

Low-temperature deposition of ZnO thin films on PET and glass substrates by DC-sputtering technique

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Abstract

The structural, optical and electrical properties of ZnO thin films (260–490 nm thick) deposited by direct-current sputtering technique, at a relatively low-substrate temperature (363 K), onto polyethylene terephthalate and glass substrates have been investigated. X-ray diffraction patterns confirm the proper phase formation of the material. Optical transmittance data show high transparency (80% to more than 98%) of the films in the visible portion of solar radiation. Slight variation in the transparency of the films is observed with a variation in the deposition time. Electrical characterizations show the room-temperature conductivity of the films deposited onto polyethylene terephthalate substrates for 4 and 5 h around 0.05 and 0.25 S cm⁻¹, respectively. On the other hand, for the films deposited on glass substrates, these values are 8.5 and 9.6 S cm⁻¹ for similar variation in the deposition time. Room-temperature conductivity of the ZnO films deposited on glass substrates is at least two orders of magnitude higher than that of ZnO films deposited onto polyethylene terephthalate substrates under identical conditions. Hall-measurements show the maximum carrier concentration of the films on PET and glass substrate around 2.8 × 10¹⁶ and 3.1 × 10²⁰ cm⁻³, respectively. This report will provide newer applications of ZnO thin films in flexible display technology.

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1. Introduction

Light-weight, flexible display technologies have recently gained tremendous interest in the display industry for the development of highly demanding future product applications in efficient portable devices such as pagers, personal digital assistants (PDA), smart cards, cell phones, digital cameras, camcorders, remote control circuits and the future “electronic paper” [1–10]. These flexible displays incorporate transparent conducting oxide (TCO) films on plastic substrates and therefore also called ‘plastic displays’ [8,11]. These plastic displays have several advantages over glass-substrates based

displays, which include robustness, lesser weight, thinness (which provides wide viewing angles), flexibility (for varying the device shape to optimize visibility and thus suppress reflections), durability, easy scaling-up to large format for large volume roll-to-roll production [8,10,12] etc. The substrate materials, commonly used for the above applications include polycarbonate (PC), polyarylate (PAR), polyestersulfone (PES), polyimide (PI), polyethylene terephthalate (PET), polyolefin, polytetrafluoroethylene (Teflon), thermoplastic polymethyl methacrylate (Perpex, Plexiglas), polyethylene naphthalate, cellulose triacetate etc. [8,10,11,13–15]. Amongst the above materials, PET and PC are the most commonly used substrates in plastic display applications because of their superior optical properties over other polymer substrates [8]. Indium tin oxide (ITO) is commonly used as the transparent conducting coatings on these polymer substrates because of its better electro-optical properties over other TCOs [8,11,16,17]. But in plastic display technology the most important issue is the

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low-temperature deposition of ITO onto the plastic substrates as these plastic substrates are very much temperature sensitive and the low temperature deposition of ITO film onto plastic substrates severely deteriorate the quality of the as-deposited film [11]. So some alternatives to ITO is needed for the low-temperature deposition of good quality TCO films onto plastic substrates. ZnO can become a good alternative to ITO because of its suitability for low-temperature deposition [18,19].

ZnO thin films are technologically important materials due to its wide range of optical and electrical properties. These characteristics have made ZnO thin films very adequate for several promising applications such as in solar cells [20], gas sensors [21], transducers [22], luminescent materials [23], transparent conductors [24], heat mirrors [25] etc. ZnO thin films have been prepared by many techniques like thermal evaporation [26], chemical vapor deposition [27,28], radio-frequency (RF) magnetron sputtering [29], spray pyrolysis [30], pulsed laser deposition [31], sol–gel-dip-coating [32], electro-deposition [33] etc. As far as ZnO thin film deposited on PET substrate is concerned, Yamabi and Imai [34] deposited ZnO films onto PET substrates by wet-chemical procedure. In the present work, we have synthesized ZnO films onto PET and glass substrates by direct-current (DC) sputtering technique and studied the corresponding structural, optical and electrical properties. This report may give an added impetus on the applications of this technologically important material and give newer alternatives to ITO in the display industries.

2. Experimental

2.1. Target preparation

Commercially available ZnO powder (99.99%) was first taken into a grooved aluminum holder and pressed into a free-standing pellet by hydrostatic pressure (150 kgf cm^{-2}). This pellet was then used as the target for sputtering and placed into the sputtering chamber by appropriate arrangements as the upper electrode. PET, glass and Si (111) substrates were placed on the lower electrode. Negative terminal of the power supply was connected to the target and the lower electrode was kept at ground potential.

2.2. Film deposition

Our sputtering system consists of a conventional vacuum system, which was evacuated to 10^{-6} mbar by a rotary and diffusion pump arrangement. The chamber was back filled with argon. The target was pre-sputtered for 10 min to remove contamination, if any, from the surface and then the shutter was displaced to expose the substrates in the sputtering plasma. PET (DuPont Torray-100), glass and Si (111) were used as substrates. Before placing into the deposition chamber, the PET substrates were washed by alcohol and then ultrasonically cleaned in alcohol for 10 min. The glass substrates were at first cleaned by mild soap solution, then washed thoroughly in deionized water and also in boiling water. Finally they were ultrasonically cleaned in acetone for 15 min. On the other hand, Si substrates

Table 1
Summary of deposition parameters

Target	ZnO pellet
Substrate	PET, glass, Si (111)
Substrate-to-target distance	2.0 cm
Base pressure	0.05 mbar
Sputtering pressure	0.4 mbar
Sputtering gas	Argon
Substrate temp.	363 K
Sputtering voltage	2.5 kV
Current density	4.0 mA/cm ²
Deposition time	4 and 5 h

were immersed in 20% HF solution for 5 min for removing surface oxide layers. Then they were cleaned in deionized water and finally with alcohol in an ultrasonic cleaner. The summary of deposition conditions is shown in Table 1. The sputtering was done in a lower substrate temperature of 363 K and all the three types of substrates (PET, glass and Si) were placed together under the sputtering plasma. Therefore the films were deposited simultaneously on all the three types of substrates under identical sputtering conditions. Also the deposition time was varied to observe any change in the properties of the films.

2.3. Characterization

The deposited films were characterized by X-ray diffraction (XRD, BRUKER D8 ADVANCE, by CuK_α radiation) measurements. Optical transmission spectra of the films deposited onto PET and glass substrates were measured by a UV-Vis-NIR spectrophotometer (SHIMADZU-UV-3101-PC) in the wavelength range of 300 to 2600 nm, taking similar bare substrates as reference, and hence the spectra give transmittance of the films only. Thicknesses of the films were measured by an ellipsometer (NANO-VIEW SG SM 1000). Room-temperature electrical conductivity of the films was studied by the standard four-probe method under vacuum condition (10^{-3} mbar). The contact was made with silver paint, which showed linear I–V characteristic over a wide range of applied voltages. Hall-measurements were done under room temperature by standard methods.

3. Results and discussions

3.1. Structural properties

Fig. 1 shows the XRD pattern of ZnO target, which was used for sputtering. All the peaks originate from the hexagonal ZnO [35]. Fig. 2 shows the XRD patterns of as-deposited ZnO films on PET substrates with deposition times 4 and 5 h, respectively. XRD pattern of ZnO films onto PET deposited for 4 h (thickness ~ 260 nm) shows poor crystallinity. But the film deposited for 5 h (thickness ~ 470 nm) on PET confirmed the formation of crystalline ZnO and three peaks originated from (100), (002) and (101) reflections of hexagonal ZnO [35]. The XRD pattern for 4 h deposited ZnO films on PET substrates shows weak intensity as well as broad peaks. The broad peaks indicate poor crystallinity and small crystallite size. With the 5 h deposited film along with the increase of thickness the

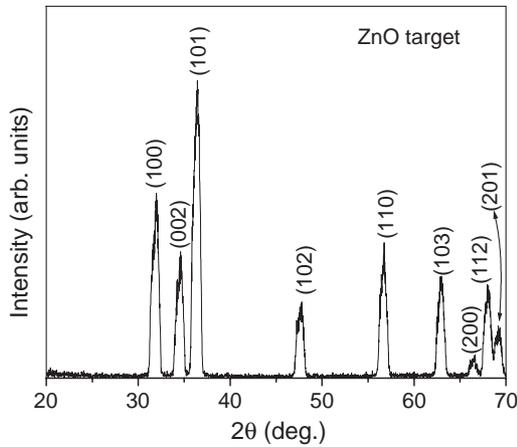


Fig. 1. XRD pattern of ZnO pellet used as sputtering target.

crystalline quality of the films also become better, which is also reflected by the improvement in the electrical properties of the films, discussed later. Fig. 3 shows the XRD patterns of as-deposited films on glass substrates under the identical conditions as that deposited onto PET substrates. The crystallinity in these cases is slightly better than that deposited onto PET substrates. Similar observation was reported by Kulkarni et al. [17] in their ITO films deposited onto polymer and glass substrates. For films on glass substrate with deposition time 4 h, a preferred (002) orientation is observed. However the orientation is lost for the films deposited with 5 h, as is evident from the XRD spectra shown in Fig. 3 (b). ZnO films deposited on glass substrate in general shows some (002) orientations indicating c-axis perpendicular to substrate. But in our case for 5 h deposited films the orientations are lost. This may be due to the fact that, with increase in the film thickness the surface roughness evolved, and the incoming species would have less freedom (adatom mobility decreases) to seek the minimum energy site and the growth becomes random. This is particularly important in our deposition conditions, as the substrate temperature was low. Also the generation of intrinsic stress may have some effect on the loss of orientation in the film growth.

We have estimated the film thickness by the ellipsometric measurements. For films deposited on transparent substrates

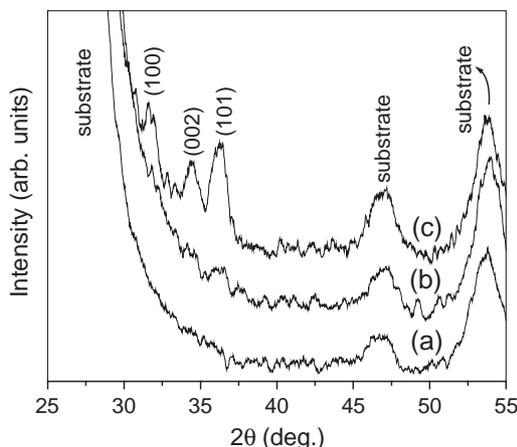


Fig. 2. XRD pattern of (a) bare PET substrate, (b) ZnO film on PET; deposition time=4 h, and (c) ZnO on PET; deposition time=5 h.

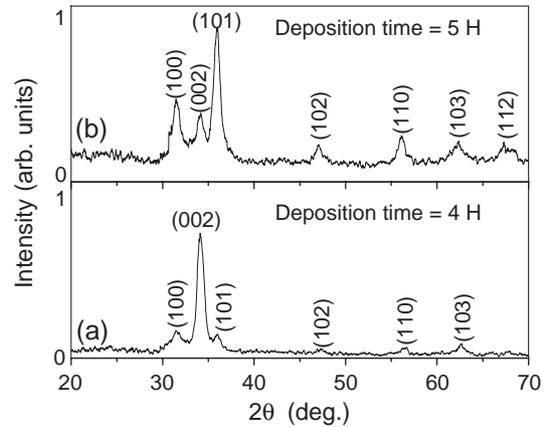


Fig. 3. XRD pattern of ZnO films on glass substrates for (a) deposition time=4 h, and (b) deposition time=5 h.

(i.e., films on glass and PET) this was done by roughening the back side of the substrates by rubbing with a diamond powder coated paper and was also blackened. This approach helped to reduce significantly the reflection from the lower interface of the substrate. The thickness of the films on PET and glass substrates were obtained as 260 and 275 nm (deposition time 4 h), 470 and 480 nm (deposition time 5 h), respectively. It may be mentioned that these values nearly matches with that obtained from interference oscillations from the transmittance spectra (Fig. 4) of films deposited on glass substrates (285 and 490 nm for 4 and 5 h deposited films respectively), which is discussed later. But there is much difference in the thickness of 4 and 5 h deposited films. It certainly indicates that the thickness is not linearly dependent on deposition time and may be related either with the change in deposition conditions or to the substrate effect. As far as the deposition conditions are concerned, sputtering current density, sputtering voltage, substrate temperature and pressure were all kept constant throughout the deposition time. Hence the above variation in thickness with deposition time is dependent on effects related to the substrate. The thickness of the growing films depends on the sticking coefficient of the incoming flux of material with the substrate among others factors. The sticking coefficient

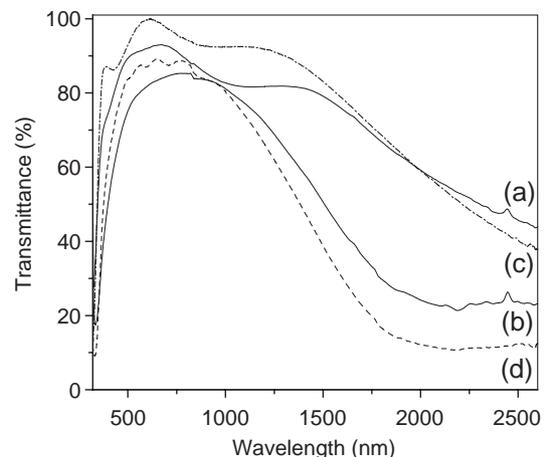


Fig. 4. Optical transmittance spectra of ZnO films deposited onto PET substrates for (a) 4 h, (b) 5 h and glass substrates for (c) 4 h, (d) 5 h.

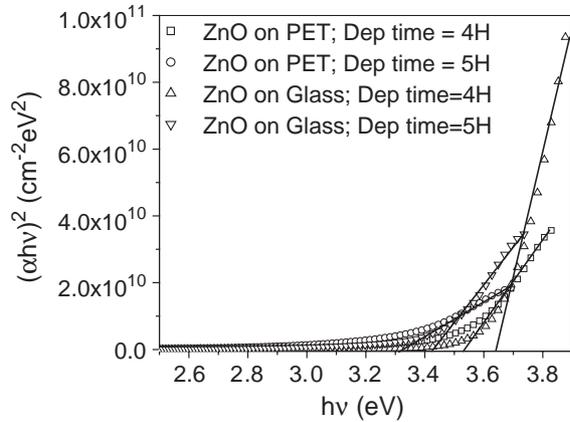


Fig. 5. Plot to determine the direct bandgaps of ZnO films deposited on PET and glass substrates under different deposition times.

depends on the substrate temperature and also on surface roughness. The initial layer, including nucleation stage sees the highly polished substrate but after long time the films are deposited on the already grown ZnO layer, and the surface roughness also evolved. This may be the reason of above mentioned thickness variation with time.

3.2. Optical properties

The optical transmittance spectra of ZnO thin films deposited onto PET and glass substrates are shown in Fig. 4, which indicate that the films are highly transparent in the visible region (400 to 800 nm). Also from the interference oscillations in Fig. 4 (c) and (d) we have estimated the film thickness of ZnO films on glass substrates using Manifacier model [36]. The values calculated as 285 and 490 nm for 4 and 5 h deposited films. These values approximately agree with those calculated from ellipsometric measurements, as discussed earlier. With the known film thickness, as obtained from the ellipsometric measurements, the absorption coefficients (α) were determined from the region of strong absorption of the transmittance data, by using Manifacier model [36]. The fundamental absorption, which corresponds to electron excitation from the valance band to conduction band, can be used to determine the nature and value of the optical band gap. As the films are crystalline in nature, the relation between the absorption coefficients (α) and the incident photon energy ($h\nu$) can be written as [37],

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (1)$$

where A is a constant and E_g is the band gap of the material and exponent n depends on the type of transition. For direct allowed transition, $n=1/2$, for indirect allowed transition, $n=2$, and for direct forbidden transition, $n=3/2$. To determine the possible transitions, $(\alpha h\nu)^{1/n}$ vs. $h\nu$ were plotted for different values of n . The $(\alpha h\nu)^2$ vs. $h\nu$ plots are shown in Fig. 5. Extrapolating the linear portion of the graphs to the $h\nu$ axis we have obtained the direct band gap values of the material from the intercept on $h\nu$ axis. For the ZnO films deposited onto PET substrates, the direct bandgap values come out as 3.53 eV,

for deposition time 4 h and 3.31 eV, for deposition time 5 h, respectively. On the other hand, for the films deposited on glass substrates, these values are 3.64 and 3.42 eV, respectively. All these values well-agree with that reported previously [24]. Different optical parameters of ZnO films deposited onto PET and glass substrates for different deposition times are furnished in Table 2.

3.3. Electrical properties

Room temperature conductivity (σ_{RT}) of the ZnO films deposited on both PET and glass substrates for various deposition times were measured. For the films deposited onto PET substrates for 4 and 5 h, these values are 0.05 and 0.25 S cm^{-1} , respectively. On the other hand, for ZnO films deposited on glass substrates, these values are 8.5 (for deposition time 4 h) and 9.6 S cm^{-1} (for deposition time 5 h), respectively. A variation of almost three orders of magnitude in the values of σ_{RT} has been observed between the films deposited onto PET and glass substrates as furnished above. This type of variation is not unusual even for commercially available ITO films deposited onto PET and glass substrates [11]. In fact, Lewis and Paine [11] stated that there was a difference of almost 5 orders of magnitude between ITO coated PET and glass substrates currently used in flat-panel-display industries.

Room-temperature Hall-measurements of the ZnO films deposited onto PET substrates for deposition time 5 h were determined successfully. The Hall-mobility (μ_H) and carrier concentration (n) are obtained around 19.82 $\text{cm}^2 \text{V}^{-1} \text{S}^{-1}$ and $2.8 \times 10^{16} \text{cm}^{-3}$, respectively. But Hall-study could not be performed for 4-h-deposited ZnO films on PET substrate, due to the high resistivity of the film. On the other hand, Hall-studies were successfully done for the films deposited on glass substrates, deposited for two different deposition times. The values of μ_H and n are found to be 7.80 $\text{cm}^2 \text{V}^{-1} \text{S}^{-1}$ and $4.86 \times 10^{19} \text{cm}^{-3}$, respectively (for deposition time 4 h) and 3.73 $\text{cm}^2 \text{V}^{-1} \text{S}^{-1}$ and $3.10 \times 10^{20} \text{cm}^{-3}$, respectively (for the films deposited for 5 h). Similar types of values had been reported by Webb et al. [38] for their ZnO films synthesized by RF-magnetron sputtering technique. Different electrical parameters of ZnO films deposited onto PET and glass substrates for different deposition times are furnished in Table 2.

Table 2

Different opto-electrical parameters of ZnO thin films deposited onto PET and glass substrates for different deposition times

	ZnO thin films onto PET		ZnO films on glass	
	Deposition time=4 h	Deposition time=5 h	Deposition time=4 h	Deposition time=5 h
Thickness (nm)	260	470	275	480
α at 800 nm (cm^{-1})	3.63×10^3	3.40×10^3	1.84×10^3	2.62×10^3
Direct bandgap (eV)	3.53	3.31	3.64	3.42
Room-temp. conductivity (S cm^{-1})	0.05	0.25	8.5	9.6
Carrier concentration (cm^{-3})	–	2.8×10^{16}	4.86×10^{19}	3.10×10^{20}

4. Conclusions

Low-temperature depositions of ZnO films were successfully done on PET and glass substrates. XRD patterns of the films deposited on both PET and glass substrates show the proper formation of hexagonal ZnO. The optical properties of the films deposited onto both PET and glass substrates show almost 80% to more than 98% visible transmittance. Calculations of the bandgap values show the existence of direct bandgap of the material ranging from 3.31 to 3.64 eV for the films deposited on both PET and glass substrates. Room-temperature conductivities of the films deposited onto PET substrates are found to be ranging around 0.05 to 0.25 S cm⁻¹ with a variation in the deposition time of 4 and 5 h, respectively. On the other hand, these values are 8.5 and 9.6 S cm⁻¹ for the films deposited on glass substrates for the similar variation in the deposition times as that deposited onto PET substrates. Room-temperature Hall measurements for the ZnO films deposited on PET and glass substrates give maximum carrier concentrations around 2.8×10^{16} cm⁻³ and 3.10×10^{20} cm⁻³, respectively. The low-temperature deposition of highly transparent and good-conducting ZnO thin films onto both PET and glass substrates indicate that this material can become a good candidate for TCO materials in the plastic-display industries. Work is going on for the synthesis of doped ZnO film so that higher conductivities could be achieved on PET substrates without compromising the transparencies.

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