Thickness Dependence of Optical and Electrical Properties of Zinc Oxide Thin Films

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Abstract

This study addresses the optical and electrical properties of 200 nm – ca. 500 nm thick pristine zinc oxide (ZnO) films, fabricated with spray pyrolysis on quartz substrate. Particular attention was given for achieving high transparency (in visible and near-infrared region of solar spectrum) and low resistivity, simultaneously, by fine tuning the thickness of the film. The structural, optical and electrical properties were studied using X-Ray Diffraction (XRD), (UV-Vis) Ultraviolet-visible spectroscopy and room temperature Hall Effect measurements, respectively. The XRD spectrum showed the polycrystalline films with a preferential orientation along the c-axis. The transmittance of the ca. 225 nm thick ZnO film, particularly, at the wavelength 425 nm, was approximately 30 percent higher than the one with thickness ca. 476 nm. While at ca. 600 nm and above, the transparency of the later film diminished only by 15%. The band gap of ZnO thin film, derived with the aid of measured transmittance curves employing Swanepoel approximation, was ca. 3.26 eV and was almost independent to the film's thickness (decreased only by a very amount to ca. 3.22 eV, when the thickness increased to 476 nm). In contrast, with increase in thickness, film's resistivity decreased and electron mobility (μ) enhanced remarkably.

Keywords: Transparent thin films; Spray pyrolysis; Optical properties; Electrical properties

Introduction

Current PV devices in market, mostly, are made of crystalline silicon and amorphous silicon based solar cells. However, because of the considerably high material costs and long energy payback time, effort has been made to find alternative materials such as compound semiconductor (for example Gallium arsenide, (GaAs) [1,2], copper indium gallium selenide [3,4] and thin film based solar cells [5-7]. But, for practical use, they still require major breakthroughs to meet the long term goal of low cost, high stability and short payback time so that the technology can be affordable for their adoption.

Zinc oxide (ZnO) thin film based dye-sensitized solar cells (DSSCs) have attracted large attention to the scientific community of this domain for the past two decades [8-11], due to possession of similarity of the wide energy band gap (ca. 3.37

eV), but much higher (7 orders of magnitude) electron mobility to that of Anatase Titania (TiO_2). The DSSCs are devised with a thin film of wide band gap compound semiconductor (as an Electron Transport Layer, ETL), metal-organic complex dye (as a sensitizer) and a liquid electrolyte (as a Hole Transport Layer, HTL). About a micron thick layer of metal oxide, TiO_2 or ZnO is coated on top of ITO or FTO coated glass substrate, on top of which dye molecules are physically adsorbed. The later layer is then sandwiched between the counter electrode and TiO_2 layer. HTL layer carries holes produces in the dye molecule up to the counter electrode. This arrangement creates the large particle-dye-electrolyte interface needed for cell operation. In brief, operating principle of ZnO based DSSCs cell can be understood as: When photons (from sunlight) hit the photo-sensitive dye layer, the freed electrons accumulate on the ZnO layer and create an electrical current which transport to the counter electrode via load. However, one of the measure problems of the ZnO based DSSC is still low solar to light conversion efficiency (η).

In this regard, the highest overall η obtained so far for ZnO based DSSCs is only about 5% -7% depending on the nature of ZnO composition and dye used for its (ZnO film) sensitization [8]. In particular, it has been understood that quality of ZnO film (porosity of ZnO nanoparticles, geometry and surface morphology) greatly affects the optical and electrical properties of the film and, eventually, the photovoltaic properties of the cell. Therefore, the present investigation is aimed to reveal co-relation of ZnO films' optical properties with electrical resistances, which are prepared by a simple and low cost homemade spray pyrolysis setup on quartz substrate. Also, comparison of above properties of ZnO films with similar thickness, but synthesized by two different techniques, spray pyrolysis and spin coating have been made.

Materials and Methodology

Well known spray pyrolysis technique was employed for fabricating ZnO films on quartz substrate ($\sim 2.5 \times 2.5 \times 0.25$ cm) [12]. In short, the setup consists of a cylindrical nebulizer mounted vertically on a horizontal table to spray the aerosol jet aimed upwards at a substrate through a 5 mm nozzle. The

substrate was mounted on a temperature controlled heating block 25 mm above the nozzle. Humid air at atmospheric pressure is used as a carrier gas at a 2 - 3 mL/h flow rate. The precursor solution consists of 0.2 M zinc acetate dissolved in distilled water and ethanol (at ratio of 1:3) and quartz plates were used as substrates, purchased from Merck, Germany. Spraying times was variable to control the thicknesses of the film. Alternatively, thicker films can be obtained in shorter times by increasing the concentration of the solution. After deposition, samples were annealed in a standard furnace 450 °C for 1h in air. During the time of deposition the substrate temperature was maintained around 425 °C ± 10 °C. The substrate temperature was measured by IR thermometer (spectral response 6214 µm).

For comparison, we also employed spin coating technique for ZnO thin film preparation following our previous contribution [13], in which zinc acetate dehydrate $\text{Zn}(\text{CH}_3\text{COOH})_2 \cdot \text{H}_2\text{O}$, 2-methoxy ethanol and monoethanolamine (MEA) were used as a starting material, solvent, and stabilizer, respectively. The aged precursor solution was dropped onto the surface of ordinary glass substrate or a conducting side of FTO glass substrate and placed on the holder of the spin coater set at a rotating speed of 3000 rpm for 60 seconds. After deposition, the substrate was dried at 350 °C for fifteen minutes in a muffle furnace to completely evaporate solvent and organic residuals. The coating and drying processes were repeated for ten cycles for each sample. Then, finally, the samples were annealed at a temperature of 450 °C for one hour.

Transmission measurements were performed on films supported by quartz substrate using Genesis-10 UV Spectrophotometer (Thermo Scientific, UK) in the wavelength range from 310 to 1100 nm from which the thickness (d) and optical bandgap (E_g) of the film were estimated. Specifically, the d value was evaluated by employing the well-known Swanepoel method and the E_g was estimated by the plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$), where α is the absorption coefficient. The later parameter can be related with measured transmittance (T) and thickness of the film as,

$$\alpha = \frac{1}{d} * \ln\left(\frac{1}{T}\right) \quad (1)$$

The electrical properties were characterized with Four Probe method.

Results and Discussions

Structural characterization

The structural characterization of ZnO thin films was studied by the X-ray diffraction (XRD) pattern recorded by Broker D2 Phaser, Germany ($\lambda = 1.5418 \text{ \AA}$). The XRD JCPDS peaks were indexed by comparing the peak position with XRD data profile for ZnO thin film. Figure 1 shows the XRD pattern of thin film prepared with 20 min deposition time on quartz substrate at substrate temperature of 420°C.

The peaks at $2\theta = 30.5^\circ, 36.5^\circ, 38^\circ, 49^\circ, 58^\circ, 64.5^\circ$ and 69.5° are associated with crystal orientations (100), (002), (101), (102), (110), (103) and (112) respectively. The two unknown peaks at

Figure 1: XRD pattern of ZnO thin film.

$2\theta = 40^\circ$ and 44° were also observed. Specifically, the appearance of two intense peaks at $2\theta = 36.5^\circ, 38^\circ$, corresponding to the (002) and (102) planes, infer that the crystallites of the pure ZnO thin films are strongly oriented along c-axis (perpendicular to the plane of the substrate) with hexagonal structure.

ZnO films thickness dependence of transmittance

Figure 2A shows precursor solution deposition time (proportional to the thickness) dependence transmittance of quasi transparent ZnO thin films as a function of wavelength (λ). One can clearly notice, in the shorter wavelength region (380 nm – ca. 500 nm), a gradual decreasing trend of transmittance curves with the deposition times of the precursor solution. For example, the transmittance value at $\lambda \approx 420 \text{ nm}$ (the first peak position) of the film obtained after depositing precursor solution for 12 min was found to be about 92%, while for the film with 20 min deposition time the transmittance decreased down to 65 %. Moreover, the presence of noticeable oscillations in the transmittance versus wavelength spectra indicates that the films are of good quality [14] and it also allow estimating the thickness of a film with the help of minima and maxima in the measured transmittance [14-15]. The thicknesses of the films were extracted by using Swanepoel method (an envelope was drawn using the maxima and minima of each curve and also used value of refractive index of quartz glass was 1.46). The estimated values, listed in Table 1, show increment of the film's thickness with the elevation of deposition time of the precursor solution as expected.

Figure 2B compares the transmittance curves of ZnO films of similar thicknesses fabricated with two different methods (spray pyrolysis and spin coating) as a function of wavelengths. The curves with solid red and blue lines, respectively, represent the transmittance curves for films prepared by spray pyrolysis (deposited for 12 min.) and spin coating (10-cycle at 3000 rpm). As indicated in Table 2, both the films have very close thicknesses and one can clearly notice that even the films fabricated by two different techniques (but with approximately equal thicknesses) show similar values of transmittance for all the wavelengths of the investigated. Also, included in Figure 2B is of curve (green

Figure 2A: Precursor solution deposition time dependence of transmittance as a function of radiation wavelength.

Figure 2B: Transmittances as a function of radiation wavelength of ZnO films prepared by spray pyrolysis and spin coating.

line) with 18 min deposition time of which electrical properties were compared with above two films (discussed below in the consecutive section).

The plot of $(\alpha h\nu)^2$ versus $h\nu$ Figure 3 is linear over a wide range of photon energies, indicating a direct type of transitions. The intercepts of extrapolated lines and abscissa (the energy axis) reflect the energy band gaps (E_g). The extracted E_g values from Figure 3 are shown in Figure 4, which indicate a very small variation on optical band gap with thickness of thin film. Although there is monotonic decrease of E_g values with increasing thickness, it may be concluded that there was almost no effect of alteration of film's thickness on optical band gap.

Thickness dependence of electrical properties

The relationship between film thickness and electrical properties was studied, with Room Temperature Hall Effect

measurements using a Keithley Hall setup, for both kinds of films deposited with spray pyrolysis and also for a sample with spin coating (see Figure 2B). In particular, Hall effect measurements were carried out only for films with thicknesses 265 nm and 435 nm (prepared by spray pyrolysis), and also for a film thickness 262 nm (prepared by spin coating). And observed results are summarized in Table 2. As shown in Table 2, the significantly low resistivity value of 22.86 Ωcm was measured for film with $d = 435$ nm compared to other two samples: For film with 265 nm the resistivity was quite high, as a result, Hall measurement was impossible. While for the spin coated film (thickness - 262 nm) the resistivity was found to be 32.7 Ωcm ($0.031 \Omega^{-1}\text{cm}^{-1}$) which is about 30 percent higher compared to resistance of former film (film with thickness 435 nm). In contrast, the corresponding carrier mobility was quite low for film with thickness 435 nm compared to film with thickness - 262 nm. This may be due to difference in fabrication method.

Conclusion

The thickness dependence optical and electrical properties of transparent thin film of zinc oxide on quartz substrate have been investigated. Clear co-relation was observed between precursor solution deposition time and film's thickness: The film's thickness found to increase with the deposition time, while

Table 1: Thicknesses of ZnO films calculated with Swanepoel method.

Precursor solution deposition time (minutes)	Estimated Thickness (nm)	Band gap (eV)
12	265	3.255
14	314.9	3.251
16	384.6	3.243
18	415.9	3.232
20	476.4	3.224

Figure 3: $(\alpha h\nu)^2$ as a function of photon energy, $h\nu$, (in eV). For estimating band gap linear fit was made near the rising edge of each curve and extrapolated up to the abscissa.

Table 2: Thicknesses of ZnO films calculated with Swanepoel method.

Sample	Thickness [nm]	Mobility [cm ² /Vs]	Conc. [cm ⁻³]	Cond. [Ω ⁻¹ cm ⁻¹]	Res. [Ωcm]	Carrier
12min. ^{*SP}	265	High resistivity layer. Hall measurement was impossible				
18min. ^{*SP}	435	2.22	1.23×10 ¹⁷	0.0437	22.857	n
10 cycle ^{*SC}	262	40	4.77×10 ¹⁵	0.0305	32.712	N

^{*SP}, spray pyrolysis, ^{*SC}, spin coating

Figure 4: Variation in band gap with film thicknesses.

the transmittance found to diminish only ca. 15% above 600 nm and in the near IR region when the film's thickness increased by two fold. Also, there was almost no effect on optical band gap of change in film's thickness. Electrical conductivity of the film found to enhance from almost zero for film with thickness 265 nm to ca. 0.044 Ω⁻¹cm⁻¹ for 435 nm.

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References

1. Ward JS, Ramanathan K, Hasoon FS, Coutts TJ, Keane J, Contreras MA, et al. A 21.5% efficient Cu(In,Ga)Se₂ thin-film concentrator solar cell. *Prog Photovoltaics*. 2002;10:41-46.
2. Afzaal M, Brien PO. Recent developments in II-VI and III-VI

semiconductors and their applications in solar cell. *J Mater Chem*. 2006;16:1597-1602.

3. Schock HW. Thin film photovoltaics. *Appl Surf Sci*. 1996;92:606-616.
4. Birkmire RW. Compound polycrystalline solar cells:: Recent progress and Y2 K perspective. *Sol Energ Mat Sol*. 2001;65:17-28.
5. Regan BO, Gratzel M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature*. 1991;353:737-740.
6. Gratzel M. Dye-sensitized solar cells. *J Photochem Photobiol C*. 2003;145-153.
7. Yella A, Lee HW, Tsao HN, Yi C, Chandiran AK, Nazeeruddin MK, et al. Porphyrin-sensitized solar cells with cobalt (II/III)-based redox electrolyte exceed 12 percent efficiency. *Science*. 2011;334(6056):629-634.
8. Anta JA, Guillen E, Tena-Zaera R. ZnO-Based Dye-Sensitized Solar Cells. *J Phys Chem C*. 2012;116(21): 11413-11425.
9. Saito M, Fujihara S. Large photocurrent generation in dye-sensitized ZnO solar cells. *Energy Environ Sci*. 2008;1:280-283.
10. Lin CY, Yi-Hsuan L, Chen HW, Chen JG, Kung CW, Vittal R, Ho KC. Highly efficient dye-sensitized solar cell with a ZnO nanosheet-based photoanode. *Energy Environ Sci*. 2011;4:3448-3455.
11. Xu C, Wu J, Desai UV, Gao D. Multilayer assembly of nanowire arrays for dye-sensitized solar cells. *J Am Chem Soc*. 2011;133(21):8122-8125.
12. Huczko A, Dabrowska A, Madhup DK, Subedi DP, Chimouriya SP. Al-doped ZnO nanofilms: Synthesis and characterization. *Phys Status Solidi*. 2010;247:3035.
13. Kafle B, Acharya S, Thapa S, Poudel S. Structural and optical properties of Fe-doped ZnO transparent thin films. *Ceramics International*. 2016;42(1):1133-1139.
14. Ilcan S, Caglar M, Caglar Y. Determination of the thickness and optical constants of transparent indium-doped ZnO thin films by the envelope method. *Materials Science Poland*. 2007;25(3):709.
15. Dorrnanian D, Dejam L, Mosayebian G. Optical characterization of Cu₃N thin film with Swanepoel method. *Theoretical and Applied Phys*. 2012;6:13.