Proc. XXXVII International School of Semiconducting Compounds, Jaszowiec 2008

Characterization of ZnO Films Grown at Low Temperature

E. Przeździecka[a], T. Krajewski[a], Ł. Wachnicki[a,b], A. Szczepanik[a,b], A. Wójcik-Głodowska[a], S. Yatsunenko[a], E. Łusakowska[a], W. Paszkowicz[a], E. Guziewicz[a] and M. Godlewski[a,b]

[a]Institute of Physics, Polish Academy of Sciences
al. Lotników 32/46, 02-668 Warsaw, Poland
[b]Dept. of Mathematics and Natural Sciences College of Science
Cardinal S. Wyszyński University, Dewajtis 5, 01-815 Warsaw, Poland

ZnO thin films were grown by atomic layer deposition method at extremely low temperature using a reactive diethylzinc as a zinc precursor. Optical properties, electrical properties and surface morphology were examined by photoluminescence, Hall effect and atomic force microscope. The study shows correlation between optical, electrical properties and surface morphology in a series of samples of different thickness.

PACS numbers: 78.55.−m, 81.10.−h, 85.30.Fg

1. Introduction

ZnO is a direct wide band gap semiconductor ($E_{\mathrm{g}} \approx 3.35$ eV at room temperature) with high exciton binding energy (60 meV, compared to 25 meV in GaN). The present interest in ZnO properties relates to the fact that ZnO is a superior candidate for minority-carrier-based devices, such as gas sensors, transparent *p–n* junctions, light emitting diodes and transistors. Moreover, ZnO combines semiconductor and oxide properties. Thus, it can likely replace ITO (Indium Tin Oxide) as transparent conductive oxide material. This wide band gap material has unique electrical properties: mobility in monocrystalline ZnO layer is about 250 cm^2/(V s), which is not record high, but the carrier mobility in polycrystalline low temperature layers was reported even at the range of 50–100 cm^2/(V s) [1]. This is considerably better than in the case of other semiconductors. For example, in silicon, the mobility in a monocrystalline layer is about 1000 cm^2/(V s), whereas in a polycrystalline one it is only at the level of 1 cm^2/(V s). Therefore, polycrystalline ZnO layers may work in transistors [2–5] and sensors [6, 7].

ZnO thin films can be prepared by a variety of growth techniques such as: sol-gel method, sputtering [8, 9], oxidation of zinc based materials [10–12], metal organic chemical vapor deposition (MOCVD) [13], molecular beam epitaxy (MBE) [14, 15] or atomic layer deposition (ALD) [16]. Recent studies show that low temperature (LT) ZnO growth is crucial to avoid the foreign phases in a material doped with a transition metal [17]. Moreover, low temperature growth makes it possible to obtain ZnO on flexible or organic substrates, as reported separately at this conference.

In order to obtain a good quality Schottky junction one has to optimize ZnO layer. The typical method involves decreasing concentration and increasing mobility of the carriers. But still the quality of the diode is improved when we correlate electrical and optical parameters of the samples. The present research reveals that the best results are obtained when both, a low free electron concentration and simultaneously low deep defect-related luminescence, are achieved.

In this paper we show how to control optical and electrical properties of polycrystalline LT ZnO thin film grown by ALD using diethylzinc (DEZn) as a zinc precursor and water as an oxygen precursor at temperatures ranging from 60 to 240°C.

2. Growth conditions

In the ALD technique, the precursors are introduced sequentially into the growth chamber and the cycles in which individual precursors reach the substrate are separated by the cycles of purging with an inert gas. In the deposition processes we used deionized water as an oxygen precursor, reactive DEZn [$Zn(C_2H_5)_2$] as a zinc precursor and high purity nitrogen as a purging gas. ZnO thin films were deposited on (100) silicon substrates. Both precursors were kept at room temperature, whereas the substrate temperature was 100°C.

Pulse time of DEZn was 60 ms and pulse time of water was 15 ms. Purging time after DEZn was 8 s and after H_2O was 20 s. In the series of samples we changed the number of cycles (thickness of the sample) from 100 to 1000 cycles (from 0.032 μm to 0.171 μm).

3. Results and discussion

In photoluminescence (PL) measurements, the samples were excited by the 325 nm He–Cd laser line or by the xenon lamp. The measurements were performed at 10 K and 300 K. Electrical properties were obtained from the Hall measurements at room temperature. The samples surface morphology was examined by atomic force microscope (AFM). A structural characterization on the ZnO layers was assessed by X-ray diffraction (XRD) measurements.

3.1. Surface morphology and structural characterization

Thin ZnO layers obtained by ALD in LT show atomically flat surfaces, as it was derived from the AFM studies. The root-mean-square (RMS) of surface roughness varied between 1 and 7 nm depending on the thickness of samples (Fig. 1). When thickness of samples increased roughness also increased. XRD investigations related this observation to a gradual improvement of film crystallinity.

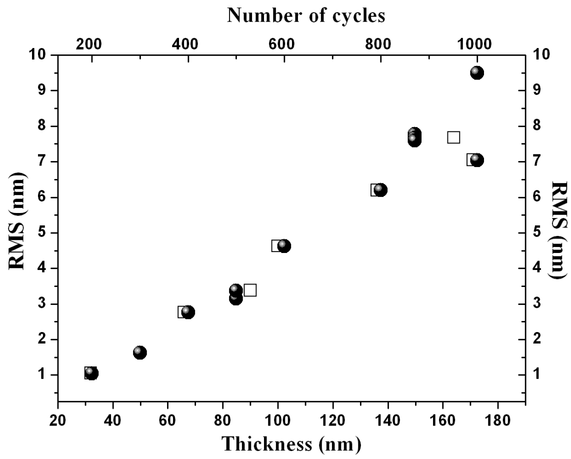

Fig. 1. RMS obtained from AFM study, for series of different thickness samples grown under 100°C at the same growth conditions. Black circles — RMS versus number of cycles; open squares — RMS versus thickness.

Even though all samples were found to be polycrystalline, thicker films were more ordered, showed narrower XRD peaks and columnar structure with larger diameter. Diffraction maxima corresponding to (10.0), (00.1), (10.1) and (11.0) crystallographic planes were observed in the ZnO sample grown at above specified conditions. The intensities of XRD maxima depend on growth conditions (temperature and purging time). In the studied series of ZnO films we observed domination of (00.1) and (10.0) crystallographic orientation [18].

3.2. Optical properties

Figure 2a and b show PL spectra measured at 9 K and 300 K. One can notice a clear correlation between film thickness and the PL observed. When we increased the thickness of samples we observed increase in the blue and UV luminescence (P_1 in Fig. 2a) and decrease in the defects related luminescence in thick (1000 cycles sample) (P_2 and P_3 in Fig. 2a and b). Intensities of the defects related luminescence have maximum at 600 cycle's samples, and in thicker samples decrease (Fig. 2c). Origin of the broad PL band in red-green colors is still disputed, as reviewed recently [19–21]. The green ZnO PL may be related to oxygen vacancy (V_O) or zinc interstitial (Zn_i). Yellow-red band may be related to Li [21, 22] or hydrogen [20]. Thus, the decrease in defects-related PL means that the concentration of deep defects is decreasing when thickness of sample is increasing. At the same time the electron concentration in our samples is increasing, indicating a smaller compensation of shallow donors by some unidentified deep defects.

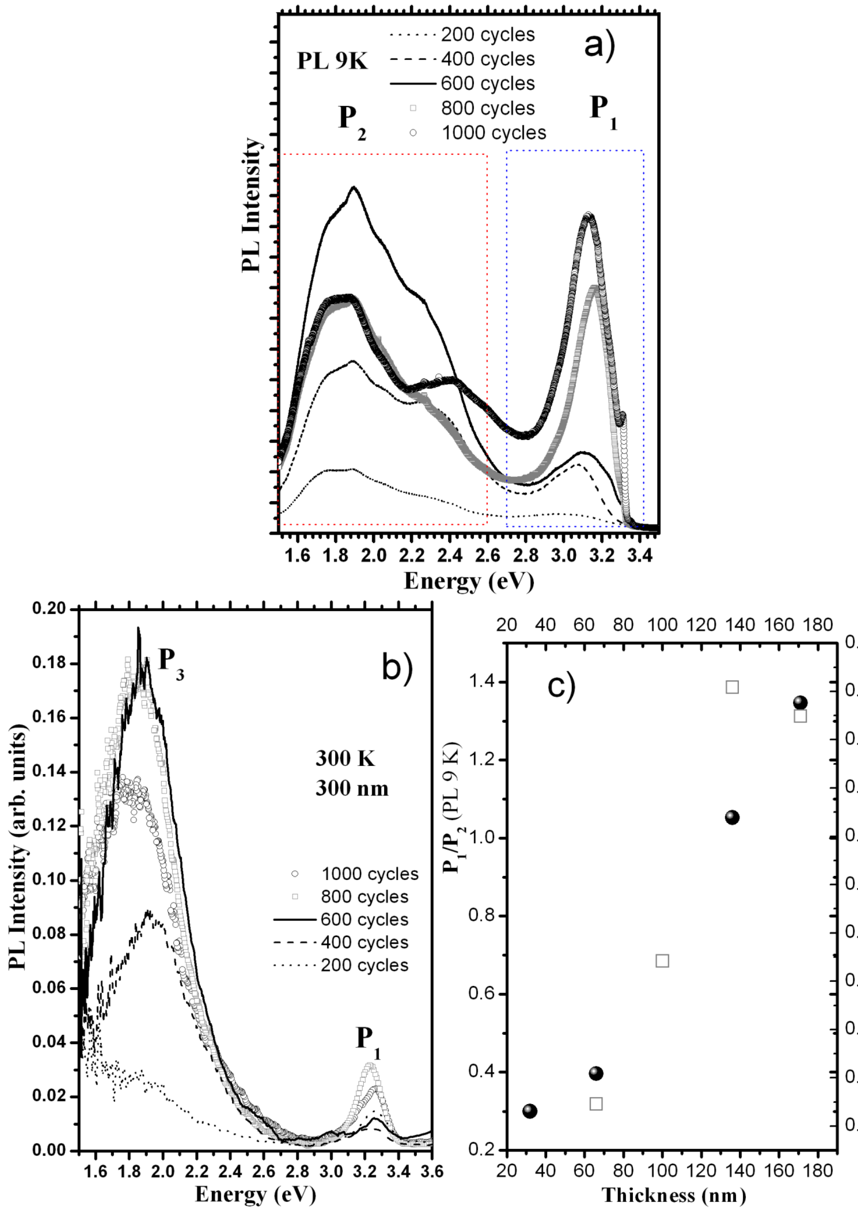

Fig. 2. Photoluminescence spectra of series of samples with different thickness: open circles — 171 nm, open grey squares — 136 nm, solid line — 100 nm, dash line — 66 nm, and dot line — 32 nm; measured: (a) at 9 K, (b) at 300 K, and (c) defects PL peaks intensities versus thickness of samples, black circles — at 300 K; grey squares — at 9 K.

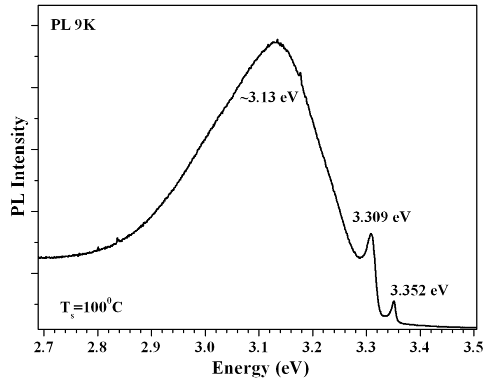

Fig. 3. Photoluminescence spectra of ZnO sample (after optimization growth parameters), measured at 9 K.

In low temperature PL spectra (Fig. 3) we observed a small peak at 3.352 eV corresponding probably to a donor bound exciton (D^0X). Peak at 3.309 eV is probably associated with a free to band transmission or alternatively with deep acceptor. We also observed broad line located at 3.13 eV. The third line may be associated with zinc vacancies [23] or other defects. Because our samples were grown at an extremely low temperature, observation of excitonic luminescence suggested that we have a good quality ZnO layer.

3.3. Electrical properties

Electrical parameters of LT ZnO thin films were obtained from the Hall effect measurements, which were carried out by the direct current (dc) four probe method at room temperature in the magnetic field up to 0.5 T. For the Hall measurements we deposited Cr/Ag ohmic contacts which were evaporated at low temperature. The linear current–voltage characteristics of these contacts are shown in the inset of Fig. 4.

From the Hall effect measurements we found that free carriers concentration increases when thickness of samples increases (Fig. 4). In a 32 nm, n-type sample we have concentration of $n = 2 \times 10^{16}$ cm^{-3} and in a 171 nm sample $n = 4.6 \times 10^{17}$ cm^{-3}. We may control the free carrier concentration in a broad range by changing only the thickness of a sample.

3.4. Correlation between electrical and optical properties of ZnO films

The aim of the present study was to optimize growth conditions to get ZnO films with appropriate doping level for device applications (for cross-bar memories). It turned out that the Schottky junction optimization required not only selection of samples with appropriate room temperature free electron concentration, but also a control of deep defects. This is why we searched for relations between electrical, optical and junction properties. It turned out that the best Schottky junctions were observed (see [5, 24] for the details) for samples grown

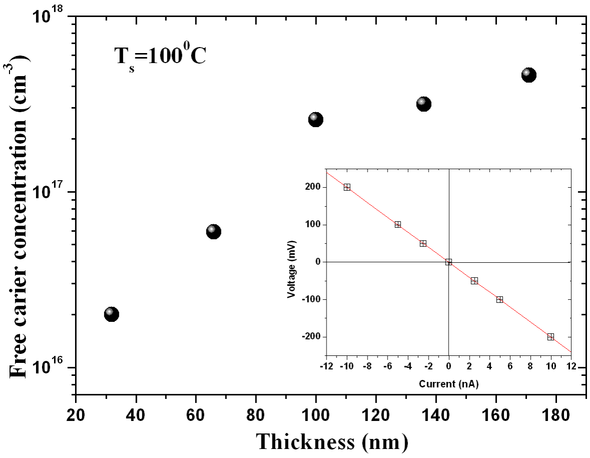

Fig. 4. Free carrier concentration versus thickness of samples as obtained from the Hall measurements at 300 K. Inset shows *I–V* characteristic of Cr/Ag contacts on 100 nm thick sample.

at 100°C with free electron concentration at the level of 10^{17} cm^{-3} and with low deep defect related PL.

4. Summary

The present results show that optical properties, electrical properties and surface morphology of ZnO thin films, grown at extra-low temperature using DEZn precursor, vary with the thickness of the sample. We correlate PL with carrier concentration; when defects PL decreases, electron concentration increases, which suggests that in the thicker sample we have a lower concentration of some deep defects.

Our results demonstrate that a good quality ZnO material can be obtained at the growth temperature as low as 100°C. ZnO thin films grown at extremely low temperature are interesting materials for some applications, e.g. as the Schottky diodes and hybrid organic/semiconductor junctions.

Acknowledgments

The work was supported by Polish grant SPUB No. 180/6.PR UE/2006/7 (6 Framework Programme — priority 2 (IST)) and European project FP6 026714 VERSATILE.

References

[1] T. Krajewski, E. Guziewicz, M. Godlewski, L. Wachnicki, I.A. Kowalik, A. Wójcik-Glodowska, K. Kopalko, V. Osinniy, M. Guziewicz, *Microelectronics Journal* DOI: 10.1016/j.mejo.2008.07.053 (2008).

[2] P.F. Carcia, R.S. McLean, M.H. Reilly, J. Nunes, *Appl. Phys. Lett.* **82**, 1117 (2003).

[3] E. Fortunato, P. Barquinha, A. Pimentel, A. Gonçalves, A. Marques, L. Pereira, R. Martins, *Thin Solid Films* **487**, 205 (2005).

[4] F.M. Hossain, J. Nishii, S. Takagi, A. Ohtomo, T. Fukumura, H. Fujioka, H. Ohno, H. Koinuma, M. Kawasaki, *J. Appl. Phys.* **94**, 7768 (2003).

[5] N. Huby, S. Ferrari, E. Guziewicz, M. Godlewski, V. Osinniy, *Appl. Phys. Lett.* **92**, 023502 (2008).

[6] K.S. Weißenrieder, J. Müller, *Thin Solid Films* **300**, 30 (1997).

[7] M. Bender, E. Gagaoudakis, E. Douloufakis, E. Natsakou, N. Katsarakis, V. Cimalla, G. Kiriakidis, E. Fortunato, P. Nunes, A. Marques, R. Martins, *Thin Solid Films* **418**, 45 (2002).

[8] T. Hiramatsu, M. Furuta, H. Furuta, T. Matsuda, T. Hirao, *Jpn. J. Appl. Phys., Part 1* **46**, 3319 (2007).

[9] L. Jianguo, Z. Yinzhu, Y. Zhizhen, W. Lei, Z. Binghui, H. Jinhyun, *Mater. Lett.* **57**, 3311 (2003).

[10] E. Kaminska, A. Piotrowska, J. Kossut, A. Barcz, R. Butkute, W. Dobrowolski, E. Dynowska, R. Jakiela, E. Przezdziecka, R. Lukasiewicz, M. Aleszkiewicz, P. Wojnar, E. Kowalczyk, *Solid State Commun.* **135**, 11 (2005).

[11] E. Kaminska, E. Przezdziecka, A. Piotrowska, J. Kossut, E. Dynowska, W. Dobrowolski, A. Barcz, R. Jakiela, E. Lusakowska, J. Ratajczak, in: *Proc. Progress in Semiconductor Materials V-Novel Materials and Electronic and Optoelectronic Applications*, Eds. L.J. Olafsen, R.M. Biefeld, M.C. Wanke, A.W. Saxlar, Materials Research Society, Warrendale; Boston 2006, p. 363.

[12] E. Przezdziecka, E. Kaminska, I. Pasternak, A. Piotrowska, J. Kossut, *Phys. Rev. B* **76**, 193303 (2007).

[13] L. Xiaonan, S.E. Asher, S. Limpijumnong, B.M. Keyes, C.L. Perkins, T.M. Barnes, H.R. Moutinho, J.M. Luther, S.B. Zhang, Wei S HS, T.J. Coutts, *J. Cryst. Growth* **287**, 94 (2006).

[14] D.C. Look, D.C. Reynolds, C.W. Litton, R.L. Jones, D.B. Eason, G. Cantwell, *Appl. Phys. Lett.* **81**, 1830 (2002).

[15] F.X. Xiu, Z. Yang, L.J. Mandalapu, D.T. Zhao, J.L. Liu, W.P. Beyermann, *Appl. Phys. Lett.* **87**, 152101 (2005).

[16] A. Wojcik, M. Godlewski, E. Guziewicz, R. Minikayev, W. Paszkowicz, *J. Cryst. Growth* **310**, 284 (2008).

[17] A. Wojcik, M. Godlewski, E. Guziewicz, K. Kopalko, R. Jakiela, M. Kiecana, M. Sawicki, M. Guziewicz, M. Putkonen, L. Niinisto, Y. Dumont, N. Keller, *Appl. Phys. Lett.* **90**, 082502 (2007).

[18] I.A. Kowalik, E. Guziewicz, K. Kopalko, S. Yatsunenko, A. Wójcik, M. Godlewski, P. Dluzewski, E. Lusakowska, W. Paszkowicz, *J. Cryst. Growth*, in press.

[19] S.J. Peatron, D.P. Norton, K. Ip, Y.W. Heo, T. Steiner, *Superlattices Microstruct.* **34**, 3 (2003).

[20] O.F. Schirmer, D. Zwingel, *Solid State Commun.* **8**, 1559 (1970).

[21] B.J. Bierce, R.L. Hengehold, *J. Appl. Phys.* **47**, 644 (1976).

[22] S.A. Studenikin, N. Golego, M. Cocivera, *J. Appl. Phys.* **84**, 2287 (1998).

[23] F.X. Xiu, Z. Yang, L.J. Mandalapu, D.T. Zhao, J.L. Liu, *Appl. Phys. Lett.* **87**, 252102 (2005).

[24] M. Godlewski, E. Guziewicz, J. Szade, A. Wójcik-Glodowska, Ł. Wachnicki, T. Krajewski, K. Kopalko, R. Jakieła, S. Yatsunenko, E. Przeździecka, P. Kruszewski, N. Huby, G. Tallarida, S. Ferrari, *Microelectronic Engineering* DOI: 10.1016/j.mee.2008.09.012 (2008).