) shows AFM image (20×20 μm^2) of ZnCdO nanowires resting on a Si wafer.

Figure 3b presents a comparison at RT of PL spectrum of as-grown ZnCdO nanowires (line 1) and dispersed in ethanol solution (line 2). For clarity, in Fig. 3b we present the PL spectrum of pure ethanol (line 3). An increase in intensity and the redshift of green emission related to structural defects and impurities is observed for ZnCdO NWs dispersed in ethanol. Immersion in ethanol results in a change of the charge state on the NW surface. This change is related to adsorption and desorption of molecular oxygen on the NW surface. The influence of the presence of oxygen on the surface was previously reported for ZnO nanorods [7],

In-doped ZnO nanowires [8], and nanocrystalline ZnO particles [9]. It gives prospects for the applications of ZnO nanostructures for the construction of gas sensors.

4. Conclusions

ZnO and ZnCdO nanowires were obtained by a low-pressure vapor phase synthesis at various temperatures. X-ray diffraction and transmission electron microscopy measurements show that ZnO and ZnCdO nanowires are single crystalline and have wurtzite hexagonal structure. Both types of nanowires show strong near band edge emissions, a signature of good optical quality. The emission caused by radiative recombination of excitons bound to neutral acceptor (A^0X) dominates PL spectra at low temperatures. The results of PL studies confirm that the optical properties of ZnO and ZnCdO nanowires as well as their temperature dependence are comparable to the properties of bulk material.

Acknowledgments

The research was partially supported by the Ministry of Science and Higher Education (Poland) through grant N515 015 32/0997 and by the network "New materials and sensors for optoelectronics, information technology, energetic applications and medicine".

References

[1] M. Yan, M. Lane, C.R. Kannewurf, R.P.H. Chang, *Appl. Phys. Lett.* **78**, 2342 (2001).

[2] Ü. Özgür, Ya.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Doğan, V. Avrutin, S.J. Cho, H. Morkoç, *J. Appl. Phys.* **98**, 041301 (2005).

[3] B.P. Zhang, N.T. Binh, Y. Segawa, K. Wakatsuki, N. Usami, *Appl. Phys. Lett.* **83**, 1635 (2003).

[4] C.X. Shan, Z. Liu, Z.Z. Zhang, D.Z. Shen, S.K. Hark, *J. Phys. Chem. B* **110**, 11176 (2006).

[5] F.Z. Wang, H.P. He, Z.Z. Ye, L.P. Zhu, *J. Appl. Phys.* **98**, 084301 (2005).

[6] K. Vanheusden, W.L. Warren, C.H. Seager, D.R. Tallant, J.A. Voigt, B.E. Gnade, *J. Appl. Phys.* **79**, 7983 (1996).

[7] Y. Lin, D. Wang, Q. Zhao, Z. Li, Y. Ma, M. Yang, *Nanotechnology* **17**, 2110 (2006).

[8] L.M. Li, C.C. Li, J. Zhang, Z.F. Du, B.S. Zou, H.C. Yu, Y.G. Wang, T.H. Wang, *Nanotechnology* **18**, 225504 (2007).

[9] A. van Dijken, E.A. Meulenkamp, D. Vanmaekelbergh, A. Meijerink, *J. Phys. Chem. B* **104**, 4355 (2000).