HRTEM study of ZnO thin films deposited by magnetron sputtering

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Recent developments in the field of ZnO thin films for optoelectronic devices have been focused on the optimization of the film structure since it was found that particularly (002)-oriented ZnO films exhibit highly enhanced optical and photoluminescence properties.

In this paper we report the results of our investigation on the structure of ZnO thin films deposited on glass substrates by using DC and RF magnetron sputtering.

Experimental

- Zinc oxide thin films were prepared by DC and RF magnetron sputtering technique. Metallic Zn (Aldrich, 99.99%) was used as target in DC magnetron sputtering process. ZnO target used in RF magnetron sputtering deposition process was obtained from ZnO powder (Umicore Zinc Chemicals, 99.99%). The ZnO powder was mecanically milled, then pressed as a disc with the diameter of 4.5 cm and thickness of 3.5 - 4 mm. The target was sintered at 1200°C for 1 h.
- The sputtering processes were carried out in Ar atmosphere. The sputtering time was 1 min and the deposited film thickness was about 120 nm. The substrate was glass in both experiments.

ZnO films obtained by oxidation of metallic Zn films are referred as "films A" and ZnO films deposited from ZnO target are reffered ti as "films B".

- The surface mophology was investigated by using a QUANTA INSPECT F Scanning Electron Microscope (SEM) with X-ray energy dispersive spectrometer (EDAX) and an Alpha 300 S *Witec alpha 300S* System with Atomic Force Microscopy (AFM).

The film structure was analysed by using a High Resolution Transmision Electron Microscope (HRTEM) TECNAI F30 and a X-ray Diffraction System (XRD) - *SmartLab* Rigaku Corporation, Japan.

Conclusions

- SEM images of films "A" show grains of ~ 100 nm in average size, with columnar structure and a relative large porosity.

Films "B" present smooth surfaces with spherical grains of ~ 35 nm in average size.

The characteristics of the films morphology, structure and opto-electrical properties related to the two method of deposition were previously reported [1,2].

- HRTEM images of films "A" show nanocrystalline regions of ~10-15 nm in size. The nanocrystalline domains have different orientations and are separated by well defined grain boundaries.

Various [0001] tilted grain boundaries may be observed, as previously revealed in ZnO bicrystals [3].

HRTEM images of the films "B" show small crystalline volumes. Nanocrystalline domains are surrounded by large and strongly defective grain boundaries.

- EDAX spectra evidence a reduced I_{Zn}/I_O ratio in films "A" oxidized in air at 450°C for 3h, that indicates an increased oxygen content comparatively with the as-deposited ZnO films (films "B").

The dependence of the crystallinity on the oxygen content was previously reported [4]; it has a strong influence on the structure of the grain boundaries and electrical properties.

- 2D and 3D AFM images and topography profiles reveal that regions of columnar grains with an abnormal size are randomly distributed on the surface of films "A".

Grains with more uniform size distribution are present in films "B". A mechanism for the grain growth in ZnO films was proposed and related with the surface morphology [5].

- The XRD pattern of film "A" reveals their polycrystalline structure with (100), (002) and (101) oriented nanocrystalls. The nanocrystalls size is ~ 10.5 nm.

The XRD pattern of as-deposited film "B" shows that the film has a poor crystallinity, with (002) preferential orientation. The nanocrystalls size is ~ 11.7 nm.

- The reflectivity profiles reveal the increased porosity and surface roughness of films "A" comparatively with the as-deposited ZnO films "B".

References

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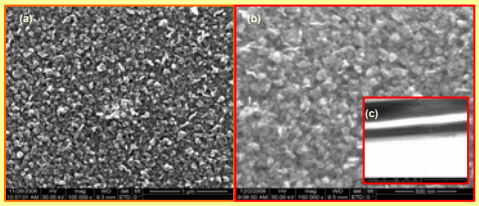
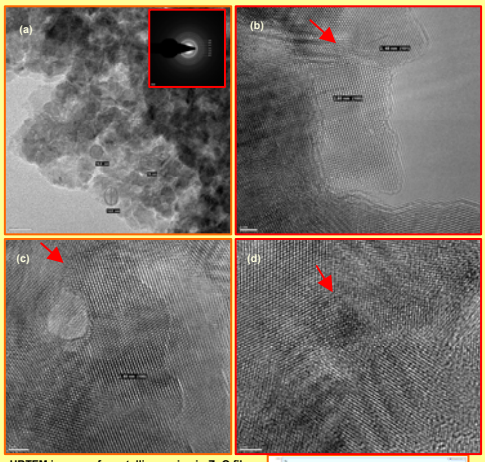
[5] J.M. Yuk, J.Y. Lee, Y.S. No, T.W. Kim, W.K. Choi, Evolution mechanisms of the surface morphology of grains in ZnO thin films grown on p-InP substrates due to thermal annealing, Appl. Phys. Lett. 93, 021904 (2008).

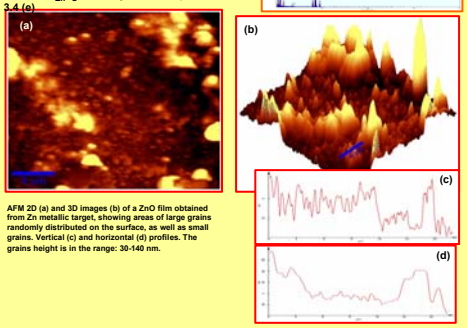
ZnO films deposited by DC magnetron sputtering from Zn target



SEM images of ZnO film deposited from Zn metallic target and oxidized in air at 450°C, 3h (a,b). The film thickness in the SEM cross section image is 92.5 nm (c).

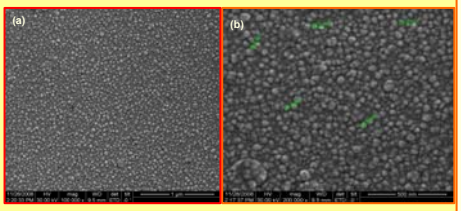


HRTEM images of crystalline grains in ZnO film deposited from Zn metallic target (a). Magnified HRTEM image of grains surrounded by defective region of grain boundaries (b, c, d). The ratio I_{Zn}/I_O intensity in EDAX spectrum is 3.4 (e).

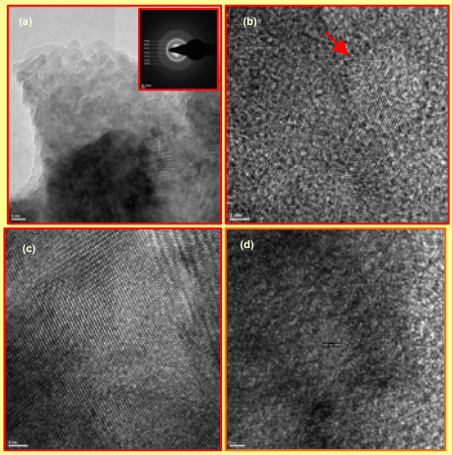


AFM 2D (a) and 3D images (b) of a ZnO film obtained from Zn metallic target, showing areas of large grains randomly distributed on the surface, as well as small grains. Vertical (c) and horizontal (d) profiles. The grains height is in the range: 30-140 nm.

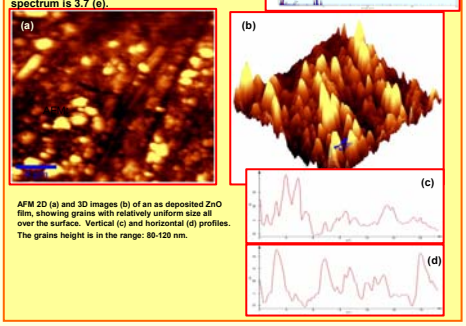
ZnO films deposited by RF magnetron sputtering from ZnO target



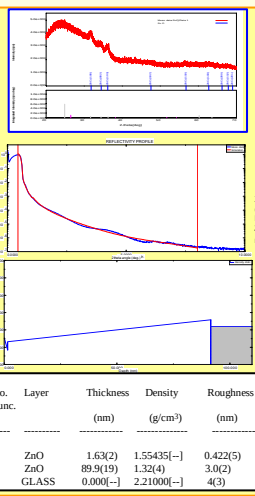
SEM images of the as deposited ZnO film surface (a). Relative uniform grains size about 22-35 nm (b).



HRTEM images of crystalline grains in as deposited ZnO film (a). Magnified HRTEM image of crystalline grains surrounded by defective regions. Crystalline order on the smal volumes (b, c, d). The ratio I_{Zn}/I_O intensity in EDAX spectrum is 3.7 (e).



AFM 2D (a) and 3D images (b) of an as deposited ZnO film, showing grains with relatively uniform size all over the surface. Vertical (c) and horizontal (d) profiles. The grains height is in the range: 80-120 nm.



X-ray diffraction: pattern (a), Reflectivity profile (b), Density distribution (c) of ZnO film deposted from Zn metallic target.

No. Func.	Layer	Thickness (nm)	Density (g/cm³)	Roughness (nm)	Period
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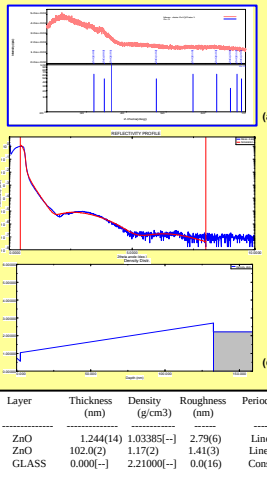
2	ZnO	1.63(2)	1.55435[--]	0.422(5)	Linear
1	ZnO	89.9(19)	1.32(4)	3.0(2)	Linear
0	GLASS	0.000[--]	2.21000[--]	4(3)	Const.



X-ray diffraction: pattern (a), Reflectivity profile (b), Density distribution (c) of ZnO film deposted from ZnO target.

No. Func.	Layer	Thickness (nm)	Density (g/cm3)	Roughness (nm)	Period
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2	ZnO	1.244(14)	1.03385[--]	2.79(6)	Linear
1	ZnO	102.0(2)	1.17(2)	1.41(3)	Linear
0	GLASS	0.000[--]	2.21000[--]	0.0(16)	Const.

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