Properties of low-temperature deposited ZnO thin films prepared by cathodic vacuum arc technology on different flexible substrates

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ABSTRACT

Un-doped zinc oxide (ZnO) films were deposited on three different substrates (polyethylene terephthalate (PET), polyvinyl butyral (PVB) and polyimide (PI)) at a low temperature (<75 °C) by cathode vacuum arc deposition. The microstructure, optical and electrical properties of the deposited films were investigated and discussed. All the deposited films reveal a preferred orientation with the c-axis perpendicular to the substrate, and an average transmittance of over 85% in the visible region. The calculated optical band gaps are around 2.6, 3.14 and 3.18 eV, respectively, for the ZnO films deposited on the PI, PVB and PET substrates. The lowest resistivity and the highest Hall mobility are 5.31×10^{-3} Ω-cm and 15.16 cm²/V-s for the ZnO film deposited on the PET substrate.

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1. Introduction

Flexible electronic devices are increasingly being applied in fields such as thin film transistor liquid crystal display, solar cells, light-emitting diodes, personal digital assistants, cell phones, digital cameras and "e-paper". Transparent conductive oxide (TCO) thin films play an important role in achieving the performance required for flexible electronic technology [1]. In recent years, pure or doped zinc oxide (ZnO) thin films have been seen as a good candidate TCO material because of their high conductivity, good optical transmittance and low-cost fabrication [2–9].

ZnO films with high transparency and conductivity have been deposited by several different methods, including chemical vapor deposition [2], thermal oxidation [3], radio frequency magnetron sputtering [4], pulsed laser deposition [5], electron beam evaporation [6], spray pyrolysis [7], electrodeposition [8] and cathodic arc plasma deposition (CAPD) [9–14]. However, most of these deposition methods require high substrate temperatures or in-situ annealing (>300 °C) to obtain the desired optical and/or electrical properties of the deposited films. Thus these methods are not suitable for use in low temperature deposition for flexible substrates. Therefore, depositing high quality ZnO thin films with the desired optical and/or electrical properties at low temperatures remains a challenge. The CAPD technique provides certain advantages such as readily-adjustable deposition parameters, low growth temperatures, and convenient in situ doping using the

overlying plasma [10–12]. For flexible electronic devices, polycarbonate and polyethylene terephthalate (PET) are the most popular substrates due to their superior optical properties [11]. In addition, polyvinyl butyral (PVB) is commonly used as a protective interlayer due to its properties of toughness and ductility, and is now applied in solar modules. Moreover, the thermal stability of polyimide (PI) has lead to its wide use in high-temperature applications in the aerospace, electronics, and electrical industries. The choice of the substrate is based on the requirements of the device. Therefore, the properties of the film deposited on different substrates should be investigated and identified.

This paper investigates the microstructure, mechanical, optical and electrical properties of the un-doped ZnO films on different polymer substrates using CAPD. The results are discussed through X-ray diffraction (XRD), ultraviolet–visible (UV–vis) spectrophotometry, four point-probe and Hall measurement.

2. Experiment

A CAPD system was used to deposit ZnO films onto three substrates individually made of polyethylene terephthalate (PET), polyvinyl butyral (PVB), and polyimide (PI). A cathode target of metallic Zn with a diameter of 100 mm and a purity of 99.99% was held in an alumina ceramic tube, while O_2 gas with a purity of 99.99% was used as the reactant gas. Before deposition, PET, PVB, and PI substrates with a thickness of 0.1 mm were washed by 2-propanol and then ultrasonically cleaned in alcohol for 10 min. In the deposition of the ZnO films, base pressure was kept at 2.25×10^{-6} Pa, flow rates directly controlled by a mass flow controller at 20 and 160 sccm for

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Ar and O$_2$, respectively, and an arc current of 40 A was used to generate a cathode plasma. Substrate rotation of 2 rpm and a substrate–anode distance of approximately 21 cm were kept constant during the deposition process. Since the power flux to the substrate, associated with the energetic ion flux, would heat the substrate, the substrate temperature increased slightly during deposition to temperatures above room temperature. Without any extra heating, the depositions of ZnO films was performed at a maximum temperature (<75 °C) [1].

An X-ray diffraction system (XRD, BRUKER D8 ADVANCE), with CuK$_\alpha$ radiation of an average wavelength of 1.5406 Å was used to specify the existent phases and the orientation of the ZnO thin films. X-ray patterns were taken at 2θ between 20° and 80° and with a scan speed of 4.5°/min. A UV–vis spectrometer (Thermo Evolution-300) was used to measure the optical properties of the ZnO films in a wavelength range of 200–800 nm. Moreover, from the absorption spectra, the absorption coefficient α could be determined to calculate the energy band gap of the ZnO/polymer ensemble. The standard four-point probe method was used to determine the room-temperature sheet resistance of the films and Hall-measurements were used to determine the carrier concentration and mobility.

3. Results and discussion

3.1. Structural properties

Fig. 1 shows the X-ray diffraction pattern for ZnO thin films deposited on the various polymer substrates. For all as-grown films, the XRD patterns revealed a polycrystalline hexagonal wurtzite crystal structure and no metallic Zn characteristic peak is observed. It is known that the film has a preferred crystal orientation as (002) is still the highest peak, but the film should have a fully random crystal structure with (101) as the highest peak. Therefore, in this study, all the deposited films reveal a preferred orientation with the c-axis perpendicular to the substrate. The grain sizes calculated from the XRD results and the mechanical properties of the ZnO thin films deposited on the various substrates are shown in Table 1. The grain sizes of the ZnO thin films deposited on different substrates were calculated using Scherrer's formula [1]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad (1)$$

where β is the calibrated full width at half maximum (FWHM) of the selected diffraction line in radians, θ is the Bragg angle and λ is the
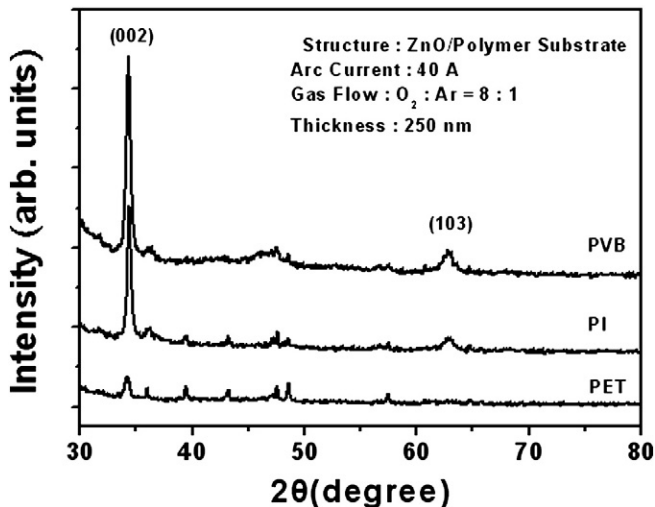

Fig. 1. The XRD patterns of ZnO films deposited on the different substrates.

Table 1
Grain sizes calculated from XRD results and mechanical properties of ZnO thin films deposited on different substrates.

	PET	PVB	PI
2θ (°)	34.22	34.34	34.4
Full width at half maximum (FWHM, nm)	0.46	0.41	0.343
Crystal size (D, nm)	14.06	20.86	24.53
Crystal lattice constant (c, nm)	0.5231	0.522	0.5209
Inter-planar distance (d, nm)	0.2615	0.261	0.2604
Strain (ε_z, %)	−0.476	−0.478	−0.479
Stress (σ, $\times 10^9$ Pa)	−2.58	−1.53	−0.259

X-ray wavelength (0.15406 nm). The grain sizes of the ZnO thin films deposited on various substrates range from 18 to 24 nm.

3.2. Mechanical properties

From the peak position of the (002) peak we calculate the grain size, the FWHM, interplanar distance d, stress σ, strain ε_z and crystal lattice constant c. The diffraction peak degree (2Θ) of (002) for ZnO films deposited on PET, PI, and PVB is 34.22, 34.34, and 34.40, respectively. The strain in the ZnO films along c-axis perpendicular to the substrate is given by the following equation [15]

$$\varepsilon_z(\%) = \frac{C_{film} - C_{bulk}}{C_{bulk}} \times 100\% \qquad (2)$$

where C is the lattice parameter of the ZnO film, C$_{bulk}$ (5.2066 Å) is the unstrained lattice parameter of ZnO [15], C$_{film}$ is the measured c-axis lattice constant calculated from the (002) reflection peak using Bragg's law. The parameter of strain ε_z of all the deposited films is close to 0.4%, indicating that the strains of the prepared films were all tensile.

The stress in the plane of a ZnO film with a hexagonal crystal structure can be expressed as [10]

$$\sigma(\text{Pa}) = -4.5 \times 10^{11} \left(\frac{C_{film} - C_{bulk}}{C_{bulk}} \right) \qquad (3)$$

The calculation of film stress is based on the biaxial strain model. The strain along the c-axis, i.e., perpendicular to the substrate surface, was calculated by XRD data. The respective stresses of the ZnO films deposited on the PET, PI and PVB substrates are -2.58×10^9, $-.1.88 \times 10^9$ & -2.59×10^9 Pa. If the stress is positive, the biaxial stress is tensile; if the stress is negative, the biaxial stress is compressive [16]. Usually, the energetic bombardment of the deposited film tends to be compressive due to the atomic peening of an energy dependent process [10]. Since no external heating was provided during the deposition, the thermal stress caused by the various linear thermal expansion coefficients of the substrate and the ZnO film was insignificant as compared to the measured stress [10]. In addition, a significant fraction of the energy of a bombarding ion is known to be transferred to the violent motion of the atoms in the area of impact, thus such a high ion deposition energy causes stress relaxation due to a 'thermal spike' [17]. Therefore, despite the lack of external heating during this deposition, intense local heating such as a thermal spike could provide energy to release the deposited atoms from their meta-stable positions within the film, thus causing stress relaxation [18]. This competition between stress generation and relaxation determines the final stage of the intrinsic stress in the films, with the energetic bombardment apparently playing an important role in the generation of compressive stress in the current experiment.