Results in Physics 8 (2018) 249–252

Contents lists available at ScienceDirect

Results in Physics

journal homepage: www.journals.elsevier.com/results-in-physics

Annealing effect on the structural, morphological and electrical properties of TiO_2/ZnO bilayer thin films

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ARTICLE INFO

Article history:
Received 19 October 2017
Received in revised form 26 November 2017
Accepted 10 December 2017
Available online 15 December 2017

Keywords:
ZnO
TiO_2
XRD
AFM
Electrical properties

ABSTRACT

The effect of annealing temperature on the structural, morphological and electrical properties of TiO_2/ZnO (TZ) thin films has been observed. Bilayer thin films of TiO_2/ZnO are deposited on FTO glass substrate by spray pyrolysis method. After deposition, these films are annealed at 573 K, 723 K and 873 K. XRD shows that TiO_2 is present in anatase phase only and ZnO is present in hexagonal phase. No other phases of TiO_2 and ZnO are present. Also, there is no evidence of other compounds like Zn-Ti etc. It also shows that the average grain size of TiO_2/ZnO films is increased by increasing annealing temperature. AFM (Atomic force microscope) showed that the average roughness of TiO_2/ZnO films is decreased at temperature 573–723 K and then increased at 873 K. The calculated average sheet resistivity of thin films annealed at 573 K, 723 K and 873 K is 152.28×10^2, 75.29×10^2 and 63.34×10^2 ohm-m respectively. This decrease in sheet resistivity might be due to the increment of electron concentration with increasing thickness and the temperature of thin films.

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Introduction

Nowadays, multilayer thin films are intensively used for the designing of various electronic and optoelectronic devices like computer disks, solar cells and optical reflectors [1]. Titanium dioxide (TiO_2) is most studied material for optoelectronic devices because of low cost, durable, non-toxic, exceptionally stable material with a high refractive index [2]. However, in solar cells, TiO_2 has high recombination rate which decrease its efficiency [3]. Recently, enhancing the optoelectronic efficiency of TiO_2 is a hot topics; one approach is to dope some kind of transition metals into TiO_2, which would modify both physical and optical properties of TiO_2 [4], but the results are still unsatisfying. Another one is to couple other oxides in order to achieve higher optoelectronic efficiency, such as WO_3 [5], ZnO [6–8], SiO_2 [9,10], SnO_2 [11], Fe_2O_3 [12], and MoO_3 [13,14]. Among all of these, ZnO is found a suitable candidate for coupling with TiO_2 because it has same photocatalytic mechanism and has approximate equal band gap energy like TiO_2 [8]. ZnO has high mobility of electrons and low recombination rate of electrons as compared to TiO_2. Therefore, its electronic properties are higher than TiO_2. Also, it has found in literature [15] that ZnO layer on TiO_2 suppress the recombination rate of electron mainly occurred from TiO_2 to electrolyte.

Like coupling, annealing also effects on the electrical properties of TiO_2/ZnO thin film. The crystallinity and grain size have been changed by annealing the materials. At room temperature TiO_2 has amorphous nature, It should be annealed at thigh temperature to obtained crystallinity [16]. Also, at high temperature ZnO has poor electrical properties [17]. Therefore, in this study we have used couple TiO_2/ZnO thin films and check its structural, morphological and electrical properties at different annealing temperatures (i.e. 573 K, 723 K and 873 K). The purpose of this study is to enhance the efficiency of low cost dye sensitized solar cells.

Experimental technique

By using spray pyrolysis method, TiO_2/ZnO thin films have been deposited on FTO substrates. To prepare TiO_2 solution, TiO_2 powder (0.4 g) was added in ethanol and diethylene glycol (5 ml + 5 ml). The mixture was stirred for 15 h at 60 °C. 0.2 M solution of ZnO was obtained by adding zinc acetate dehydrate (0.88 g) in 2-methoxyethanol (20 ml) and stirred this solution for 30 min at 60 °C. After that, Mono-ethanol-amine was added and the mixture was continuously stirred for 90 min, a clear homogeneous ZnO solution was obtained. These solutions were then used to prepare

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https://doi.org/10.1016/j.rinp.2017.12.030
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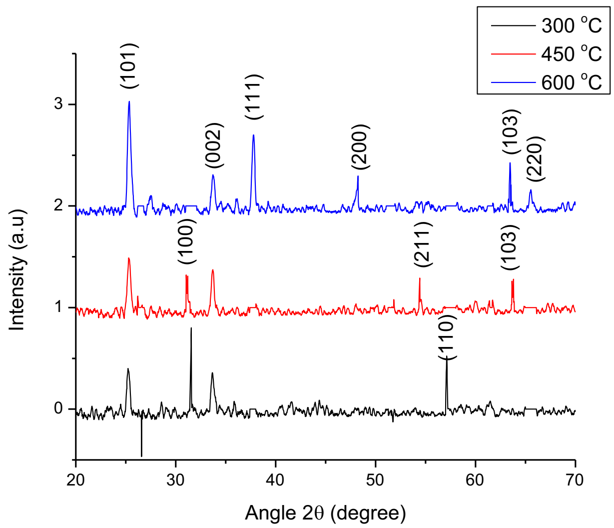

Fig. 1. XRD pattern of thin films annealed at temperatures 300 °C, 450 °C and 600 °C.

TiO_2/ZnO thin films. 2 cm × 2 cm FTO substrates were used. Before using, the FTO substrates were washed with organic solvent.

By using Spray pyrolysis method TiO_2/ZnO thin films were deposited. Firstly, TiO_2 solution was sprayed three times on the FTO glass substrate and annealed at 140 °C for 15 min. Then ZnO was deposited by spraying for three times and annealed at 120 °C for 10 min. By using this spray pyrolysis method three thin films were prepared. First film was annealed at 573 K, second film was annealed at 723 K and third film was annealed at 873 K in furnace.

The structural properties of TiO_2/ZnO thin films were studied by using a PW 3050/60 Analytical X'Pert PRO diffractometer (XRD). The surface morphology of films was observed by using atomic force microscope (AFM) (Park XE7). The electrical properties of the thin films were studied by using KIETHLEY (2400) instrument (four point probe technique) .

Result and discussion

XRD analysis

XRD graph of TiO_2/ZnO thin films annealed at 573 K, 723 K and 873 K is shown in Fig. 1.

XRD graph of TiO_2/ZnO thin film annealed at temperature 573 K showed four peaks. The anatase peak is obtained at 25.23° (1 0 1). Also three hexagonal peaks are obtained at 31.82° (1 0 0), 33.66° (0 0 2) and 57.168° (1 1 0) according to card number 00-001-1136. These results are matched with the previous results in literature [18–20]. Film annealed at temperature 723 K has five peaks. Two anatase peaks are obtained at 25.29° (1 0 1) and 54.5° (2 1 1) [18–20]. Three hexagonal peaks are obtained at 31.82° (1 0 0), 33.7° (0 0 2) and 63.204° (1 0 3) according to card number 00-001-1136. Film annealed at temperature 873 K has six peaks. Four peaks of TiO_2 having anatase phase are obtained at 25.35° (1 0 1), 37.78° (1 1 1), 48.16° (2 0 0) and 65.84° (2 2 0) [18–20]. The two hexagonal peaks are obtained at 33.71° (0 0 2) and 63.20° (1 0 3) according to card number 00-001-1136. This XRD pattern confirmed that TZ thin films consist of TiO_2 (anatase) and ZnO (hexagonal) atoms only. Also, there is no presence of any other phases of TiO_2 and ZnO or any compound like ZnTi etc. It has been found that at high temperature (i.e. 873 K), ZnO peaks are reduced. This is found in literature that at high temperature the electrical properties of ZnO are decreased. Therefore, our results matched with the available literature [15].

The Scherrer's formula is used to calculate the grain size [21,22].

The summary of structural properties obtained from Fig. 1 is shown in Table 1.

The effect of annealing temperature on the average grain size is shown in Fig. 2.

This graph shows that by increasing the temperature, the grain size is increased because by increasing the annealing temperature small grains fused collectively to increase grain size [23,24].

AFM (Atomic Force Microscope) explanation

The morphology of TiO_2/ZnO films annealed at 573 K, 723 K and 873 K is measured by AFM, as shown in Fig. 3(a–c).

It was observed that the surface morphology is changed by increasing temperature of the films. Fig. 3 indicates the existence of grains in the form of cluster but they have no definite grain boundaries [25]. Surface roughness, as a component of the surface texture, gives an indication about the quality of the surface. The average roughness of TiO_2/ZnO films annealed at temperature 573 K, 723 K and 873 K is 0.831, 0.2017 and 0.2732 respectively. This shows that as the temperature of films increases, average roughness decreases and then increases. The decrease in roughness

Table 1
XRD parameters extracted from Fig. 1.

Number of peaks	Peak position (2 theta)	Relative Intensity (%)	d-spacing (A°)	HKL	FWHM	Crystallite size (nm)	Phase	Dislocation line density (× 10^{18})
TZ annealed at temperature 300 °C								
1	25.23	53.62319	3.53	(1 0 1)	0.37	0.38	Anatase	6.77
2	31.7	100	3.37	(1 0 0)	0.25	0.57	Hexagonal	3.08
3	33.66	44.56522	2.66	(0 0 2)	0.33	0.44	Hexagonal	5.18
4	57.168	97.10145	1.78	(1 1 0)	0.11	1.40	Hexagonal	0.51
TZ thin films annealed at temperature 450 °C								
1	25.29	64.94505	3.52	(1 0 1)	0.39	0.37	Anatase	7.52
2	31.7	100	3.37	(1 0 0)	0.27	0.53	Hexagonal	3.59
3	33.7	47.91209	2.66	(0 0 2)	0.29	0.50	Hexagonal	4.01
4	54.5	92.30769	1.68	(2 1 1)	0.32	0.49	Anatase	4.20
5	63.204	15.82418	1.51	(1 0 3)	0.53	0.31	Hexagonal	10.8
TZ annealed at temperature 600 °C								
1	25.35	100	3.52	(1 0 1)	0.36	0.39	Anatase	6.41
2	33.71	37.1124	2.66	(0 0 2)	0.41	0.35	Hexagonal	8.01
3	37.78	74.22481	2.38	(1 1 1)	0.31	0.47	Anatase	4.47
4	48.16	20.63953	1.89	(2 0 0)	0.24	0.63	Anatase	2.49
5	63.204	16.37597	1.51	(1 0 3)	0.28	0.58	Hexagonal	3.01
6	65.54	18.50775	1.42	(2 2 0)	0.32	0.52	Anatase	3.76

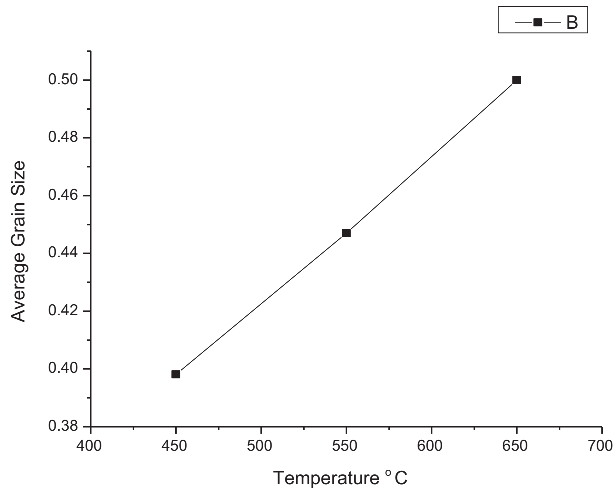

Fig. 2. Graph between annealing temperature and average grain size.

leads to good homogeneity of films. It indicates the good interaction of TiO2 and ZnO particles in different layers of films. As a result, good film has been formed. The increase in roughness is due to nucleation of the particles with increment of temperature [26]. The film is crack less. These cracks less films with homogeneity of surface play an important role in enhancing the efficiency of optical and electro optical devices [26].

Resistivity measurement

The performance of electrical device depends on the resistivity of material use in that device. I-V measurement of TiO_2/ZnO thin films at different temperature (573 K, 723 K and 873 K) is shown in Fig. 4, which shows that current is proportional to the magnitude of the voltage applied [27] according to ohm's law. Linear I-V curve is obtained for all thin films at different temperatures. The linear curve shows ohmic behavior of films [28]. This ohmic behavior increases by increasing the temperature of film. However, due to some factors, the result shows schottky response. One of the important factor of this response is defects which are produced at the interface of TiO_2/ZnO film [29]. Schottky response reduces by increasing the temperature of TiO_2/ZnO thin films.

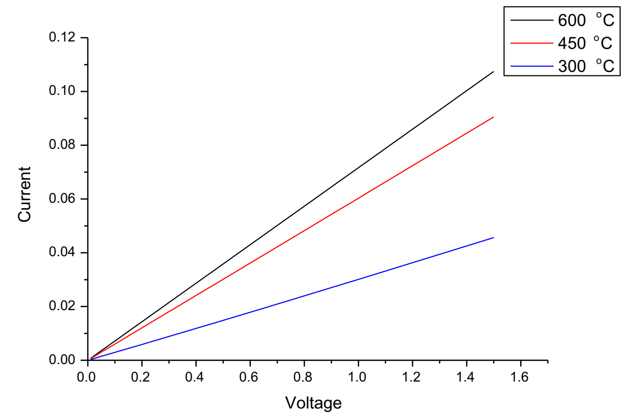

Fig. 4. Graph between voltage and current at different annealing temperatures.

Following relationship is used to find the sheet resistivity of the thin film [30]

$$\rho = \frac{\pi}{\ln(2)} \cdot \frac{V}{I} \quad (1)$$

where ρ is average resistivity, V is the voltage and I is the current. The calculated average sheet resistivity of thin films annealed at 573 K, 723 K and 873 K is 152.28×10^2, 75.29×10^2 and 63.34×10^2 ohm-m respectively [1]. From Fig. 5, it is observed that the average sheet resistivity of films is decreased by increasing the

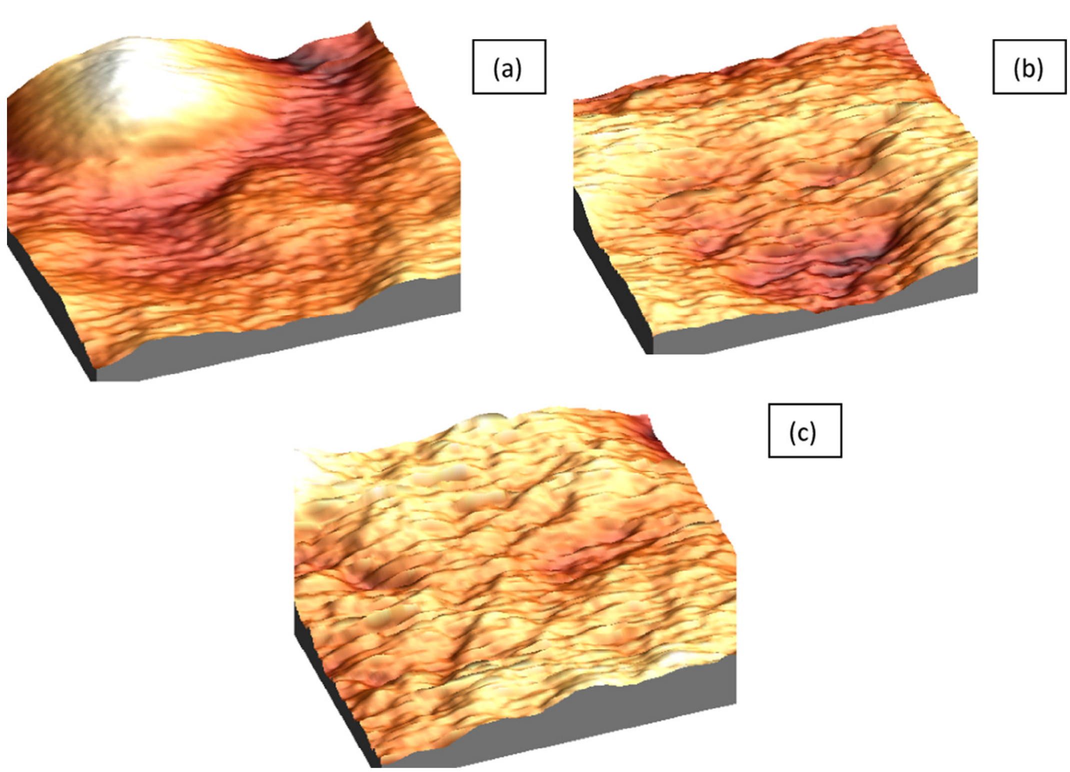

Fig. 3. AFM image of TZ thin film annealed at (a) 300 °C, (b) 450 °C and (c) 600 °C.

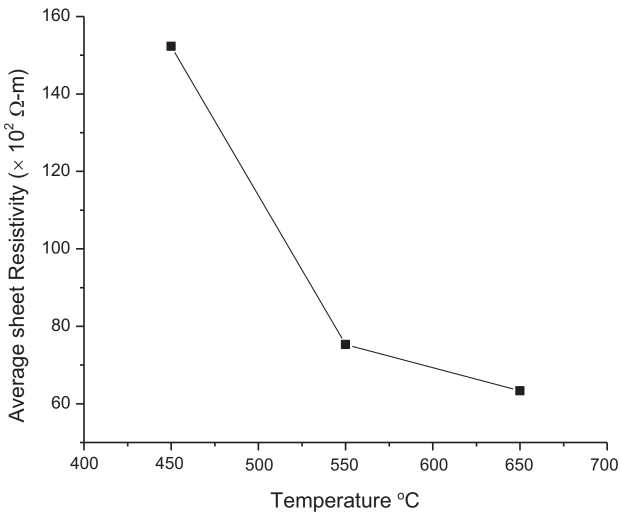

Fig. 5. Graph between temperature and average resistivity at different annealing temperatures.

annealing temperature. This decrease in sheet resistivity might be due to the increment of electron concentration with increasing the temperature of thin films [31]. Also, XRD results indicate that by increasing annealing temperature, particle size also increases. The surface contact between particles improves due to increment in particle size which produces better electron mobility in the thin films [28]. That's why the resistivity of film decreases.

Conclusion

TiO_2/ZnO thin films have been deposited on FTO substrate by spray pyrolysis method. Effect of annealing temperature on the properties of TiO_2/ZnO thin films has been observed. XRD pattern confirmed the hexagonal phase of ZnO and anatase phase of TiO_2. This also shows that by increasing the annealing temperature, grain size is also increases. This is due to collective fusion of small grains into large grain at high temperature. TZ thin film has highest average roughness at temperature 573 K and low roughness at temperature 723 K. The low roughness has high homogeneity which shows good interaction of TiO_2 and ZnO particles in different layers of films; result the formation of good film. The average sheet resistivity of thin films annealed at 573 K, 723 K and 873 K is 152.2766 ohm-m, 75.28774 ohm-m and 63.3379 ohm-m respectively. By increasing the annealing temperature, resistivity is decreased because of increment in particle size.

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