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Structure, optical and electrical properties of ZnO thin films on the flexible substrate by cathodic vacuum arc technology with different arc currents

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Abstract

ZnO thin lms were successfully deposited onto PET substrates prepared by using cathodic arc plasma deposition (CAPD) technique at a low temperature (<75 °C). Their structure, optical and electrical properties were investigated with various arc currents (40, 45, 50 and 55 A). ZnO (0 0 2) peak was clearly observed, and increased as the arc current increased from 40 A to 55 A. The calculated average crystallized sizes were around 15.9–17.7 nm. The films have an average transmittance over 85% in the visible region, and calculated values of the band gap around 3.33–3.31 eV with increase of the arc current. It was also found that a slight blue shift of optical transmission spectra was observable when decreasing the arc current. The deposited ZnO films had the lowest resistivity; about 3×10^{-3} Ω cm for the ZnO lm with the arc current of 40 A.

Keywords: ZnO thin lms; PET substrate; Cathodic arc plasma deposition

1. Introduction

Recently, there has been considerable interest in Zinc oxide (ZnO) research due to its wide and direct band gap (3.3 eV), which is desirable for optoelectronic devices such as photodetectors, solar cells light emission diodes, and ultraviolet laser diodes. Pure or doped ZnO thin films have been considered as good candidates for transparent conductive oxide (TCO) materials, due to their high conductivity, good optical transmittance, and low-cost fabrication [1–8]. Moreover, ZnO thin films show thermal stability, and do not suffer from dislocation degradation during operation.

Various methods were reported to deposit a ZnO films on glass for TCO use, such as radio frequency (RF) magnetron sputtering [1], pulsed laser deposition [2], electron beam evaporation [3], chemical vapor deposition (CVD) [4], thermal oxidation [5], spray pyrolysis [6], and cathodic arc plasma deposition (CAPD) [7–9]. Recently, polycarbonate (PC) and polyethylene terephthalate (PET) have proved to be popular flexible electronic device substrates, due to their superior optical properties [10]. However, most of these deposition methods require an in situ annealing process (>300 °C) to obtain the desired optical and/or electrical properties, and are therefore unsuitable for the low temperature deposition required by the flexible substrate. Of the deposition methods described previously, the CAPD technique has a high ionization ratio and high ion drift energy of 10–200 eV at the cathode, depending on the ion mass [9]. The CAPD technique can therefore enhance surface atom mobility, and is in turn able to deposit high crystal quality films at relatively low substrate temperature, which is preferable in order to avoid the reactive and elemental diffusion of different layers and protect substrates such as the flexible substrate of polymers [7]. In addition, the CAPD technique has several other advantages, including high deposition rate, convenient in situ doping using an overlying plasma, and readily adjustable deposition parameters such as substrate temperature, arc current and gas flow rate [8,9]. However, very few papers address the preparation and properties of ZnO films on PET substrates using the CAPD technique, and the deposit of high quality ZnO thin films with desired optical and/or electrical properties at a low temperature, remains a challenge.

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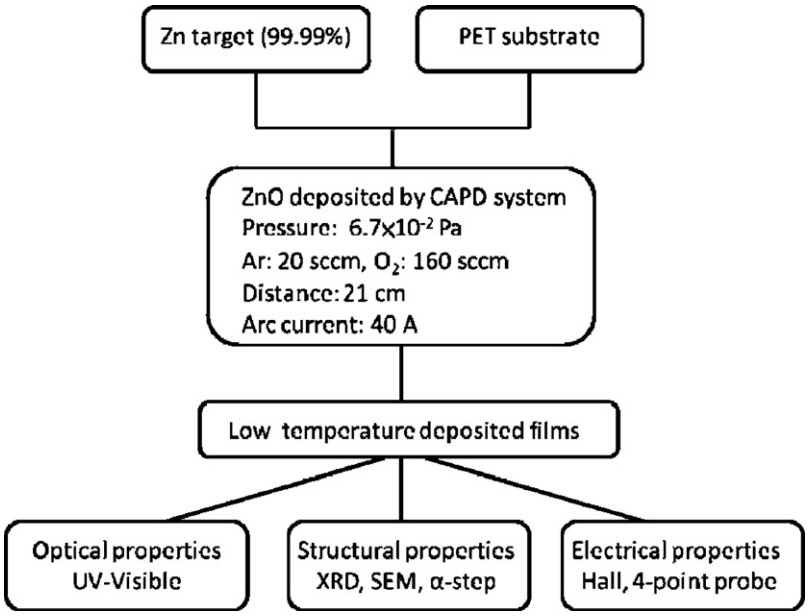

Fig. 1. Process flow chart.

This paper, presents the successful deposition of un-doped ZnO films on PET substrates at a low temperature, using the CAPD technique. The structure, and optical and electrical properties of ZnO films are discussed with regard to different arc currents.

2. Experimental procedure

PET substrates with a thickness of 0.1 mm were washed by alcohol and then cleaned in alcohol ultrasonically for 10 min before deposition. Metallic Zn with a diameter of 100 mm and purity of 99.99% was used as a cathode target, held in an alumina ceramic tube. O_2 gas with high purity of 99.99% was used as the reactant gas. When depositing ZnO films, base pressure was kept at 6.7×10^{-2} Pa, and flow rates of Ar and O_2 (controlled directly by a mass flow controller), were 20 and 160 sccm, respectively. Substrate rotation of 2 rpm and a substrate–anode distance of approximately 21 cm remained constant during the deposition. Though no external heating was used, the substrate temperature still increased slightly during deposition, since the power flux to the substrate (associated with the energetic ion flux), heated the substrate to temperatures above room temperature. It is reported that the process temperature, without any extra heating for the depositions of ZnO films, was performed at a maximum temperature (<75 °C) [9]. Different arc currents of 40, 45, 50 and 55 A were used. The deposition times (13–23 min) were controlled to maintain the ZnO film thicknesses at 200 nm, confirmed by the measurement of Alpha-step (α-step, Kosaka Laboratory Ltd. ET-4000).

To specify the existent phases and the orientation of ZnO thin films, an X-ray diffraction system (XRD, BRUKER D8 ADVANCE), equipped with CuKα radiation of average wavelength 1.5406 Å was used, and scans were taken 2θ between 20° and 70° with a scan speed of 3°/min. A UV–vis spectrometer (Thermo Evolution-300), was used to measure the optical properties of ZnO films in the wavelength range of 200–800 nm. The absorption coefficient α was also determined from absorption spectra, to obtain the energy band value. The standard four-point probe method, operated at room temperature, was used for sheet resistance. Hall-measurements were used to determine the carrier concentration and mobility of the deposited films. The flow chart of the process is described in Fig. 1.

3. Results and discussion

Fig. 2 shows deposition rates of the deposited ZnO thin films on PET substrates using the CAPD technique, with different arc currents. The deposition rate was obtained from the film thickness and the corresponding deposition time. It is clearly observable that the deposition rate of zinc oxide film increases from 13 nm/min to 23 nm/min with an increasing arc current from 40 A to 55 A, since both the zinc atoms generated by the

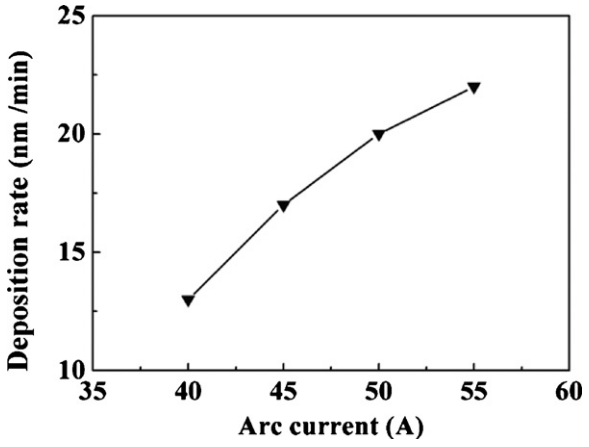

Fig. 2. Deposition rates of the deposited ZnO thin films on PET substrates using the CAPD technique with different arc currents.

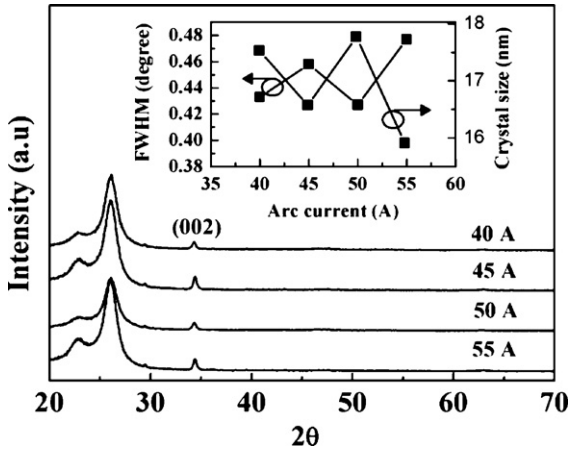

Fig. 3. XRD patterns of the deposited ZnO thin films on PET substrates using the CAPD technique with different arc currents. Inserted are the FWHM of (0 0 2) peaks and crystal size as a function of arc currents.

evaporation and the probability of the zinc atoms arriving to the substrate, increase when the arc current increases. It is known that deposition rates depend on arc current, oxygen pressure, and substrate temperature. The deposition rates in this study are similar to those reported in [7–9].

3.1. Microstructure

Fig. 3 shows the XRD patterns of the ZnO films on PET substrates using the CAPD technique with different arc currents. The (0 0 2) preferred orientation can be clearly observed for all the deposited films, indicating a hexagonal wurtzite crystal structure oriented to the *c*-axis normal to the substrate. It is reported that the *c*-axis preferred orientation of ZnO thin films is a result of a self-ordering effect resulted from the interaction between the deposited material and the substrate surface, as well as the minimization of the crystal surface free energy. The crystallographic structure of the PET substrate does not therefore affect the film crystal orientation [11]. It is found that the lms were successfully deposited at low temperature without extra substrate heating. The average crystalline size (D) of the ZnO lms is calculated using the Scherrer equation, as given by:

$$D = \frac{0.9\lambda}{\omega \cos\theta} \quad (1)$$

where ω is the calibrated FWHM of the (0 0 2) peak in radians, θ is the Bragg angle, and λ is the X-ray wavelength (0.15406 nm). As shown in the insert of Fig. 2, the crystallite size was within the range of 15.9–17.7 nm, as the arc current varies from 40 A to 55 A. The crystallite size does not increase obviously with an increasing arc current, indicating the crystallinity of ZnO films is not directly dependent on the arc current from 40 A to 55 A.

Fig. 4 shows a microscopic surface scan of AFM results of the deposited ZnO thin films on PET substrates using the CAPD technique with different arc currents. The scanning area is 1 μm × 1 μm. It is found that the surface roughness of the deposited ZnO thin films decreases from 4.8 nm to 4.3 nm with

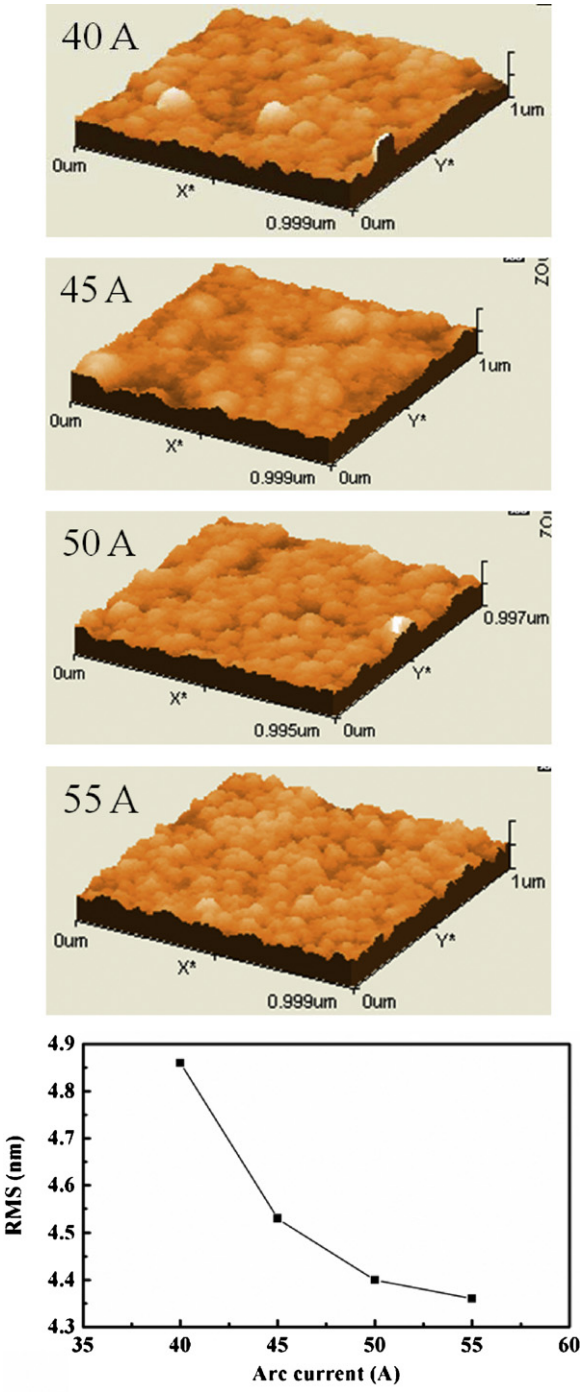

Fig. 4. Surface morphology of AFM results of the deposited ZnO thin films on PET substrates using the CAPD technique with different arc currents.

an increasing arc current from 40 A to 55 A. This is because that the higher arc current causes the Zn atom to arrive at the desired location, resulting in a smoother surface. Xu et al. [12] studied the effect of the substrate temperature on the ZnO films, and found the roughness to be within a similar order; 1 nm to 4 nm. They suggested that the increased roughness may be due to the increased grain size of ZnO crystals as the substrate temperature increases [12]. The higher arc current does not therefore enhance the grain growth as also calculated from the XRD data, shown in Fig. 2.

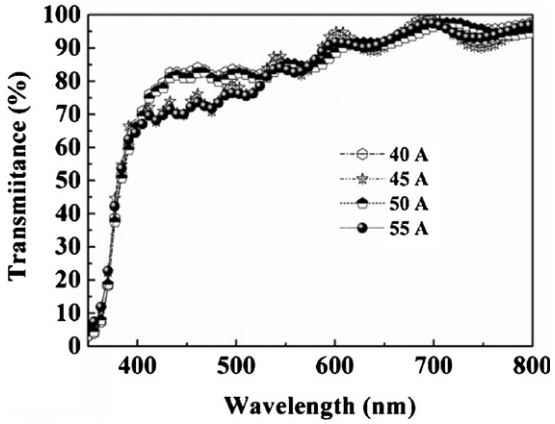

Fig. 5. Optical transmittance spectra in ultraviolet-visible region of the deposited ZnO thin films on PET substrates using the CAPD technique with different arc currents.

3.2. Optical properties

Fig. 5 shows the optical transmittance spectra of the deposited ZnO films on PET substrates using the CAPD technique with various arc currents. It is noted that all the film thicknesses are kept to approximately 200 nm. It is found that the ZnO films deposited at a low temperature using the CAPD technique with various arc currents all have an excellent transparent property wavelength region, and a high transparent spectrum with an average transmittance over 85% in the visible wavelength. The film with 40 A has higher transmittance in the wavelength between 300 nm and 500 nm, than that with 55 A. The position and the shape of the absorption edge seem independent of the arc currents [13]. To determine the optical energy gap (E_g) of the deposited ZnO films, transmission spectra based on assuming a direct transition between the edges of the valence and the conduction band was used. The variation of the absorption coefficient α with the photon energy $h\nu$ can be given as Eq. (2) [9,13]:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (2)$$

where α was estimated from the transmittance data and A is a constant, depending on material properties. It is known that $(\alpha h\nu)^2$ is a function of $h\nu$, and the optical energy gaps of the ZnO film can be obtained by extrapolating $\alpha = 0$ from the linear region of "Tauc" plots. It is found that values of the optical energy gaps decrease from 3.33 eV to 3.31 eV with an increasing arc current from 40 A to 55 A, as shown in Fig. 6. That is to say, reduction of the arc current causes a slight blue shift of energy gap. It is reported that various mechanisms are responsible for the shifts of energy gap, such as: (1) the quality of crystallinity, (2) the change of the crystallite dimension, (3) quantum size effects and (4) the density of impurities or carriers, produced in the films [9,13]. As discussed in the XRD data, the quality of crystallinity and the crystalline orientation did not vary greatly with an increase of the arc current. It is also known that the Burstein–Moss effect notes that the energy band broadening (blue shift), effect would be caused by the lifting of the Fermi level into the conduction band of the degenerate semiconductor [14]. Since the value of the carrier concentration increases slightly as the arc current decreases in this study, it is believed that the origin of the energy gap blue shift may be attributable to the mechanisms of impurity or carrier density, as discussed later.

3.3. Electrical properties

Fig. 7 shows the resistivity (ρ), carrier concentration (n) and Hall mobility (μ) with different arc currents for ZnO films on PET substrates measured at room temperature. When reducing the arc current from 55 A to 40 A, the resistivities fall from $3.7 \times 10^{-2}\ \Omega$ cm to $3 \times 10^{-3}\ \Omega$ cm. It is found that the ZnO films prepared by the CAPD show relatively low resistivity even without doping. Hall measurement results indicate that the ZnO thin films deposited by the CAPD technique with various arc currents all exhibit n-type conductivity. Hall mobility decreases from 10.6 $cm^2\ V^{-1}\ s^{-1}$ to 4.3 $cm^2\ V^{-1}\ s^{-1}$ as the arc current increased from 40 A to 45 A, then increased to 15.39 $cm^2\ V^{-1}\ s^{-1}$ as the arc current further increased to 55 A. It is believed that the higher arc current improves surface roughness, as shown in Fig. 4, reducing the carrier scattering and improving the mobility [15]. The carrier concentration values are from 3.53×10^{19} to $3.6 \times 10^{19}\ cm^{-3}$ as the arc current increases from 40 A to

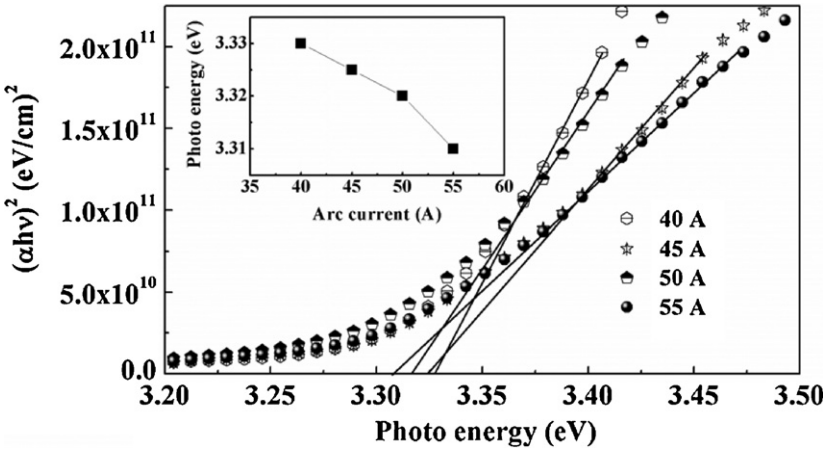

Fig. 6. $(\alpha h\nu)^2$ as a function of the photon energy ($h\nu$) for the deposited ZnO films on PET substrates using the CAPD technique with different arc currents.

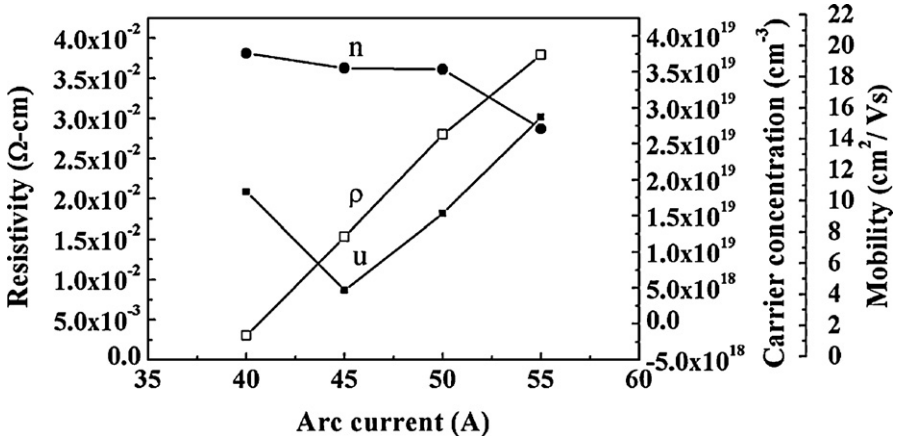

Fig. 7. Resistivity (ρ), carrier concentration (n) and Hall mobility (μ) for the deposited ZnO films on PET substrates using the CAPD technique with different arc currents.

50 A, then fall to 2.7×10^{19} cm^{-3} as the arc current further increases to 55 A. The ZnO films deposited by the CAPD technique obtain a high concentration of the electron. In room temperature deposited and un-doped ZnO films, n-type carriers are usually generated by the interstitial Zn atoms acting as donors. Wang et al. suggested that the generation of a high concentration of zinc interstitials in the films by the filtered cathode vacuum arc (FCVA) can be attributed to two factors [7]. One is that high ion energy of the cathodic arc plasma achieves the implantation of the zinc atom into the interstitial position, thus increasing the formation probability of zinc interstitials. The other is that use of low temperature deposition would prevent the diffusion of zinc interstitials into the ZnO crystal lattice, thus stabilizing the zinc interstitials [7,9].

The deposited ZnO films have the lowest resistivity; about 3×10^{-3} Ω cm for the ZnO lm with an arc current of 40 A. It is known that the resistivity is related to carrier concentration and mobility, and may be attributable to intrinsic donor defects such as donor vacancies and Zn interstitials, which are influenced by experimental conditions [7,9,15]. Since the ZnO films prepared in this study were room temperature deposited and un-doped, the lowest resistivity about 3×10^{-3} Ω cm for the ZnO lm is caused mainly by the improved mobility and increased carrier concentration. It is found that the lowest resistivity of the deposited ZnO film on PET substrates can be competitive with those in the previous reports [10,13]. The experimental results verify that the CAPD technique can deposit high quality ZnO based TCO films at low temperature for flexible substrates.

4. Conclusions

We have demonstrated the deposition of un-doped ZnO films on PET substrates using the CAPD technique with a different arc current. Structure and optical and electrical properties depending on the deposition conditions of arc currents, were investigated. All film thicknesses were kept at approximately 200 nm. The zinc oxide film deposition rate increased from 13 nm/min to 23 nm/min with an increasing arc current from 40 A to 55 A. XRD results showed the deposited ZnO films to form a hexagonal structure with (0 0 2) preferred orientation, and the calculated crystal sizes to be around 15.9–17.7 nm. The ZnO films all had an excellent transparent property wavelength region, and a high transparent spectrum with an average transmittance over 85% in the visible wavelength. The values of the optical energy gaps decreased from 3.33 eV to 3.31 eV with an increase of arc current from 40 A to 55 A, while the resistivity decreased from 3.7×10^{-2} Ω cm to 3×10^{-3} Ω cm when reducing the arc current from 55 A to 40 A. The lowest resistivity of about 3×10^{-3} Ω cm for the ZnO lm was caused mainly by the improved mobility and increased carrier concentration. The results have verified that the low temperature deposition of ZnO thin films onto PET substrates using the cathodic arc plasma technique shows high transparency and good conducting properties, and is therefore a suitable method for next generation flexible industries.

Acknowledgments

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