Vol. **114** (2008) *ACTA PHYSICA POLONICA A* No. 5

Proc. XXXVII International School of Semiconducting Compounds, Jaszowiec 2008

Substrates Grown from the Vapor for ZnO Homoepitaxy

P. Skupiński[a], K. Kopalko[a], K. Grasza[a,b], E. Łusakowska[a], V. Domukhovski[a], R. Jakieła[a] and A. Mycielski[a]

[a]Institute of Physics, Polish Academy of Sciences
al. Lotników 32/46, 02-668 Warsaw, Poland
[b]Institute of Electronic Materials Technology
Wólczyńska 133, 01-919 Warsaw, Poland

The novel method of preparation of epi-ready ZnO substrates is demonstrated. The substrates were made of unique ZnO crystals grown by chemical vapor transport method using hydrogen as the transport agent. The effect of low-level doping (Mn, Co, Cu, and V) on the structural quality of the crystals was investigated. Atomic layer deposition was used to verify usability of the substrates for homoepitaxy. The thermal annealing prior to the atomic layer deposition process and effect of thermal annealing of the epitaxial layers was studied. The X-ray diffraction and atomic force microscopy methods were applied to study the structural quality of the ZnO layers. Detection of the dopants in the substrates by secondary ion mass spectroscopy made possible the measurement of the thickness of the layers. The obtained root mean square roughness for both the substrates and layers ranged between 0.2 nm and 5 nm, and was dependent on the sample crystallographic orientation and sequence of polishing and annealing procedures. The optimal recipe for the epi-ready substrate preparation was formulated.

PACS numbers: 81.05.Dz, 68.47.Fg, 68.55.J−, 68.37.Ps, 81.10.Bk, 81.15.−z

1. Introduction

ZnO is a material with a great future in the field of optoelectronic devices. The interest in ZnO results from its unique properties such as the wide band-gap (3.37 eV) and large exciton binding energy (60 meV) [1]. The production of ZnO optoelectronic elements is being restrained due to problems with *p*-type conductivity [2, 3]. The homoepitaxial growth [4] can provide ZnO layers with a better quality as compared to results of heteroepitaxy. The ZnO substrates accessible on the market are grown by the hydrothermal method. The epi-ready substrate preparation procedure in the case of ZnO is not yet extensively described in the open literature. Only a few papers contain the superficial descriptions [5]. Up to the knowledge of the authors, satisfactory results are achieved in the Tokyo Denpa (important hydrothermal method ZnO crystals producer), which managed the complete substrate preparation procedure. Also, the European Novasic achievements are among the most frequently mentioned by ZnO crystal growers.

In this paper, we demonstrate a novel technique of combined mechanical polishing, two-phase mechano-chemical polishing and thermal annealing, which we found optimal for ZnO crystals. The recipe was developed in a long process of experimentally verified study. The atomic layer deposition (ALD) [6] was used to grow ZnO layers. The effect of the thermal annealing on the quality of substrates and layers was also studied.

2. Experimental procedure

The substrates were prepared by the multi-step procedure: mechanical polishing, two-phase mechano-chemical polishing, and thermal annealing. Table shows the succeeding steps applied for preparation of five substrates presented in this work. In the initial phase of the first step (mechanical polishing), the powders of 20–30 μm and 5–6 μm grain size were used. The resulting surface was smooth when observed with a naked eye. The samples prepared in this way were subjected to the two-phase mechano-chemical polishing, which removed microscopic scratches. The first phase of mechano-chemical polishing was performed in an aquatic colloid solution of SiO_2 nanoparticles mixed with hydrochloric acid. In the second phase, the polishing in a colloidal solution mixed with nitric acid took place. Finally, the samples were double rinsed in hot methanol, acetone and trichloroethylene. This way the root mean square (RMS) value of 0.5 nm was obtained. The exemplary result is shown in Fig. 1. In our experiments, we used ZnO substrates grown by the chemical vapor transport (CVT) method in our laboratory [7], using hydrogen as the transport agent. The substrates were doped with Mn, Co, Cu, and V. The concentration of the dopants was 3×10^{18} cm^{-3} for the ZnO:Mn, 10^{19} cm^{-3} for the ZnO:Co, 3×10^{18} cm^{-3} for the ZnO:Cu and 3×10^{18} cm^{-3} for the ZnO:V (Table). The doping made possible the measurement of the depth of diffusion of the dopant from the substrate into the layer and the layers thickness by the secondary ion mass spectroscopy (SIMS) method. Simultaneously, the effect of low-level doping on the structural quality of the crystals was investigated.

In the step 2 (Table) two substrates doped with Cu and V were additionally annealed at 930°C for 3 h in air. To grow the undoped ZnO layers, the ALD method was used (step 3 in Table). The process parameters were as follows: the number of cycles 800, velocity of gas flux 20 sccm, and substrate temperature 170°C. Diethylzinc was applied as the zinc precursor. In the step 4 all samples were annealed at 930°C for 12 h in air. The substrates and layers were investigated by the atomic force microscopy (AFM) and X-ray diffraction (XRD) techniques.

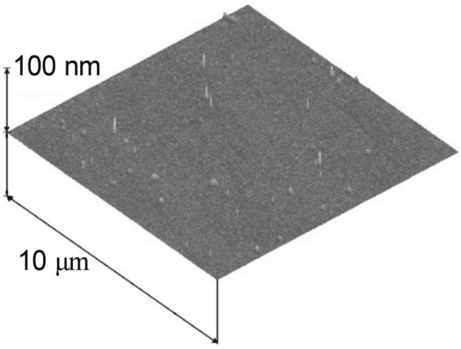

Fig. 1. ZnO:Co after the two-phase mechano-chemical polishing. RMS is equal to 0.5 nm.

TABLE

The four steps applied for preparation of the five substrates. The FWHM values are given for two X-ray diffraction peaks before and after 90° rotation of the samples.

Sample number		1	2	3	4	5
dopant in substrate [cm^{-3}]		Mn 3×10^{18}	Co 1×10^{19}	Cu 3×10^{18}	V 3×10^{18}	Cu 3×10^{18}
crystallographic orientation		(0001)	polycrystal	(11-20)	first seed (1-100); second seed deviated 0.2° from (1-100)	(11-20)
step 1		mechanical polishing and two-phase mechano-chemical polishing				
step 2		–			thermal annealing at 930°C for 3 h in air	
step 3		ZnO atomic layer deposition				
FWHM for two peaks [arcsec]	0°	95	–	252	–	144
	90°	99	–	226	–	151
step 4		thermal annealing at 930°C for 12 h in air				
FWHM for two peaks [arcsec]	0°	77	–	–	–	–
	90°	82	–	–	–	–

3. Results

The XRD study of the as-grown layers proved that the layers and the substrates have the same crystallographic orientation. The rocking curve full widths at half maximum (FWHM) for samples No. 1 (ZnO:Mn), 3 (ZnO:Cu), and 5 (ZnO:Cu) are presented in Table. The quality of layers varied due to the substrate preparation procedure and sample orientation. No evident signs of influence of the kind of dopant on the crystallographic quality of the substrates and layers grown on these substrates were found. That was in opposition to our observation of ZnO crystals doped with Cr, Fe, Ni, As, and Sb, which are not under the scope of this paper.

Figures 2a–c show the AFM pictures of the films grown on the substrates No. 1 (ZnO:Mn), 2 (ZnO:Co), and 3 (ZnO:Cu). These substrates were not annealed

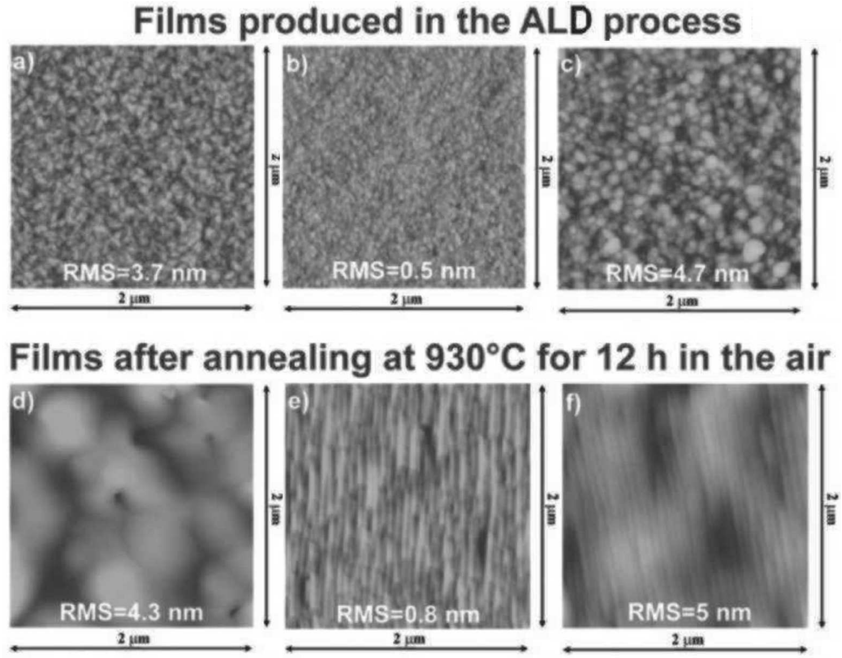

Fig. 2. Parts (a–c) show films grown by ALD on the substrates No. 1 ZnO:Mn, 2 ZnO:Co and 3 ZnO:Cu, respectively. Parts (d–f) show the same samples after annealing. In Fig. 4 these samples are denoted by filled symbols.

before the ALD process and are characterized by RMS equal to 0.5 nm after the mechano-chemical polishing. The RMS of the layers obtained on these substrates was lower than 5 nm (Fig. 2). Figures 2d–f show the same samples after annealing at 930°C for 12 h in air. One can see the evident changes of the morphology of these surfaces. Low roughness of the sample No. 2 (ZnO:Co) is striking and the step-like structure of the ALD layer after thermal annealing is visible.

After the mechano-chemical polishing, the samples No. 4 doped with vanadium and No. 5 doped with copper were annealed at 930°C for 3 h in air, prior to the ALD. The surfaces obtained in this way are shown in Fig. 3a–c. One can see that the annealing produced regular steps on the sample No. 5 doped with copper. It is the effect of the crystallographic orientation (11-20) of the sample [8, 9]. On the sample No. 4 (ZnO:V) one can see two seeds with different surface morphology: the flat surface for seed oriented (1-100) in Fig. 3a, and the surface with terraces (the deviation of its orientation is about 0.2° from (1-100)) in Fig. 3b. The films grown on these substrates are presented in Fig. 3d–f. Some of the films (Fig. 3e, f) have the same step-like structure of the surfaces as the substrates visible in Fig. 3b and c. These samples were additionally annealed at 930°C for 12 h after ALD processing and are presented in Fig. 3g–i. In Fig. 4, the RMS values for all samples are compared.

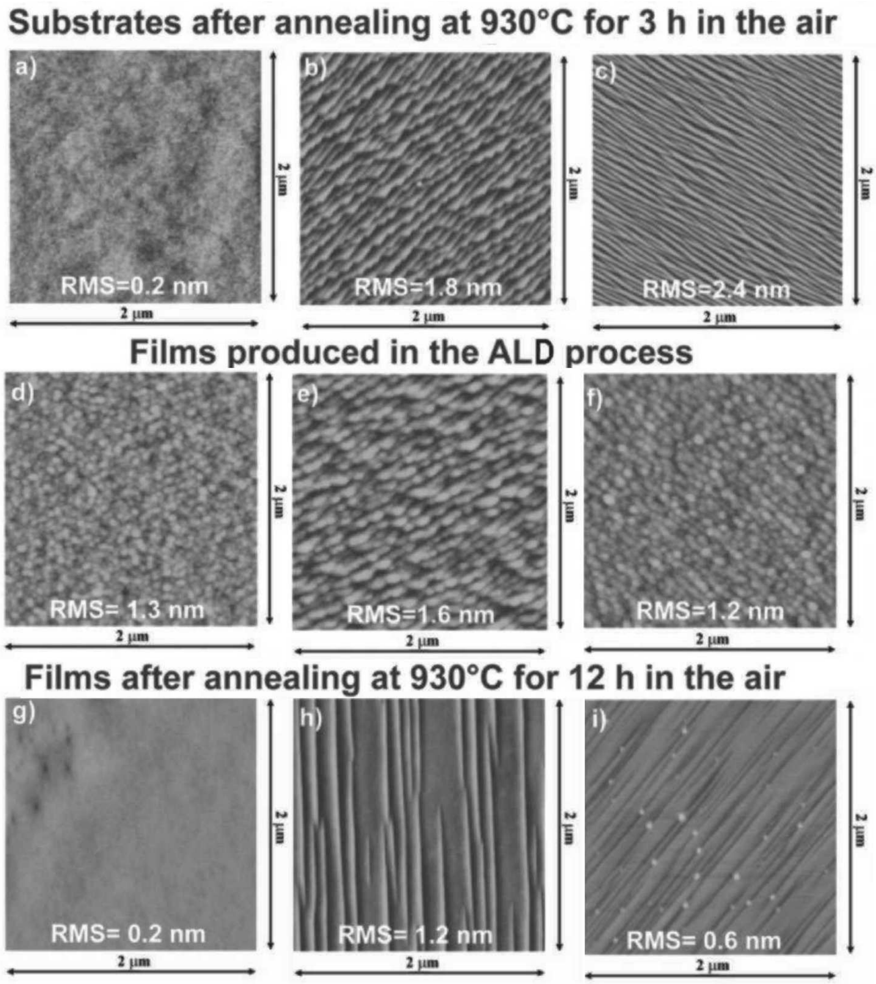

Fig. 3. On the left hand side: first (1-100) and second (deviation of 0.2° relative to the (1-100) plane) seeds from sample No. 4 (ZnO:V). On the right hand side: sample No. 5 (ZnO:Cu) oriented (11-20). In Fig. 4 these samples are denoted by empty symbols.

The thickness of ALD layers was measured by the SIMS method. The average result of this measurement is 0.2 μm. Figure 5 shows a typical result of SIMS measurement for the sample No. 2 doped with Co. In this figure, one can observe two regions: the film (with lower concentration of dopant) and the substrate (with higher concentration of dopant).

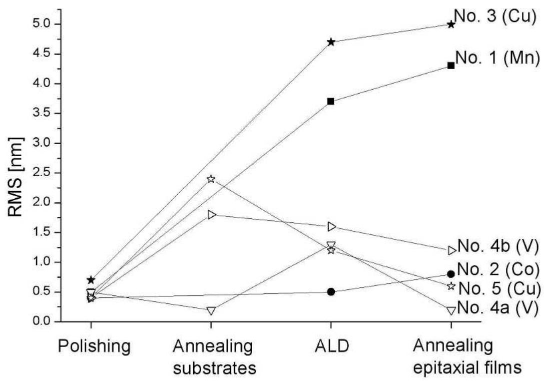

Fig. 4. The comparison of the RMS for all substrates and preparation steps. Samples No. 4a and 4b are seeds oriented (1-100) and 0.2° deviated from (1-100), respectively.

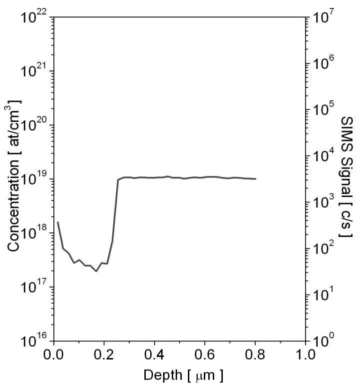

Fig. 5. The SIMS study of the ZnO:Co sample.

4. Discussion

The RMS of ZnO ALD layers ranged between 0.5 nm (Fig. 2b) and 4.7 nm (Fig. 2c). Both extreme data characterized layers grown on non-annealed substrates. The literature data is widely ranging from 0.4 nm [10] to 20 nm [11]. These and other reports [12–14] demonstrate the dependence of the roughness on the way the substrate was prepared, the method of the film growth and the film thickness. Additionally, the quality of ALD layers was found in this work dependent on the crystallographic orientation of the samples. However, the positive effect of thermal annealing of the substrate prior to the ALD process is striking. The FWHM rocking curve is smaller for layers grown on the substrates, which were annealed before the ALD process (Table). We found the RMS in the low range, 1.2–1.6 nm, in all the layers, which were grown on the annealed substrates. This is better result as compared to RMS equal to 1.9 nm obtained in homoepitaxy by pulsed laser deposition using non-annealed perfectly prepared (RMS = 0.2 nm) substrates [4]. Comparison of the data from this work and our earlier results [15] shows similarity in structure of surface (0001) perpendicular to the *c*-axis and (1-100) parallel to the *c*-axis. They are fuzzy (Fig. 2d) or smooth (Fig. 3a and g) after annealing. On the other hand, surfaces with higher index orientation have regular atomic terraces or steps (the other samples in Figs. 2 and 3) ([8, 9] and [15]).

The grainy structure was found on all the obtained layers. However, in the films grown on the substrates annealed before the ALD process, this structure is ordered in the same way as the substrate surface (compare Fig. 3b with 3e and Fig. 3c with 3f). The grainy structure of these surfaces suggests the "column-like" growth of the film. The grainy structure disappears after annealing at 930°C for 12 h in air.

It was found that the FWHM strongly changes after the 90° rotation of the sample. It proves that the stress and deformation are present in both the substrate and film. There is a lack of data concerning ALD ZnO homoepitaxy in the literature. The FWHM value equal to 27 arcsec was reported for the chemical vapor deposition (CVD) method [9] and 0.4° [10] for the metal-organic CVD (MOCVD). According to the reported data, the parameter decreases with the increase in the film thickness (the result of 27 arcsec was reported for the thickness of 0.7 μm). The reason of this is the decrease in the film stress, which originates from the substrate. Our results prove that the stress can be reduced by annealing samples at 930°C (see Table, sample No. 1).

The interface between the film and the substrate is clearly seen in the SIMS measurements. It is marked by a quick decrease in the dopant concentration. The thickness of ZnO film equal to 0.2 μm can be determined. The SIMS measurements prove absence (samples No. 1, 3, 4 and 5) or minimal (sample No. 2) diffusion of dopants from substrates into the films after the ALD process. The annealing of the samples after the ALD process stimulated a uniform diffusion from the substrate into the films in case of Mn, Cu, and V, and partial diffusion in the case of Co.

5. Summary

The ZnO substrates were prepared using the novel multi-step polishing procedure combined with thermal annealing. The substrates were CVT grown unique crystals, low-level doped with Mn, Co, Cu, and V. The effect of the investigated dopants was found not to be essential for the structure of the substrates and ALD layers. The SIMS study made possible to observe the diffusion of the dopants to the ZnO ALD layers. The XRD analysis proved the existence of the stress and deformation in the films. This study confirms the positive influence of the substrate annealing before the epitaxy on the crystallographic quality of the substrate. The annealing after the epitaxy induces the surface ordering of the film, which strongly depends on the crystallographic orientation of the samples. In the description of experimental procedure the recipe for epi-ready substrate preparation was formulated.

Acknowledgments

This work was supported by the Ministry of Science and Higher Education, Poland, through the grant No. 3 T08A 051 28.

References

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

[2] B. Xiao, Z. Ye, Y. Zhang, Y. Zeng, L. Zhu, B. Zhao, *Appl. Surf. Sci.* **253**, 895 (2006).

[3] S. Gangi, A. Nakamura, Y. Ichikawa, K. Yamamoto, J. Ishihara, T. Aokia, J. Temmyo, *J. Cryst. Growth* **298**, 486 (2007).

[4] D.J. Rogers, F. Hosseini Teherani, A. Largeteau, G. Demazeau, C. Moisson, D. Turover, J. Nause, G. Garry, R. Kling, T. Gruber, A. Waag, F. Jomard, P. Galtier, A. Lusson, T. Monteiro, M.J. Soares, A. Neves, M.C. Carmo, M. Peres, G. Lerondel, C. Hubert, *Appl. Phys. A* **88**, 49 (2007).

[5] D.A. Lucca, D.W. Hamby, M.J. Klopfstein, G. Cantwell, *Phys. Status Solidi B* **229**, 845 (2002).

[6] T. Suntola, *Handbook of Crystal Growth. Thin Films and Epitaxy*, Vol. 3B, North Holland, Amsterdam 1994, p. 601.

[7] K. Grasza, P. Skupiński, A. Mycielski, E. Łusakowska, V. Domukhovski, *J. Cryst. Growth* **310**, 1823 (2008).

[8] K. Grasza, E. Łusakowska, P. Skupiński, K. Kopalko, J. Bąk-Misiuk, *Phys. Status Solidi B* **244**, 1468 (2007).

[9] H.-J. Koa, M.-S. Hana, Y.-S. Parka, Y.-S. Yub, B.-I. Kimb, S.S. Kimc, J.-H. Kim, *J. Cryst. Growth* **269**, 493 (2004).

[10] D. Ehrentraut, H. Sato, M. Miyamoto, T. Fukuda, M. Nikl, K. Maeda, I. Niikura, *J. Cryst. Growth* **287**, 367 (2006).

[11] Sh. Zhu, C.-H. Su, S.L. Lehoczky, M.T. Harris, M.J. Callahan, P. McCarty, M.A. George, *J. Cryst. Growth* **219**, 361 (2000).

[12] C. Neumann, S. Lautensxchläge, S. Graubner, J. Sann, N. Volbers, B.K. Meyer, J. Bläsing, A. Krost, F. Bertram, J. Christen, *Phys. Status Solidi B* **244**, 1451 (2007).

[13] Y. Kashiwaba, H. Kato, T. Kikuchi, I. Niikura, K. Matsushita, Y. Kashiwaba, *Appl. Surf. Sci.* **244**, 373 (2005).

[14] T. Abe, Y. Kashiwaba, S. Onodera, F. Masuoka, A. Nakagawa, H. Endo, I. Niikura, Y. Kashiwaba, *J. Cryst. Growth* **298**, 457 (2007).

[15] K. Grasza, E. Łusakowska, P. Skupiński, H. Sakowska, A. Mycielski, *Superlattices Microstruct.* **42**, 290 (2007).