Conference Paper

ZnO Thin Film Deposition for TCO Application in Solar Cell

S. Agrawal, R. Rane, and S. Mukherjee

Facilitation Centre for Industrial Plasma Technologies (FCIPT), Institute for Plasma Research (IPR), Gandhinagar Plot No. A-10/B, Electronic Estate, GIDC, Sector 25, Gandhinagar, Gujarat 382044, India

Correspondence should be addressed to S. Agrawal; sag.agr@gmail.com

Received 5 January 2013; Accepted 3 April 2013

Academic Editors: P. Agarwal, B. Bhattacharya, U. P. Singh, and B. Sopori

This Conference Paper is based on a presentation given by S. Agrawal at “International Conference on Solar Energy Photovoltaics” held from 19 December 2012 to 21 December 2012 in Bhubaneswar, India.

Copyright © 2013 S. Agrawal et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

ZnO is a well-known suitable candidate for the Transparent Conducting Oxide (TCO) layer of thin film compound solar cells. In this paper we have discussed the deposition of ZnO thin film on glass substrate by reactive DC magnetron sputtering using oxygen as a reactive gas. Samples are prepared by varying oxygen flow rates during the deposition process. After deposition, samples are annealed at 300°C for 2 hours in vacuum environment. All the properties of the film are measured before and after annealing. All the samples are tested for the optical transparency, band gap, and electrical resistivity before and after annealing. Band gap of film is observed to be 3.2 eV. XRD and SEM measurements of the samples show the variation in the crystal structure and surface morphology of the film with varying oxygen flow rate and annealing also. Around 600 nm thick ZnO film with $1.5 \times 10^{-3} \Omega\cdot\text{cm}$ resistivity and 80% transparency without any doping is achieved.

1. Introduction

ZnO has attracted attention as Transparent Conducting Oxide (TCO) because of its large band gap (3.3 eV), low resistivity ($5 \times 10^{-4} \Omega\cdot\text{cm}$), abundance, and nontoxicity. Optoelectric properties of ZnO depend on deposition and post-deposition treatment conditions as these properties change significantly with the conditions like nature of chosen doping element, the adsorption of oxygen during the deposition process, film deposition temperature, and postdeposition annealing atmosphere [1].

Singh et al. [1] has shown that the lowest resistivity was found at 300°C deposition in oxygen environment. Our aim is to show that if the film is annealed at 300°C after deposition in reducing environment, it would show much lower resistivity ($\sim 10^{-3} \Omega\cdot\text{cm}$).

Magnetron sputtering is a well-known technique of depositing ZnO thin film [2]. In the present study, we have investigated the effect of oxygen partial pressure during film deposition by DC magnetron sputtering technique and annealing in reducing environment after deposition. The

purpose of this work is to determine the deposition and treatment conditions that can produce highly conducting and transparent ZnO film for thin film solar cell application.

2. Experimental

Figure 1 shows the schematic of the experimental setup for magnetron sputtering deposition. Distance between the target and substrate was ~ 15 cm. Base pressure of the system was 2×10^{-5} mBar. Total operating pressure during deposition was 5×10^{-3} mBar. Deposition is done in a mixture of argon and oxygen gases. Zn target of 3" diameter, 5 mm thick, and 99.999% purity is used for sputtering. Deposition power was around ~ 275 W. Deposition process is performed for 1 hour. Total five samples are deposited by varying the oxygen percentage in argon. Deposition parameters (oxygen percentage with sample ID no.) are shown in Table 1.

After deposition, all the samples are annealed in reduced environment ($\sim 2 \times 10^{-5}$ mBar) for two hours at 300°C. Annealing treatment profile is shown in Figure 2.

FIGURE 1: Experimental setup.

FIGURE 2: Postdeposition annealing treatment profile.

TABLE 1: Deposition parameters.

Sample ID	Total operating pressure	Oxygen variation	
		O ₂ flow	O ₂ %
Unit	mBar	SCCM	%
A	4×10^{-3}	13.5	25%
B	4.5×10^{-3}	12.5	21%
C	4.5×10^{-3}	11.5	19%
D	5×10^{-3}	10.0	17%
E	5×10^{-3}	09.0	14%

3. Results and Discussion

Around 600 nm ($\pm 10\%$) thick films are deposited in argon and oxygen environments. Resistivity of all samples is measured using four-probe method. Transparency and band gap (band gap is being measured using Tauc method and while measuring band gap reflection of the film is being

assumed zero) are measured using UV-Vis (190–1100 nm) spectrophotometer. Results are shown in Tables 2 and 3.

3.1. Transparency and Band Gap. Figures 3, 4, and 5 show the transparency measurements of the films. Figure 5 clearly shows that annealing process does not affect the transparency in considerable amount, but as the oxygen percentage increases in deposition process, transparency increases.

Band gap of the films is found ~ 3.2 eV.

3.2. Resistivity. Figure 6 clearly shows that resistivity of the film varies with oxygen percentage and high for higher oxygen percentage for as deposited samples. But after annealing in reduced environment, resistivity of the all samples go down up to $\sim 10^{-3} \Omega \cdot \text{cm}$ due to desorption of extra oxygen in vacuum environment at 300°C .

3.3. XRD. Figure 7 shows the XRD results of the samples before annealing. It is clear that the film is made of mixed

TABLE 2: Results of deposited film before annealing.

Sample ID	Before annealing (as deposited)				
	Sheet resistance of the film	Thickness of film	Resistivity of the film	Transparency of the film	Band gap of the film
Unit	Ω	nm	$\Omega \cdot \text{cm}$	%	eV
A	High**	550	High**	81.6	3.14
B	2.27	650	6.69×10^{-2}	87.3	3.12
C	7.116	710	2.29×10^{-1}	87.3	3.14
D	0.304	530	7.30×10^{-3}	60.2	3.0
E	0.216	530	5.19×10^{-3}	60.3	3.12

**High Resistivity means it is such high that is not in the measurement range of the available four-probe instrument at our lab.

TABLE 3: Results of films after annealing treatment.

Sample ID	After annealing at 300°C for 2 Hrs in vacuum (2×10^{-5} mBar)				
	Sheet resistance of the film	Thickness of film	Resistivity of the film	Transparency of the film	Band gap of the film
Unit	Ω	nm	$\Omega \cdot \text{cm}$	%	eV
A	0.0616	650	1.81×10^{-3}	84.2	3.19
B	0.041	830	1.54×10^{-3}	80.8	3.2
C	0.457	580	1.20×10^{-2}	85.9	3.2
D	0.0903	640	2.62×10^{-3}	74.2	3.1
E	0.0445	645	1.30×10^{-3}	61	3.18

FIGURE 3: Transparency with oxygen percentage before annealing (as deposited).

FIGURE 4: Transparency with oxygen percentage after annealing.

phase of hexagonal phase and Face Centered Cubic (FCC) phase of ZnO and hexagonal phase of Zn. It is clear that films deposited in high oxygen percentage environment are crystalline compared to the films deposited in 14% and 17% oxygen environment. It is clear that film formation in hexagonal face is more preferred than FCC phase for

deposition in higher oxygen percentage environment. Film deposited in 19% oxygen environment is more crystalline as it shows the most intense (002) peak of hexagonal phase. But Zn phase peak (101) is clearly shown in the film deposited in 14% oxygen environment. It is a clear indication of less ZnO formation in less oxygen presence.

FIGURE 5: Transparency: comparison between as-deposited (before annealing) and annealed samples.

FIGURE 6: Resistivity: comparison between-as deposited (before annealing) and annealed samples.

Figure 8 shows the XRD results after annealing. It shows the single phase (hexagonal) formation of ZnO in the film, while film deposited at 14% oxygen environment still shows the Zn in the film. Presences of Zn in this sample also clarify the reason of low resistivity and low transparency in this particular sample.

3.4. SEM. Figure 9 shows the cross-section images of the films deposited in oxygen environment and annealed in reduced environment. It can be clearly seen from the images that, as oxygen percentage increases, columnar growth of the film increases while the film deposited at lower oxygen percentage (14%) shows no columnar growth.

FIGURE 7: XRD results with oxygen variation before annealing (as deposited).

FIGURE 8: XRD results with oxygen variation before annealing (as deposited).

Figure 10 shows the surface images of films deposited in oxygen environment and annealed in reduced environment. Annealed film shows bigger grain size compare to the as-deposited films. Film deposited at 19% oxygen shows the lowest grain size.

4. Conclusion

Approximate 600 nm thick film of ZnO deposited using DC magnetron sputtering on glass substrate. Deposited films achieve low resistivity after annealing in reduced environment due to desorption of oxygen from the film. Film deposited in 21% oxygen environment, shows 85%

FIGURE 9: SEM images of the cross-section of the films (magnification 25 K, scale $\sim 1 \mu\text{m}$).

transparency, and after annealing at 300°C for two hours in reduced environment shows the $1.5 \times 10^{-3} \Omega\cdot\text{cm}$ resistivity.

5. Future Scope of Work

Deposited ZnO film needs more improvement in terms of resistivity for TCO application of thin film solar cell. Doping

of aluminum during deposition process is an option for decreasing the resistivity of the film. Doping should be less than 2% atomic weight to keep the transparency same [3].

Acknowledgments

The authors would like to acknowledge Dr. Balasubramanian, FCIPT, IPR, Gandhinagar, Gujarat, and Dr. Rajesh

FIGURE 10: SEM images of the surface of the films (magnification 25 K, scale $\sim 1 \mu\text{m}$).

Babu, Forensic Science University, Gandhinagar, Gujarat, for arranging the spectrophotometer measurements, Mr. Narendra Chauhan, FCIPT, IPR, Gandhinagar, Gujarat, for performing SEM measurements, and Mr. Pratipal Rayjada, FCIPT, IPR, Gandhinagar, Gujarat, for performing XRD measurements. They would also like to acknowledge Department of Science and Technology, Government of India, for supporting this study under Grant DST/TM/SERI/2 K11/72.

References

- [1] A. V. Singh, M. Kumar, R. M. Mehra, A. Wakahara, and A. Yoshida, "Al-doped zinc oxide (ZnO:Al) thin films by pulsed laser ablation," *Journal of the Indian Institute of Science*, vol. 81, no. 5, pp. 527–533, 2001.
- [2] K. Ellmer, F. Kudella, R. Mientus, R. Schieck, and S. Fiechter, "Influence of discharge parameters on the layer properties of

reactive magnetron sputtered ZnO:Al films,” *Thin Solid Films*, vol. 247, no. 1, pp. 15–23, 1994.

- [3] K. Ellmer and R. Wendt, “D.c. And r.f. (reactive) magnetron sputtering of ZnO:Al films from metallic and ceramic targets: a comparative study,” *Surface and Coatings Technology*, vol. 93, no. 1, pp. 21–26, 1997.