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Research Article

Effect of O_2/Ar Gas Flow Ratios on Properties of Cathodic Vacuum Arc Deposited ZnO Thin Films on Polyethylene Terephthalate Substrate

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Cathodic vacuum arc deposition (CVAD) can obtain a good quality thin film with a low growth temperature and a high deposition rate, thus matching the requirement of film deposition on flexible electronics. This paper reported the room-temperature deposition of zinc oxide (ZnO) thin films deposited by CVAD on polyethylene terephthalate (PET) substrate. Microstructure, optical, and electrical measurements of the deposited ZnO thin films were investigated with various O_2/Ar gas flow ratios from 6 : 1 to 10 : 1. The films showed hexagonal wurtzite crystal structure. With increasing the O_2/Ar gas flow ratios, the *c*-axis (002) oriented intensity decreased. The crystal sizes were around 16.03 nm to 23.42 nm. The average transmittance values in the visible range of all deposited ZnO films were higher than 83% and the calculated band gaps from the absorption data were found to be around 3.1 to 3.2 eV. The resistivity had a minimum value in the 3.65×10^{-3} Ω·cm under the O_2/Ar gas flow ratio of 8 : 1. The luminescence mechanisms of the deposited film were also investigated to understand the defect types of room-temperature grown ZnO films.

1. Introduction

During the last few decades, flexible electronics such as thin-film transistors, solar cells, and light-emitting diodes have been studied intensively owing to their advantages of light weight and low cost over present rigid electronics [1]. Transparent conductive oxide (TCO) thin film is usually an important role to obtain the required performances of such flexible electronic devices. Typically, indium tin oxide (ITO), tin dioxide (SnO_2), and zinc oxide (ZnO) are most popular transparent conductive thin films [2]. Moreover, the high polymer flexible substrate, such as polyethylene terephthalate (PET), polycarbonate (PC), polyethersulfone (PES), polyethylene naphthalate (PEN), or polyimide (PI) [3–5] are commonly used for the above flexible applications. However, deposition of such TCO films on the plastic substrates requires a low-temperature technique since most of polymer substrates could not be used above 200°C. Thus, low temperature deposition becomes the most important issue for growing high quality TCO films on flexible polymer substrates [1].

In the past, many techniques were used to obtain high quality TCO thin film, such as physical vapor deposition and chemical vapor deposition [6]. In the above techniques, cathodic vacuum arc deposition (CVAD) method has many advantages, such as high degree of ionization in the plasma (80~100%) and high ion energy (50~150 eV) [7–13]. Therefore it can achieve good quality dense coating with a low growth temperature and a high deposition rate (~10 nm/s) [9]. In addition, ZnO film is a well-known II–VI compound semiconducting material with excellent optical, electrical, and piezoelectric properties [2]. Moreover, ZnO film has some advantages such as nontoxicity, wide band gap (3.3 eV), high thermal energy at 300 K (26 meV), and an excition binding energy of 60 meV. ZnO has a high transmittance in the visible

spectrum and a low electrical resistivity under the relative low-temperature deposition [1]. Therefore, it is desired to grow high quality ZnO film on plastic substrate at a low temperature using CVAD system. The deposition parameters of CVAD technology typically include gas flow ratio, substrate temperature, arc current, and bias voltage [9, 10]. In previous works, ZnO films were successfully deposited onto PET substrates using CVAD technique. Effect of various arc currents (40, 45, 50, and 55 A) [11] and effect of film thicknesses (150, 250, 350, 450, and 550 nm) [12] on microstructure, optical, and electrical properties were investigated. It is known that the oxygen flow rate plays an important role in the properties of the grown ZnO films under different physical vapor deposition, especially in the electrical property of pure ZnO film, since the oxygen flow rate normally affects the defect types of pure ZnO films deposited at a low temperature. However, there is no report regarding the issue.

In this paper, we reported a detailed investigation on the effects of various O_2/Ar gas flow ratios on properties of pure ZnO films deposited by using CVAD on the PET substrate at a room temperature and investigated the relation between the microstructure, optical, and electrical properties by using X-ray diffraction (XRD), ultraviolet-visible spectroscopy (UV-VIS), Hall measurement, a four-point probe, and photoluminescence (PL).

2. Experimental Procedure

Figure 1 shows the flow chart of the experiment for this study. Before deposition, PET substrates with a thickness of 0.1 mm were cleaned with isopropyl alcohol and blown dry with nitrogen. The metal Zn target with a diameter of 100 mm and purity of 99.99% as a cathode target was held in an alumina ceramic tube; oxygen and argon gas with high purity of 99.99% were used as the reactant gas. The PET substrates were loaded into the CVAD chamber with a substrate-anode distance of approximately 21 cm, and the chamber was evacuated to 10^{-5} Torr by a rotary and diffusion pump arrangement in the depositions of ZnO films. The system used a relatively low DC voltage to trigger and sustain a metal arc plasma. The O_2/Ar gas flow ratios (6 : 1 to 10 : 1) in cathodic vacuum arc deposition system were experimental variables. Substrate rotation of 2 r.p.m., discharge current in 80 A, and working pressure in 10^{-3} Torr were kept constant during the deposition work. No extra heating was provided to the depositions of ZnO films; namely, deposition was performed at room temperature. In the study, Ar was in 20 sccm and O_2 were in 120, 140, 160, 180, and 200 sccm; namely, the O_2/Ar gas flow ratios were 6 : 1, 7 : 1, 8 : 1, 9 : 1, and 10 : 1.

For the microstructure characterization, X-ray diffraction (XRD, BRUKER D8 ADVANCE) equipped with CuKα radiation of average wavelength 1.5406 Å was used to specify the existent phases, the orientation, and the stress of ZnO thin films. X-ray patterns were taken 2θ between 20° and 60° and scan speed of 4.5°/min. For the optical characterization, UV-VIS spectrometer (Thermo Evolution-300) was used to measure the optical properties of ZnO films in the wavelength range of 200–800 nm. Moreover, the absorption coefficient α could be determined from absorption spectra to further obtain the optical bandgap of the deposited films. For the electrical characterization, the four-point probe was acquired at room temperature to measure the resistivity and Hall measurement was used to determine the carrier concentration and mobility of the deposited films. Moreover, the photoluminescence (PL) spectra measurement (Jasco FP-6600) via optical excitation by a Xe lamp with an excitation wavelength of 325 nm was used to measure the defect types of the deposited films from the PL data acquired in the wavelength range of 350–800 nm.

3. Result and Discussion

3.1. Microstructure. Figure 2 shows the XRD patterns of the deposited ZnO films on PET substrate with various O_2/Ar gas flow ratios. Since the PET substrate is amorphous, the crystallographic structure of the substrate would not affect the film crystal orientation [2]. It is clearly observed that the deposited films show hexagonal wurtzite crystal structure and has a (002) peak which is close to that of the standard ZnO crystal (34.45°), indicating that the film has a preferred orientation with the *c*-axis perpendicular to the substrate [11]. However, it is observed that with O_2/Ar gas flow ratio of 6 : 1, a small broad peak (103) in 62° also appeared, showing the deposited film is polycrystalline. Namely, the grains in the film are not completely perpendicular to the substrate surface. Typically, three energy types appeared in the deposited film on a substrate, such as surface energy of the film and interface energy between film/substrate and the strain energy in the film. Among the various low index ZnO planes, the *c*-axis plane has the lowest surface energy. In general, the films are grown to achieve a minimized total energy [7]. Thus, crystal orientation of the growing film is formed from a self-ordering effect because of the minimization of the crystal surface free energy as well as the interaction between the deposited film and the substrate [10]. However, if the films are not deposited under the preferred range of the deposition parameters, *c*-axis orientation would be deteriorated and other orientations then appeared [11]. Moreover, the *c*-axis (002) oriented intensity decreases with increasing the O_2/Ar gas flow ratios from 6 : 1 to 10 : 1. This behavior reveals that with increased oxygen flow the crystallinity of the deposited ZnO films is firstly improved and then decreased. The appropriate O_2/Ar gas flow ratio is required to grow oriented crystalline ZnO film [12].

To further investigate the crystallographic quality, the film properties obtained from the XRD data are summarized in Table 1, such as the full width at half maximum (FWHM), crystallite size (D), crystal lattice constant (c), interplanar distance (d), and film stress (σ). The crystallite sizes of the grown films are estimated using the Scherrer formula [13]:

$$D = \frac{0.9\lambda}{\beta \cos\theta}, \tag{1}$$

where $\lambda = 1.541$ Å is the wavelength of X-ray, θ is the angle between the incoming X-ray and the normal of the diffracting plane, and β is FWHM form the broadening of the (002) diffraction line. The crystallite sizes are obtained as 17.3 nm, 22.2 nm, 22.8 nm, 23.4 nm, 18.3 nm, and 16.0 with the O_2/Ar

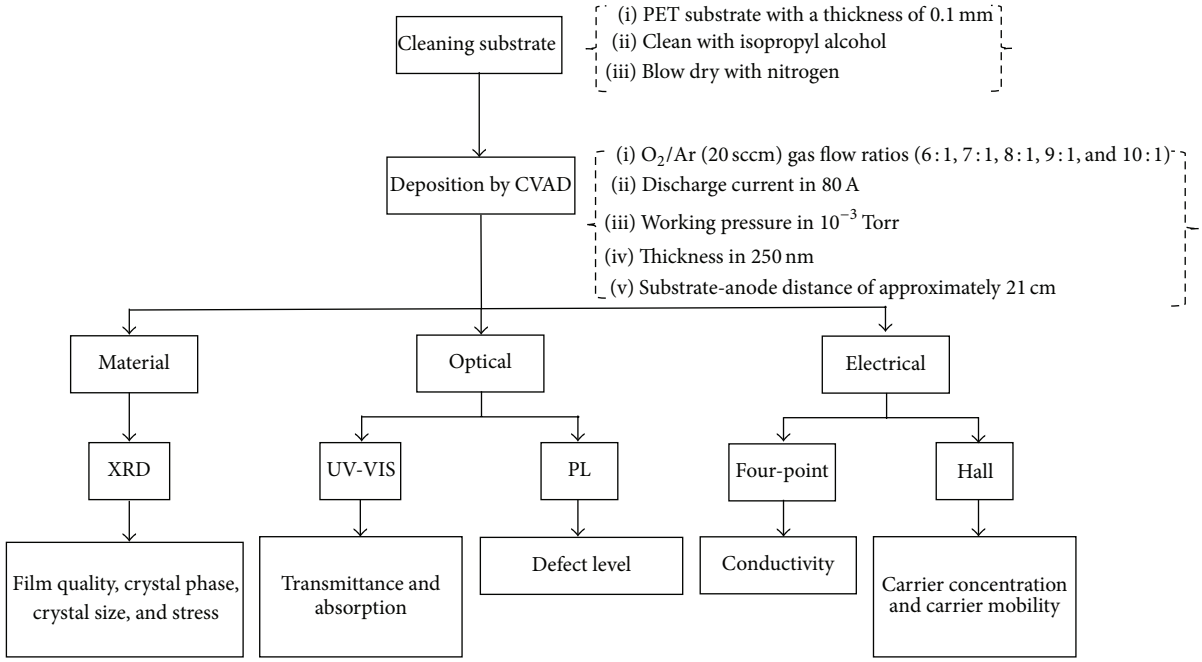

Figure 1: The flow chart of fabrication of the research.

Table 1: Material properties of the room-temperature deposited ZnO films on the PET substrate with various O_2/Ar gas flow ratios.

O_2/Ar	6 : 1	7 : 1	8 : 1	9 : 1	10 : 1
Intensity of (002) (a.u.)	620	87	87	27	3
2θ (°)	34.31	34.28	34.28	34.22	34.19
FWHM	0.38	0.37	0.36	0.51	0.526
D (nm)	22.2	22.8	23.4	16.5	16.0
d (nm)	0.2615	0.2613	0.2611	0.2612	0.2612
c (nm)	0.523038	0.522668	0.522299	0.522476	0.5243
σ (Pa)	$-2.11E+09$	$-1.79E+09$	$-1.47E+09$	$-3.20E+09$	$-3.62E+09$

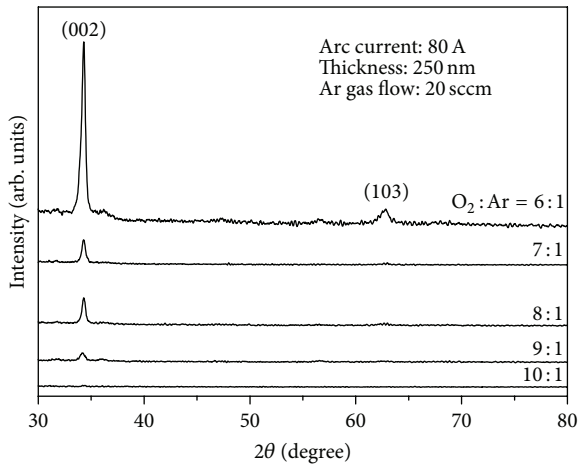

Figure 2: The XRD patterns of the room-temperature deposited ZnO films on the PET substrate with various O_2/Ar gas flow ratios.

gas flow ratios of 6 : 1, 7 : 1, 8 : 1, 9 : 1, and 10 : 1, respectively. The crystallite size increases first and then decreases when the O_2 flow increases. This result may be attributed to the reasons. First, desired introduction of oxygen in plasma generates high-energy oxygen neutral atoms and accelerates grain growth in the deposited films under the O_2/Ar gas flow ratios from 6 : 1 to 8 : 1. With more and more oxygen gas introduction, attack of high-energy neutral oxygen atoms would increase and then change the surface topology of the deposited film at the early phase during the film growth, causing the decrease of the grain aggregation [1, 7].

The c value and the d value are identified using the Bragg equation $n\lambda = 2d \sin\theta$, where n is the order of the diffracted beam. The calculation of the film stress is based on the biaxial strain model and the stress in the plane of ZnO film with a hexagonal crystal structure can be expressed as [2]

$$\sigma = 4.5 \times 10^{11} \left(\frac{C_{\text{film}} - C_{\text{bulk}}}{C_{\text{bulk}}} \right), \tag{2}$$

where C_{film} and C_{bulk} are the lattice parameters of film and the strain-free lattice parameter of ZnO thin films, respectively. The stress is −2.11, −1.79, −1.47, −3.2, and −3.26 GPa when the O_2/Ar gas flow ratio is 6 : 1, 7 : 1, 8 : 1, 9 : 1, and 10 : 1, respectively. The result indicates the compressive stress in the film

also decreases first and then increases with increasing O_2/Ar flow ratio. The energetic bombardment of the deposited film is usually compressive because of the atomic peening during the CVAD process [8].

3.2. Optical Properties. Figure 3 shows transmittance of the room-temperature deposited ZnO films on the PET substrate with various O_2/Ar gas flow ratios. The transmittance of pure PET substrate is also measured as the data reference. The average transmittance of PET substrate is in 93.32% in the visible range. The average transmittances of all the films in the visible range are over 83%, and the maximum transmittance is 86.38% as the O_2/Ar gas flow ratio is 8 : 1. Therefore, the average transmittances of the ZnO thin films deposited on the PET substrate were slightly lower than data reference of PET substrate and it is reasonably concluded that a better crystallinity reaches a higher transmittance [13]. However, the average transmittances of the ZnO thin films deposited on the PET still match the transmittance requirement of most device applications.

The absorption spectra are typically used to evaluate the optical energy band gap of the ZnO film. In the direct transition semiconductor, the relation between optical absorption coefficient (α) and the optical energy band gap (Eg) is expressed as [13]

$$(\alpha h\nu)^2 = A\left(h\nu - \mathrm{Eg}\right), \tag{3}$$

where α is estimated from the transmittance data and A is a constant depending on the materials properties. $(\alpha h\nu)^2$ is a function of $h\nu$, h is Planck's constant, and ν is the angular frequency of the incident photon. Figure 4 shows the plot of $(\alpha h\nu)^2$ as function of the incident photon energy. The Eg is obtained from intercept of the extrapolated linear part of the curve. The optical band gaps of the room-temperature deposited ZnO films on the PET substrate with various O_2/Ar gas flow ratios of 6 : 1, 7 : 1, 8 : 1, 9 : 1, and 10 : 1 are 3.16, 3.17, 3.21, 3.20, and 3.17 eV, respectively. It was reported that as the O_2 flow rate increased, the subband gap absorption at wavelengths longer than 400 nm caused by metallic Zn clusters embedded in the ZnO film would decrease notably and thus the deposited film became more transparent.

3.3. Electrical Properties. Figure 5 shows the electrical resistivity (ρ), Hall mobility (μ), and carrier concentration (n) of the deposited ZnO films. The Hall mobility (μ) is in the range from 3 to 4 $cm^2/s{\cdot}V$ and increases slightly and then decreases with increasing O_2/Ar gas flow ratios. The trend of the Hall mobility (μ) is similar to the crystal size. The different O_2/Ar gas flow ratios affect crystal size and thus affect the electrical properties. It is suggested that carriers are scattered essentially by grain boundaries as well as the intrinsic defects in an undoped film, and thus increase of crystal size would reduce the boundary and then reduce the carrier scattering, thus improving the Hall mobility (μ) [11]. The carrier concentration (n) also increases first and then decreases with increasing O_2/Ar gas flow ratios, indicating that the carrier concentration in the ZnO film can be tuned by adjusting the O_2 flow rate during the deposition. All

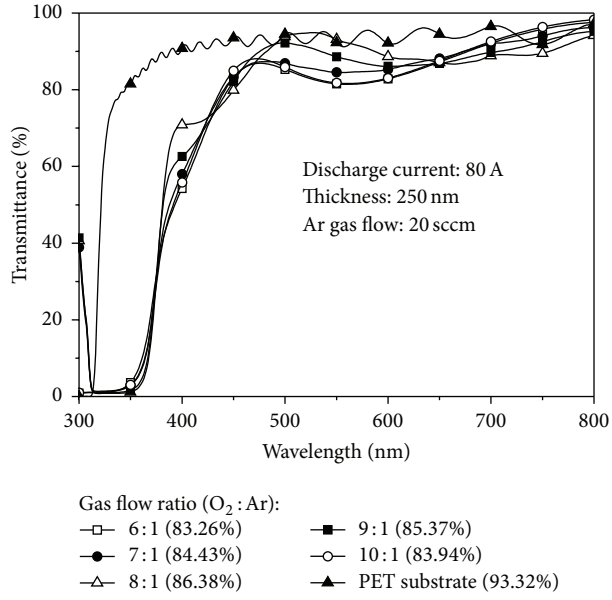

Figure 3: Transmittance of the room-temperature deposited ZnO films on the PET substrate with various O_2/Ar gas flow ratios.

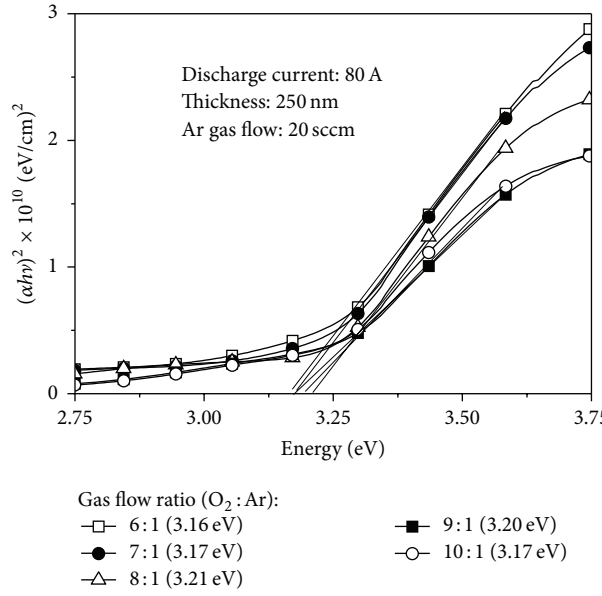

Figure 4: Absorption spectra of the room-temperature deposited ZnO films on the PET substrate with various O_2/Ar gas flow ratios.

the deposited films are shown as n-type conduction. The resistivity has a minimum value in the 3.65×10^{-3} $\Omega{\cdot}$cm, with a mobility of 4.8 $cm^2/V{\cdot}s$ and a carrier concentration of 5.89×10^{20} cm^{-3} under the O_2/Ar gas flow ratio of 8 : 1.

To consider the applications of the deposited thin films, the sheet resistance shall be known first. The sheet resistance is calculated by using the measured resistivity and the film thickness. Since all the film thickness is around 250 nm, the sheet resistivities of the deposited ZnO films are about 146 to 200 $\Omega/\square$. It is suggested that the deposited ZnO thin films on

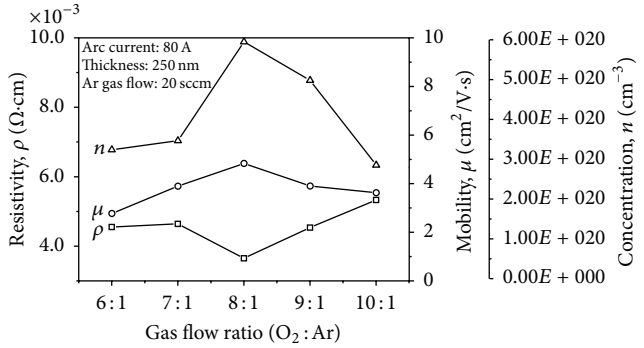

Figure 5: The resistivity (ρ), mobility (μ), and concentration (n) of the room-temperature deposited ZnO films on the PET substrate with various O_2/Ar gas flow ratios.

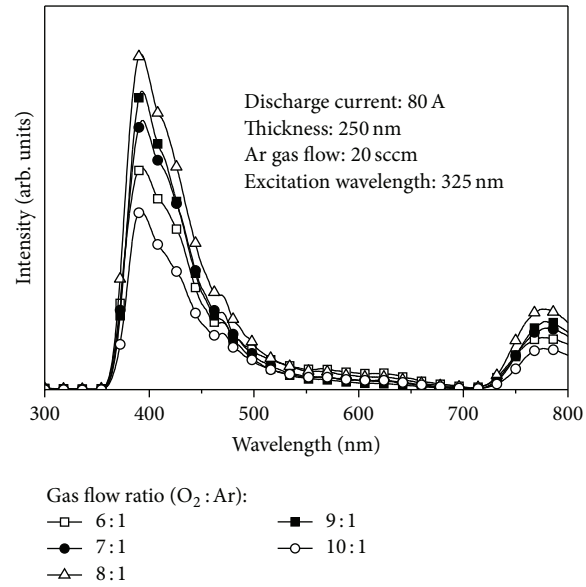

Figure 6: PL spectra of the room-temperature deposited ZnO films on the PET substrate with various O_2/Ar gas flow ratios.

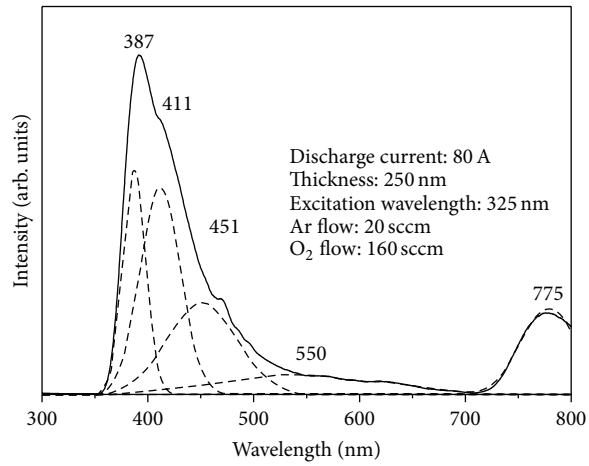

Figure 7: Typical PL spectra of the deposited ZnO thin film with O_2/Ar gas flow ratio of 8 : 1 and its Gaussian fit band.

PET substrate are considered to be suitable for the use of the flexible resistive touch penal. Moreover, if the ZnO thin films want to be used in the former electrode of solar cells, the sheet resistivities of the deposited ZnO films shall be lower since the lower sheet resistivities make lower series resistance, thus improving the output short current of the solar cell.

3.4. Defect Types. Figure 6 displays PL spectra of the ZnO thin films as functions of various O_2/Ar gas flow ratios. The result shows an obvious near ultraviolet (UV) emission peak from 380 nm to 450 nm, a broad blue-green emission peak from 450 nm to 570 nm, and a weak red emission peak from 750 nm to 800 nm. The intensity of the luminescent band is varied with the O_2/Ar gas flow ratios and has strongest UV emission intensity when O_2/Ar gas flow ratio is 8 : 1.

It is known that the oxygen flow rate typically affects the defect types of pure ZnO films deposited at a low temperature. Figure 7 shows typical PL spectra of the deposited ZnO thin film with O_2/Ar gas flow ratio of 8 : 1 and its Gaussian fit band. The peaks of five main Gaussian fit bands are at 387, 411, 451, 550, and 775 nm.

The near UV emission at approximately 387 nm typically resulted from an exciton transition related near band edge emission (NBE) of the wide band gap ZnO [1, 14]. The other visible peaks are generally correlated to the luminescence of defects. The blue-green emission mainly resulted from oxygen vacancies (V_O), zinc vacancies (V_{Zn}), oxygen interstitials (O_i), zinc interstitials (Zn_i), and oxygen displacement zinc [2]. The emission at 411 nm (e.g., 3.01 eV) in the blue emission is due to the defects from zinc interstitial (Zn_i) in the ZnO film [15]. It was reported that the formation of zinc interstitial in the ZnO film resulted from the energetic zinc particles in the cathodic plasma and low substrate temperature [6]. The optical energy for the emission at 451 nm (e.g., 2.79 eV) is close to the energy interval (2.65 eV) between the level of the zinc interstitial (Zn_i) and the level of zinc vacancy (V_{Zn}) [15]. Moreover, the luminescence mechanisms of other defect emissions at 550 nm (e.g., 2.25 eVm) and at 775 nm (e.g., 1.6 eV) in the red emission may result from the defects of oxygen interstitial (O_i) and oxygen vacancy (V_O) in the ZnO film, respectively [1, 14]. It is verified that the conductive property of the pure ZnO film is attributed to the intrinsic defects such as oxygen vacancy (V_O) and zinc interstitial (Zn_i), resulting in the origin of deep-level-emission (DLE) band [7].

4. Conclusion

We have deposited pure ZnO thin film on PET substrate using the CVAD system at different O_2/Ar gas flow ratios at a room temperature. The crystalline as well as crystal sizes are increased with adjusting O_2/Ar gas flow ratio in the optimum value of 8 : 1. The mobility and carrier concentration increased with O_2/Ar gas flow ratios and dominated by the grain boundary scattering due to the increased crystal size. The average transmittance values in the visible range of the deposited ZnO films were all higher than 83% and the calculated band gaps from the absorption data were found

to be around 3.1 to 3.2 eV. The conductive property of the deposited ZnO film resulted from the origin of deep-level-emission (DLE) band, attributed to the intrinsic defects such as oxygen vacancy (V_O) and zinc interstitial (Zn_i), and showed a minimum value in 3.65×10^{-3} Ω·cm, with a mobility of 4.8 $cm^2/V{\cdot}s$ and a carrier concentration of 5.89×10^{20} cm^{-3} under the O_2/Ar gas flow ratio of 8 : 1. For the future work, the mechanical properties of the CVAD ZnO films shall be investigated to verify the usability on the flexible electronics.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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