

Deposition of Zinc Oxide Thin Film on Calcite (CaCO_3) Substrate via PLD at Room Temperature

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Abstract

Polycrystalline zinc oxide (ZnO) films were successfully deposited on calcite (CaCO_3) by pulsed laser deposition PLD at room temperature. Zinc metal target (4N purity, analytical grade) was used for laser ablation in ambient O_2 atmosphere. XRD results show the polycrystallinity of ZnO thin film. Four probe apparatus was used to measure the resistivity of thin film. It was found to have very high resistivity $\sim 200 \text{ M}\Omega\text{m}$. High resistivity is attributed to the high-quality crystal structure of ZnO. ZnO_2 was also found to be present in the thin film. These films have great importance in fabrication of gas sensors and other applications.

Keywords: Thin films; ZnO; PLD

1. Introduction

Zinc oxide (ZnO) has attracted the scientific community for its properties, which are suitable for fabricating chemical sensors. ZnO has been proved to be suitable for both single crystal, bulk and thin film gas sensors [1]. Such sensitive thin films were successfully deposited by PLD process in the past [2]. In common practice sputtering is used to deposit good quality thin films [3].

Zinc oxide is a II-VI compound semiconductor with a wide direct band gap of 3.3 eV at room temperature [4]. This band gap is dependent on the substrate and the quality of thin film. Therefore it is of great importance as an UV emitting medium. Recently, ZnO has gained attention for its possible applications in blue and UV light emitting diodes (LEDs) and laser diodes (LDs) [5].

This paper presents study and characterization of ZnO thin film using Scanning Electron Microscopy (SEM) Hitachi S-3400N and X-Ray Diffractometer (XRD) analysis, which was deposited by employing Pulsed Laser Deposition (PLD) technique. The quality of thin film deposited at room temperature via Pulsed Laser Deposition was studied. Crystallinity of ZnO thin films can be improved by annealing of thin film after deposition [2]. F.K. Shan investigated the optimized condition for ZnO thin films relative to substrate temperature [3]. The crystallinity of ZnO thin films on various substrates is strongly dependent on substrate temperature, Laser fluence and oxygen ambient presence [6].

2. Experimental

Pulsed Laser Deposition process was carried out using Nd:YAG laser (1064 nm wavelength, 10mJ energy, 9-14 ns pulse duration and 1.1MW power) at room temperature. Zinc metal of 4N purity was used for depositing thin film on Calcite (CaCO_3) substrate. Surface of both target and substrate were polished prior to the deposition. PLD process was carried out in a computer controlled spherical PLD chamber shown in Figure 1. Pressure within the PLD chamber was kept at $\sim 10^{-3}$ torr with presence of oxygen.

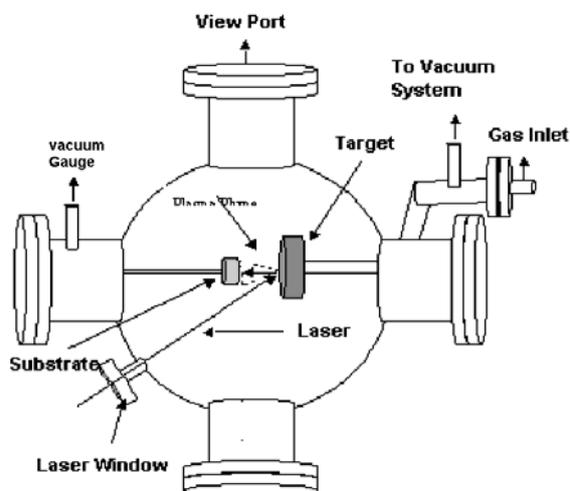


Figure 1: Computer control spherical PLD chamber for thin film deposition

The material is sputtered due to laser matter interaction following energy transfer mechanism [7]. Target was rotating with the help of a stepper motor to prevent crater formation. Crater formation can cause tilt in the plume and hence disturb film deposition process. The distance of target and substrate was optimized 5mm.

The laser was made to strike the target at an angle of 45° with respect to the normal to the surface of substrate. An IR transmitting laser window fixed at laser port of vacuum chamber was used to pass the laser from external source into the chamber as

indicated in Figure 1. It has been observed that ZnO crystalline thin films are only achieved with certain parameters and conditions for PLD process. Some of these parameters include separation of target and substrate, pressure, temperature and nature of substrate.

3. Results and discussion

Surface morphology of ZnO thin film was studied using Scanning Electron Microscope. The micrographs of substrate and deposited thin film are shown in Figure 2(a) and 2(b) respectively.

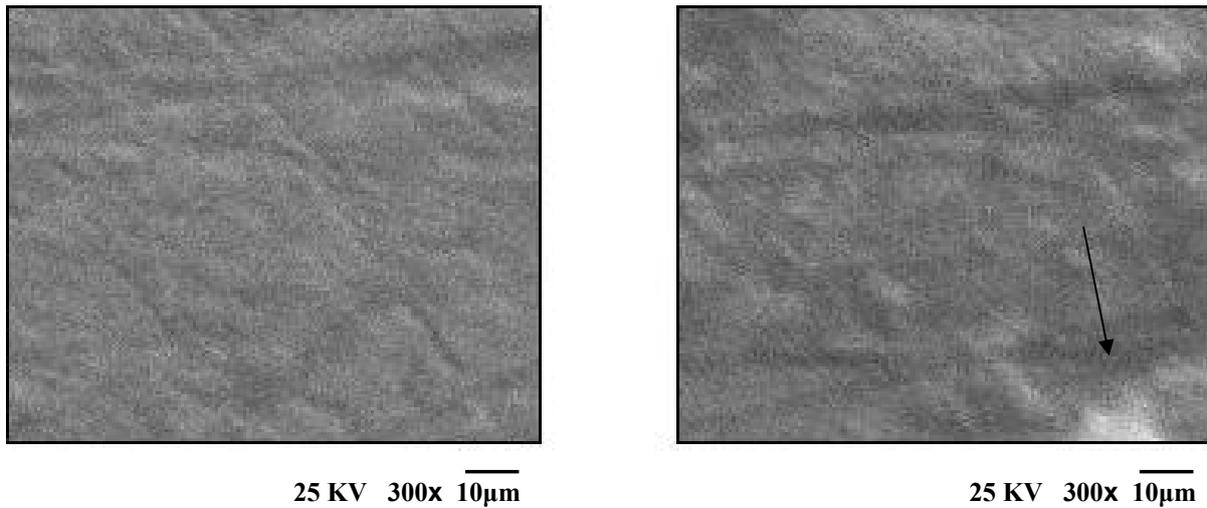


Figure 2: Scanning Electron Microscopy of (a) CaCO_3 substrate, (b) ZnO thin film deposited on CaCO_3 substrate.

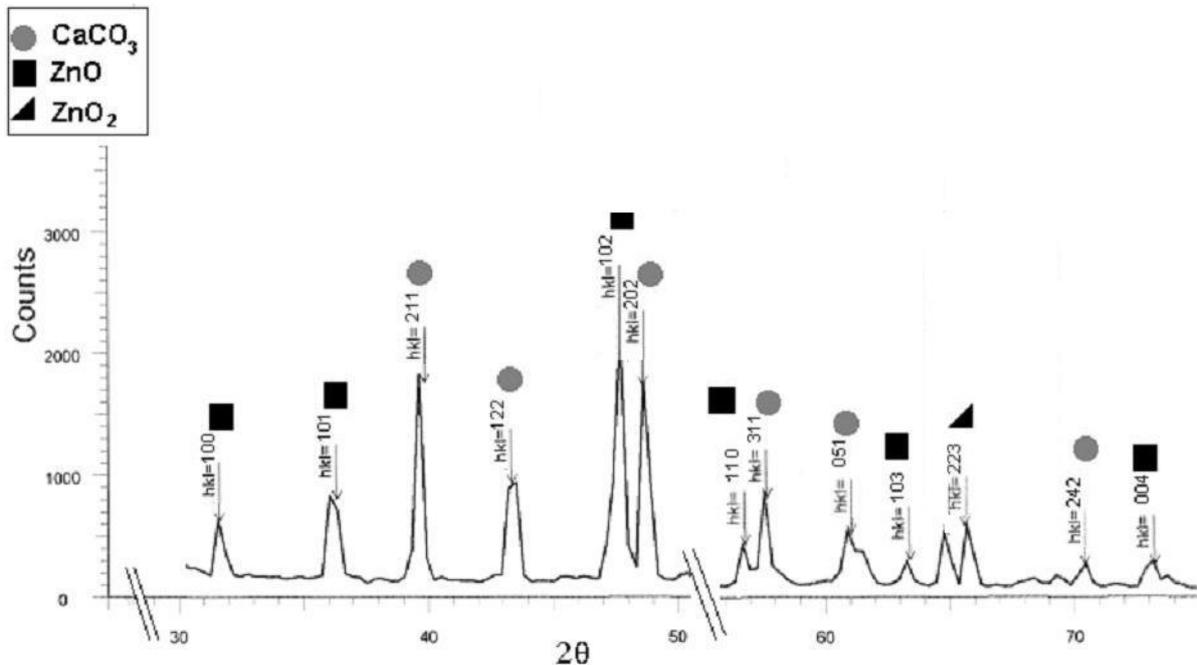


Figure 3: XRD pattern for ZnO thin film on CaCO_3 substrate

Table 1: Peak List of XRD pattern of ZnO thin film on Calcite (CaCO₃)

Sr. #	Compounds	d-spacing	2θ	hkl
1	ZnO	2.83367	31.547	100
2.	ZnO	2.47250	36.305	101
3.	CaCO ₃	2.26216	39.817	211
4.	CaCO ₃	2.08661	43.328	122
5.	ZnO	1.90760	47.633	102
6.	CaCO ₃	1.87203	48.595	202
7.	ZnO	1.61935	56.808	110
8.	CaCO ₃	1.59606	57.714	311
9.	CaCO ₃	1.51646	61.056	051
10.	ZnO	1.46520	63.435	103
11.	ZnO ₂	1.42115	65.644	223
12.	CaCO ₃	1.33510	70.474	242
13.	ZnO	1.29060	73.290	004

The micrographs show that the film is smooth, although some particulates are condensed on its surface. In the lower right corner the large white spot is a particle of radius 10 μm, which is presumably condensed on substrate during PLD process. Such particles result from sputtering of ablated target. This type of imperfection could affect the quality of thin film. It can be avoided by using loose focused laser ablation, but this may lead to an inhomogeneous film thickness due to angular distribution of plasma plume [8].

Crystal structure of the film was studied using X-ray diffractometer (BRUKER AXS D8). Figure 3 Shows XRD pattern of the thin film [9].

Peaks were observed for both Calcite and ZnO pertaining to different hkl planes. Three ZnO peaks are shown in this figure with 100, 101, 102 hkl planes at two theta angles of 31.5°, 36.3° and 47.6° respectively. These results clearly showed that under the optimized parameters of PLD technique a polycrystalline ZnO thin film was deposited. A small peak at 65.6° (Figure 3) matches the standard peak of ZnO₂ [9].

These diagnostics further confirmed the deposition of a polycrystalline ZnO thin film with different plane orientations as indicated by XRD patterns.

Resistivity of Thin film was measured with the help of four-probe and was found to be above 200 MΩm which is very high value for ZnO thin films. This high resistivity indicates that there are not enough charge carriers available for conduction in the thin film [9]. Impurities and defects in crystal structure also tend to increase conduction. Above mentioned high resistivity shows that good crystalline structure was ensured during the PLD process even at room temperature.

4. Conclusion

ZnO thin film was deposited via pulsed laser deposition (PLD) at room temperature. XRD analysis showed that the deposited thin film was polycrystalline in nature. Resistivity of deposited ZnO oxide thin film was found to have a value of the order >200MΩ, which is due to rare availability of charge carriers.

REFERENCES

- [1] J. Xu, Q. Pan, Y. Shun, Z. Tian; *Sensors and Actuators B*, 66(2000) 277–279.
- [2] Y. Nakata, T. Okada, M. Maeda; *Applied Surface Science*, 197(2002) 368-370.
- [3] F. K. Shan, B.C. Shin, S.W. Jang, Y.S. Yu; *Journal of European Ceramic Society*, 24(2004) 1015-1018.
- [4] F. K. Shan, Y. S. Yu, *Journal of the European Ceramic Society*, 24(2004) 1869–1872.
- [5] D. S. Ginley, C. Bright (eds.); *MRS Bull*, 25, (2000) 15–65.
- [6] J. N. Zeng, J. K. Low, Z. M. Ren, T. Liew, Y. F. Lu; *Applied surface science*, 197(2002) 362-367.
- [7] D. B. Geohegan; *Pulse Laser Deposition of Thin Films*, Chrisey and G. K. Hubler (eds), Wiley, New York, (1994) 59-69.
- [8] M. S. Rafique, M. Khaleeq-ur-Rahamn, M. S. Anwar, F. Mahmood, A. Ashfaq, K. Siraj; *Laser and Particle Beams*, 23(2005) 131-135.
- [9] H. Kordi Ardakani; *Thin Solid Films*, 287(1996) 280-283.