SPUTTERED OF ZnO:AI THIN FILMS FOR APPLICATION IN PHOTOVOLTAIC SOLAR CELLS

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Summary High transparent and conductive, aluminium - doped zinc oxide thin films (ZnO:Al), were prepared by radio – frequency (RF) diode sputtering from ZnO+2 wt. % Al₂O₃ target on Eutal glass substrates. Surfaces of the samples were treated by various technological steps during preparation. The ion bombardment and the substrate temperature modified their structure, surface morphology, electrical and optical parameters. In this work we present changes between samples prepared at room temperature (RT) and at 200°C, between samples on ion etched substrate and non-modified substrate, and effect of ion etching of the sample surface. We measured transmittance, resistivity and microroughness by AFM on all samples.

1. INTRODUCTION

The unique material properties in combination with a great natural abundance and low cost, make ZnO a promising transparent conductive oxide (TCO) for application in thin film solar cells, various optoelectronic devices and DNA sensors [1, 2, 3]. Improvement of existing systems and the design of new concept require continual upgrading of all steps of the electroanalytical process. The use of electrochemical biosensors is of great importance in electroanalysis. Conductive materials and biomaterials based on carbon electrodes, gold, or ZnO:Al electrodes and biological materials (e.g. DNA) are interesting alternatives for the construction of electrochemical biosensors. We studied the influence of different process parameters on properties of sputtered thin films including roughness, electrical and optical properties.

2. EXPERIMENTAL DETAILS

We prepared ZnO:Al thin films in a planar RF sputtering diode system Perkin Elmer 2400/8L, using a ceramic target (ZnO+2 wt. % Al₂O₃) in Ar working gas. The substrates were cleaned by standard chemical method. Films with thicknesses of 800 nm were deposited on Eutal glass. Two sets of samples were prepared on ion etched substrate at two different temperatures (RT and 200 °C). Further samples were prepared on non-modified substrate at two different temperatures with post-deposition treatment by RF ion etching (reduction of 80 nm in film thickness). Deposition parameters and thin film properties are given in Table 1. The film thickness was measured by Talystep instrument. The surface morphology was evaluated by means of atomic force microscopy (AFM, NT-MDT Solver P - 47) and scanning electron microscopy (SEM, LEO 1550). The resistivity of ZnO:Al thin films was obtained from 4 point method. The optical transmittance of the film was measured by optical device Avantes with AvaLight-DH-S Deuterium-Halogen Light Source, in the range from 190-1500 nm and the

AvaSpec-2048 Fiber Optic Spectrometer in the 200-1100 nm range.

3. RESULTS AND DISCUSSIONS

The most important parameters required for the application of ZnO:Al film are high optical transmittance, low electrical resistivity, and suitable roughness. The optical transmission properties of the ZnO:Al thin films deposited at different conditions are shown in the Fig.1. The integral transmittance of all the samples varies from 79 - 91% in the wavelength region of 360 - 1000 nm.



Fig. 1. The optical transmittance spectrum of films prepared at various deposition parameters



Fig. 2. Evaluation of band-gap energy from linear approximation of α^2 versus Energy plot

Absorption coefficient was calculated from transmittance data and optical band gap energy was evaluated from α^2 versus E dependence (Fig. 2). By comparison of transmittance spectra and integral transmittance of samples #1 & #2 and #3 & #5 we can see that substrate temperature during deposition has negligible influence on transmittance (Fig.1, Table 1). On the contrary, from Van der Pauw measurements it is clear that samples deposited at higher temperature exhibit lower electrical resistivities ($\rho \sim 10^{-3} \Omega cm$). Further, we can note the



Fig. 3. AFM images of ZnO:Al samples (a) prepared at RT and ion etched after deposition (sample# 4), (b) prepared at 200°C without ion etching after deposition (sample# 5), (c) prepared at 200°C and ion etched after deposition (sample# 6)

decrease of integral transmittance when we used ion bombardment of ZnO:Al films sputtered at RT and 200 °C. In our experiments, AFM was used to examine the surface morphology of ZnO:Al films. Fig. 3 presents morphologies of films deposited at different conditions. Samples show different surface morphologies and roughness (under different deposition conditions). The film deposited at RT and 200°C shown relatively high roughness (Rrms = 8 nm), (Fig. 3b). Ion bombardment caused different effects: samples deposited at 200°C had smoothed surface (Rrms = 3 nm) (Fig. 3c) and samples deposited at RT exhibited higher surface



Fig. 4. SEM images of ZnO:Al samples (a) prepared at RT and ion etched after deposition (sample# 4), (b) prepared at 200°C without ion etching after deposition (sample# 5), (c) prepared at 200°C and ion etched after deposition (sample# 6)

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Set of	Ion etching	Ion etching	Thickness	Substrate	Roughness	Resistivity	Integral	Optical
_								-
samples	of substrate	of thin film	of thin	temperature	[nm]	[Ω.cm]	transmittance	band-gap
			C1 []	[00]			F (7/ 1	F X 71
			film [nm]	[°C]			[%]	[ev]
alass	1	1	_	_	0	_	92	_
Shabb	,	,			0		72	
glass	etch.glass	/	-	-	1	-	92	-
0		-					-	
#1	250W/60 min	/	800	25	7	$3,4.10^{-2}$	89	3,27
#2	250W/60 min	/	800	200	7	4,7.10-3	90	3,33
	,	,	000	25	0	2.1.10-2	70	2.20
#3	/	/	800	25	8	3,1.10 2	79	3,28
#4	1	1	720	25	0	$2.2 \cdot 10^{-2}$	20	2.22
#4	/	/	720	23	9	2,2.10	89	5,55
#5	1	75W/30min	800	200	8	4 4 10-3	80	3 36
"3	'	75 W750mm	000	200	0	1, 1.10	00	5,50
#6	/	75W/30min	720	200	3	$3.9.10^{-3}$	91	3.35
			. 20	_ 30	,	2,2.10		2,00

 Tab. 1. The resistivity, integral transmittance and roughness of thin films deposited at different temperatures and ion bombardment

roughness (Rrms = 9 nm) (Fig. 3a). This distinctive influence of ion bombardment can be explained by differences in surface structure of thin films growing at the lower and higher temperature. The samples deposited at 200°C are more homogeneous; in consequence of ion bombardment makes the smoother surface. In the cause of deposition at RT, ZnO:Al thin films are more defective (interstitial vacancies) and ion bombardment can emphasize surface roughness. Changes in sample surface morphology observed from SEM pictures (Fig. 4(a, b, c) are equivalent to surface roughness valves obtained from AFM (Tab.1.).

4. CONCLUSION

ZnO:Al thin films were deposited on glass substrates by rf diode sputtering from a ZnO target with 2 wt % Al2O3 at RT and 200°C substrate temperatures. Finally on same samples ion etching was applied. According to our measurements, we can conclude, that deposition temperature has no influence on transmittance, but elevated deposition temperature caused lowering of electrical resistivities by one order of magnitude $(\rho \sim 10^{-3} \,\Omega \text{cm})$. The effect of ion bombardment on samples is affected by thin film structure, which is dependent on growth temperature.

Desirable properties of ZnO:Al were obtained at higher substrate temperature (200°C) during sputtering.

The results show suitability of thin films ZnO:Al in applications for solar cells and fabrication of DNA sensors.

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REFERENCES

- [1] Yoo, J., Lee, J., Kim, S., Yoon, K., Park, I. J., Dhunge, S. K., Karunagaran, B., Mangalaraj, D., Yi, J.: *High transmittance and low resistive ZnO:Al films for thin film solar cells*, Thin Solid Films, Vol. 480–481, 2005, pp. 213– 217.
- [2] Hüpkes, J., Rech, B., Calnan, S., Kluth, O., Zastrow, U., Siekmann, H., Wuttig, M.: Material study on reactively sputtered zinc oxide for thin film silicon solar cells, Thin Solid Films, Vol. 502, 2006, pp. 286 – 291.
- [3] Flickyngerova S., Ovadekova, R., Novotny, I., Tvarozek, V., Labuda, J., Breternitzc, V., Knedlik, Ch.: *Preparation of nanostructured thin-film interfaces applicable in biosensors*, Vacuum, Vol. 82, 2008, pp. 303–306.