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

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

Extra-Low Temperature Growth of ZnO by Atomic Layer Deposition with Diethylzinc Precursor

I.A. Kowalik[a], E. Guziewicz[a], K. Kopalko[a], S. Yatsunenko[a], M. Godlewski[a,b], A. Wójcik[a], V. Osinniy[a], T. Krajewski[b], T. Story[a], E. Łusakowska[a] and W. Paszkowicz[a]

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

ZnO thin films were grown on silicon substrate by atomic layer deposition method. We explored double-exchange chemical reaction and used very volatile and reactive diethylzinc as a zinc precursor. These enables us to obtain zinc oxide thin films of high quality at extremely low growth temperature (90−200°C). The films are polycrystalline as was determined by X-ray diffraction and show flat surfaces with roughness of 1–4 nm as derived from atomic force microscopy measurements. Photoluminescence studies show that an edge emission of excitonic origin is observed even at room temperature for all investigated ZnO layers deposited with the diethylzinc precursor.

PACS numbers: 78.55.Et, 78.66.Hf, 81.15.Kk

1. Introduction

ZnO has been used for a long time for pigments and protective coatings on metals. The electrical, optoelectronic, and photochemical properties of wide-band gap ZnO ($E_g \approx 3.3$ eV at 300 K) led to many applications of this material for solar cells, transparent electrodes, gas sensors, varistors, piezoelectric transducers, and optoelectronic blue/UV light emitting and light detecting devices [1, 2]. ZnO is a promising material because of high melting point, high chemical stability, and large exciton binding energy (60 meV), which is much higher than exciton binding energy in GaN and most of other semiconductor materials.

Transition metal doping of ZnO expands technological applications of this material to ferromagnetic semiconductors, which potentially leads to spintronic applications. ZnO doped with Mn is especially interesting for spintronics, due to the predicted room temperature (RT) ferromagnetism of heavily p-type doped samples [3].

ZnO is also a promising substrate material for the GaN epitaxy. Free standing GaN epilayers grown on ZnO/glass were demonstrated [2]. This is also a prospective semiconductor candidate for making hybrid organic/inorganic devices. However, some of these applications of ZnO require extremely low growth temperature.

ZnO films are usually obtained by molecular beam epitaxy, pulsed laser deposition, chemical vapour deposition, or sputtering. Our recent studies show that low temperature (LT) ZnO growth is crucial to avoid the formation of foreign phases and spinodal decomposition when transition metal atoms are introduced during the growth process [4, 5].

In this paper we report on zinc oxide thin films grown by atomic layer deposition (ALD) method at extremely LT conditions. The work was done in the Institute of Physics, Polish Academy of Sciences.

2. Growth conditions

In the ALD method reagents (precursors) are introduced sequentially into the growth chamber and cycles when precursors reach the substrate are interspersed by cycles of purging with inert gas (nitrogen). Because precursors meet only at a surface of the substrate we may use very reactive precursors and apply different type of chemical reactions (synthesis, single or double exchange).

In the zinc oxide growth reported here we used a very volatile and reactive metalorganic precursor (diethylzinc, DEZn) and achieved a successful growth at a temperature range of $90-200^{\circ}$C, which is drastically below the growth temperature reported for this material to date.

The films were grown in three series with different growth parameters. The series I and II differs with the DEZn precursor pulse time (20 ms for series I and 90 ms for series II). In the case of series III the purging time is above twice longer than for series I and II (20 s for series III and 8 s for series I and II).

3. Experimental results

In the study we explored a very low deposition temperature range of $90-200^{\circ}$C and employed the Savannah-100 reactor from Cambridge NanoTech. The results of surface morphology investigations by atomic force microscopy (AFM) confirm a good structural quality of the obtained films. We find that root mean square (RMS) clearly depends on growth temperature, thickness of the film, and purging time. We obtained the best surface quality for samples from series III. We consistently observe the lowest RMS values for the samples grown with longer H_2O purging time (20 s). Selected AFM images for samples from

this series grown at 100°C (115 nm film thickness), 130°C (90 nm), and 190°C (72 nm) are shown in Fig. 1. For all three series of ZnO samples we observe that RMS decreases with growth temperature and with increasing film thickness. For example, the RMS value for growth temperature of 100°C for samples from series III was found as 3.9 nm whereas for 200°C it was only 0.9 nm. However, when the substrate temperature (T_s) is below 100°C the increase in RMS is dramatic and films grown at a very low temperature are characterized by RMS of about 3 times higher than these grown at 130°C and above. In a temperature range above 160°C RMS is almost stable and the surface quality does not further improve with temperature.

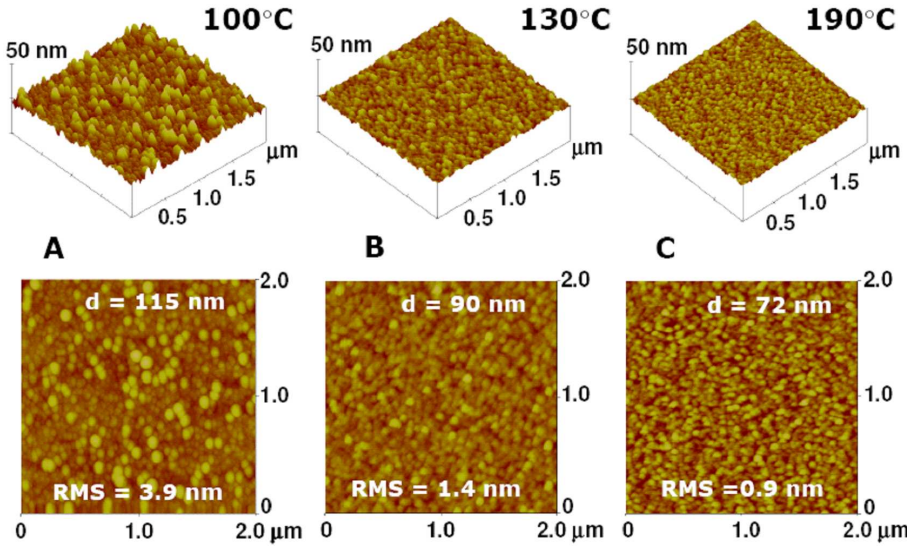

Fig. 1. AFM images from 2×2 μm ZnO samples grown at 100°C, 130°C, and 190°C — process parameters of series III.

A structural characterization of the ZnO layers was assessed by X-ray diffraction (XRD) measurements. For all three series of samples the obtained ZnO films are found to be polycrystalline and of good crystallographic quality. The investigated angular region ($2\Theta = 20{-}80°$) included the ZnO related diffraction maxima corresponding to (10.0), (00.2), (10.1), (11.0) crystallographic direction. In the case of samples grown at a relatively low temperature, we observe all the above-mentioned maxima, but their intensities depend on growth conditions (temperature and purging time). The longer purging time privileges the growth mode with the c axis perpendicular to the surface (series III), which is opposite to the samples grown with shorter purging time (series I and II) where orientation (10.0) is dominant. However, in the case of samples obtained at $T_s = 190$°C and higher only one distinguished crystallographic direction is clearly visible (see Fig. 2c).

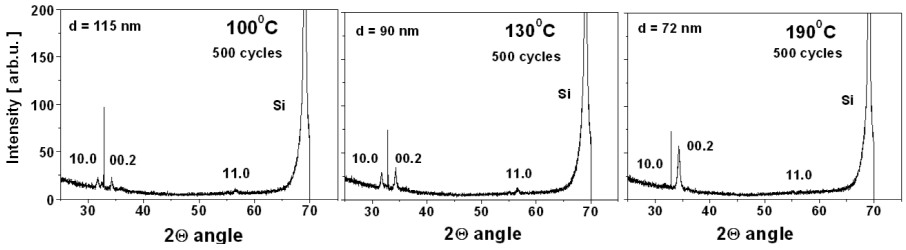

Fig. 2. Results of XRD measurements of ZnO/Si films grown at different temperatures for series III.

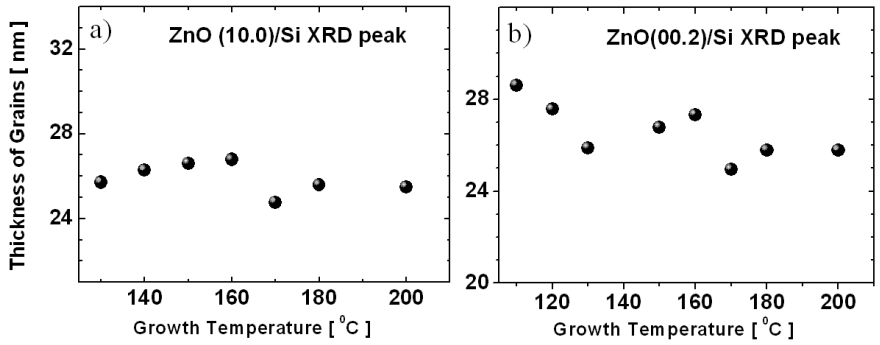

Fig. 3. Mean size of grains as function of growth temperature of ZnO films for the series III: (a) for crystallographic direction (10.0), (b) for crystallographic direction (00.2).

We also established that the growth mode (c axis parallel or perpendicular to the surface) and grain diameters depend on such growth parameters like temperature and/or purging time. We calculated grain diameters basing on XRD results and Scherrer's formula

$$D = \frac{K\lambda}{\Delta(2\Theta)\cos\Theta},$$

where $K = 180/\pi$, and λ is the X-ray wavelength (in our case it is Cu $K_{\alpha 1}$ line with $\lambda = 1.5406$ Å) [6]. The results for films from series III (long purging time) as a function of growth temperature (for 10.0 and 00.2 directions) are shown in Fig. 3. In this figure we see that sizes of grains are similar for both measured XRD reflections, they range between 24 and 27 nm and do not depend on growth temperature. This is the case of series III for which water purging time was substantially longer (20 s). In the case of shorter purging time after water precursor (8 s, series I and II) the average size of grains is considerably higher and increases with temperature (40 nm for $T_s = 140°$C and 50 nm for $T_s = 180°$C).

Grain diameters evaluated from AFM measurements show much higher scattering and range between 70 and 120 nm. The comparison of thickness of grains obtained from XRD results with the grains diameter seen at AFM images shows

that the size calculated from the Scherrer formula is approximately four times smaller. However, it should be taken into account that AFM measurements overestimate the size of objects smaller than the tip size.

Photoluminescence (PL) studies show that a strong emission of excitonic origin (so-called "edge" PL) is observed even at room temperature for all investigated ZnO films deposited with DEZn precursors. For all three investigated series we observed that intensity of the "edge" PL shows also a strong dependence on growth temperature as is demonstrated in Fig. 4. The stronger "edge" PL is observed for

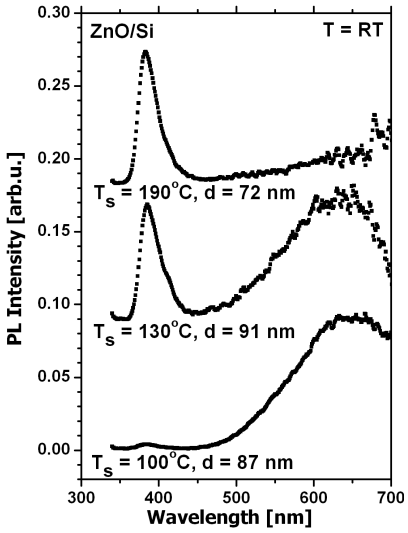

Fig. 4. PL observed at RT for LT ZnO layers from the series III grown by ALD on Si substrate at 100°C, 130°C, 190°C. All spectra are normalized to the highest point.

ZnO films grown at a temperature of 130°C and above. This is another confirmation of a high quality of this material as this is a fingerprint that nonradiative centers are not present in the material.

4. Summary

Our results show that ZnO thin films grown at extra-low temperature using DEZn precursor resulted in an unexpectedly high quality material. The parameters of obtained films like RMS, *c* axis orientation, grain diameters, and intensity of excitonic emission depend on growth temperature and other growth process parameters like deposition and/or purging time. However, for all investigated ZnO films the obtained layers are always atomically flat (RMS ranges between 1 and 4 nm) and the edge emission of excitonic origin is always observed even at room temperature pointing out the lack of nonradiative centers in the material.

Our results demonstrate that a high quality ZnO material can be obtained even at a growth temperature range of 90−200°C. Extra-low temperature grown

ZnO is an interesting material for some special applications, e.g. as an element of hybrid organic/semiconductor junctions. Such a material, when doped with transition metal elements, is also of special interest for spintronics, because low temperature deposition seems to be crucial to avoid the formation of foreign phases and spinodal decomposition as we have shown recently [4, 5].

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 with an acronym VERSATILE.

References

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

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

[3] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, D. Ferrand, *Science* **287**, 1019 (2000).

[4] A. Wójcik, K. Kopalko, M. Godlewski, E. Guziewicz, R. Jakieła, R. Minikayev, W. Paszkowicz, *Appl. Phys. Lett.* **89**, 051907 (2006).

[5] A. Wójcik, M. Godlewski, E. Guziewicz, K. Kopalko, R. Jakieła, M. Kiecana, M. Sawicki, M. Guziewicz, M. Putkonen, L. Niinistö, Y. Dumont, N. Keller, *Appl. Phys. Lett.* **90**, 082502 (2007).

[6] P. Scherrer, *Göttinger Nachrichten* **2**, 98 (1918); cf. also *Kolloidchemie*, Ed. R. Zsigmondy, 3rd ed., Sparner, Leipzig 1920, p. 394.