SNRU Journal of Science and Technology 13(1) January – April (2021) 37 – 45

SNRU Journal of Science and Technology

Journal home page: snrujst.snru.ac.th

Transparent Thin Film of Zinc Zirconate Deposited by DC Magnetron Sputtering Technique

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Received: 18 June 2020; **Revised:** 22 November 2020; **Accepted:** 27 November 2020; **Available online:** 1 January 2021

Abstract

$ZnZrO_3$ thin film was deposited by the non-reactive DC magnetron sputtering technique on glass substrates using ZnO and ZrO_2 composite target of with a mass ratio of 90:10. The composited target was pressed at a pressure of 25 MPa. The deposition process was operated with the non-reactive method and heat treatment film in the air at a temperature of about 400˚C for 1 h. The X-ray diffraction patterns revealed cubic perovskite phases of $ZnZrO_3$. The surface morphology was observed distribution of nano-granular and thickness of about 231 nm. The $ZnZrO_3$ thin film was exhibited high transparency of about 95.46% in the visible region and optical gap energy of about ~3.27 eV. The results of this research promise can develop transparent film for solar cell applications in the future.

Keywords: $ZnZrO_3$; DC magnetron sputtering; thin film; perovskite; transparent.

1. Introduction

Recently, the perovskite solar cells have become attractive in the research to development for comer espacially viable. Until now, National Renewable Energy Laboratory (NREL) was reported perovskite solar cells and materials attracted increasing efficiency up to 29.10% in laboratory scale [1], most likely with the maximum efficiency of perovskite semiconductors solar cells about 30% [2]. The perovskite materials have general stoichiometry with ABX_3 (cubic structure) where A is an organic cation, B is a metal cation and X is a halide [3, 4], the physical properties such as magnetic and good ferroelectric properties are in forms of ceramic [5]. The perovskites materials are interesting significant properties based-on earth-abundant compounds, non-toxic, and environmentally friendly for development thin film layer in the solar cells. The zinc zirconate ($ZnZrO_3$) is a one perovskites metal oxides that has been widely studied mainly in scientific research and application to ferroelectric, dielectric films ceramic capacitors, optoelectronic, sensors and actuators and magnetic fields. The optical band gap is around 2.81 − 3.15 eV [6 – 11], and invisible light region. Moreover, $ZnZrO_3$ can be used as photocatalytic [12], working electrodes for dye-sensitized solar cells (DSSC) [13 – 16] and fabrication to the transparent films of thin film solar cells (TFSC) which are important layers for the role of development on TFSC such as barrier layers [17], window layers and transparent conductive layers [18 – 22] depending on electrical properties of $ZnZrO_3$. The $ZnZrO_3$ thin films can be deposited by several methods such as hydrothermal method [7, 23], Sol-Gel Method [7 – 15], pastes coated [13], frequency magnetron sputtering [24] chemical vapor deposition [25.] and chemical solution deposition [26]. However, the physical process can be produced high-quality films higher than the chemical process [27]. The $ZnZrO_3$ material was found strong phase optimal temperature to formed at 800 °C, it can be also observed at the minimum temperatures 400 ˚C [28, 29]. The ZnO-based target can be used to deposit ZnO [30], $ZnTiO_3$ [31], and $ZnO:Al_2O_3$ [32] thin films using direct current (DC) magnetron sputtering without reactive atomic oxygen. Therefore, we proposed to use the DC magnetron sputtering technique to deposit $ZnZrO_3$ film and report a detailed investigation on the preparation the composite target of ZnO and ZrO_2.-The structural properties, morphology surface, and cross-sections and optical properties to study the possibility for developing transparent film without reactive in sputtering.

2. Materials and methods

Preparation Target

The $ZnZrO_3$ composited target was prepared using powder of ZnO, (99.99% purity, QRëC, New Zealand) ground together with ZrO_2 (99%; Sinopharm Chemical Reagent Co., Ltd) mass ratio 90:10 [33] and was compressed into the copper cap support diameter of 60 mm to produce $ZnZrO_3$ target as shown in Fig. 1.

Fig. 1 $ZnZrO_3$ composited target.

Film Deposition

Before being deposited film, a glass slide substrate size of 2.50 × 3.90 × 0.10 cm^3 (UPLINE, Model UP-209) was cleaned with detergent solution and acetone in an ultrasonic cleaner (GT -Sonic, VGT-1730QTD) for 10 min and dried in air. The conditions of DC sputtering method for deposition film were operated on base pressure 32 mT, working pressure 35 mT, DC power 32 W, deposition time 30 min [34], Ar flow rate was 35 SCCM, the process as shown in Fig. 2 (a). After the deposition, $ZnZrO_3$ film (see in Fig. 2 (b)) during heat-treatment in a furnace (in air atmosphere) from room temperature up 400 ˚C (temperature ramping rate of 5 ˚C min^{-1}) [7] and treatment time for 1 h, the temperature-time profile as shown in Fig. 3.

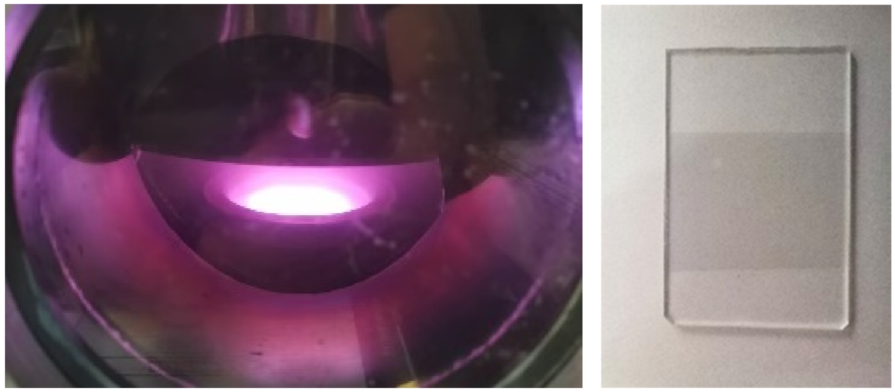

Fig. 2 Thin film deposition process (a) Sputtering plasma and (b) $ZnZrO_3$ film.

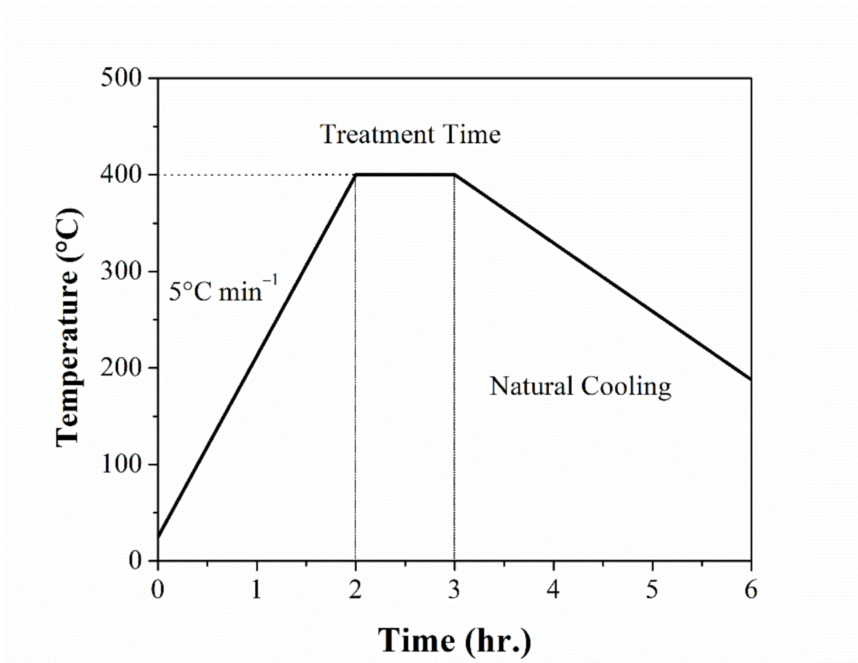

Fig. 3 Temperature-time profile used during heat treatment process of $ZnZrO_3$ film.

Characterization

The $ZnZrO_3$ thin film was studied the structural properties with X-ray Diffractometer (XRD-6100, SHIMADZU) using Cu $K_{\alpha 1}$ radiation (λ = 1.5406 Å) in the diffraction scan range $2\theta = 20^{\circ} – 80^{\circ}$, scan speed = 2˚ (deg. min^{-1}) operated at 40 kV and 30 mA, step time 0.60 s per step. The surface area and cross-section morphologies were characterized by Scanning Electron Microscope (SEM JSM-6610 LV, JEOL) operating at 20 kV. The optical properties of thin film was carried out by a UV-Vis spectrophotometer. (UV5200, Shanghai Metash Instruments Co. Ltd) in the range of 350 – 1,100 nm wavelength.

3. Results and Discussion

Fig. 4 shows the XRD diffraction patterns of $ZnZrO_3$ thin film. The diffraction patterns were observed the slightly main peak appearing at angle $2\theta = 32.06^{\circ}$ this peak can identify to the reflections from (1 1 0) plane of $ZnZrO_3$ corresponding with the $ZnZrO_3$ cubic crystal phase at ≈32˚ from the report by Reddy *et al.* [35], Zhu *et al.* [7] and Siva *et al.* [36]. The effect annealing of the $ZnZrO_3$ for 400 ˚C reveals an amorphous phase with weak lines due to temperature nonoptimized to 800 ˚C. However, $ZnZrO_3$ were found tetragonal/cubic crystal phases in the residual amorphous phases [36].

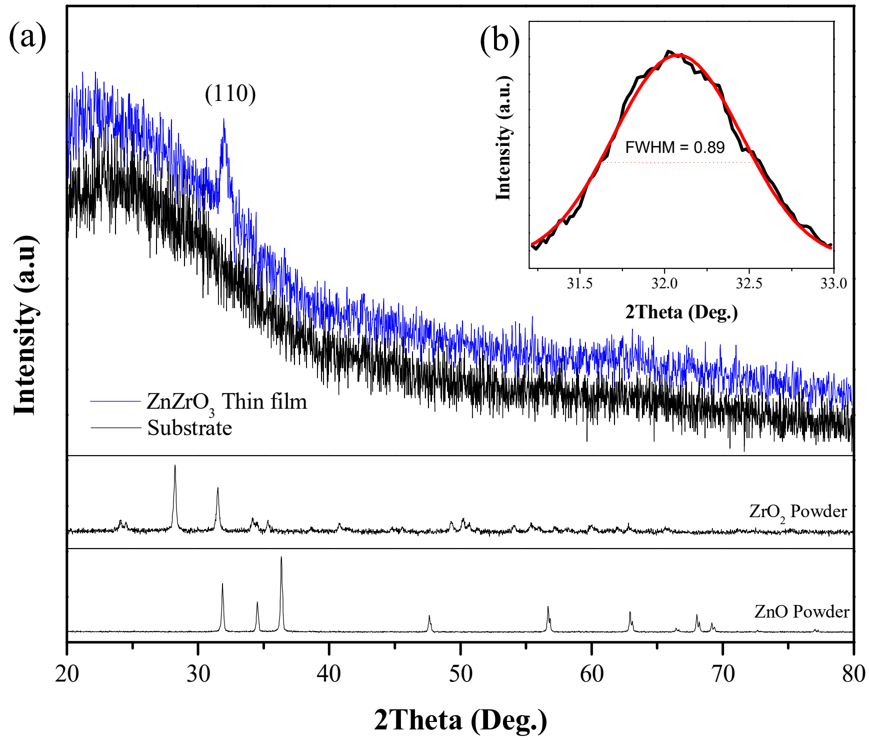

Fig. 4 X-ray diffraction patterns of glass substrate and $ZnZrO_3$ thin film ZnO-ZrO_2 .

The crystallite size (D) was evaluated from the (110) peak by Debye–Scherrer's equation as followed eq. (1) [37];

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

Where k is a constant taken to be 0.94, λ is the wavelength of X-ray radiation (λ = 1.5406 Å) and β is the full width at half-maximum (FWHM) of (110) peak of XRD pattern and the Bragg angle (2θ = 30.53˚) is 0.89. The XRD result was found that the crystallite size approximately was about 9.69 nm.

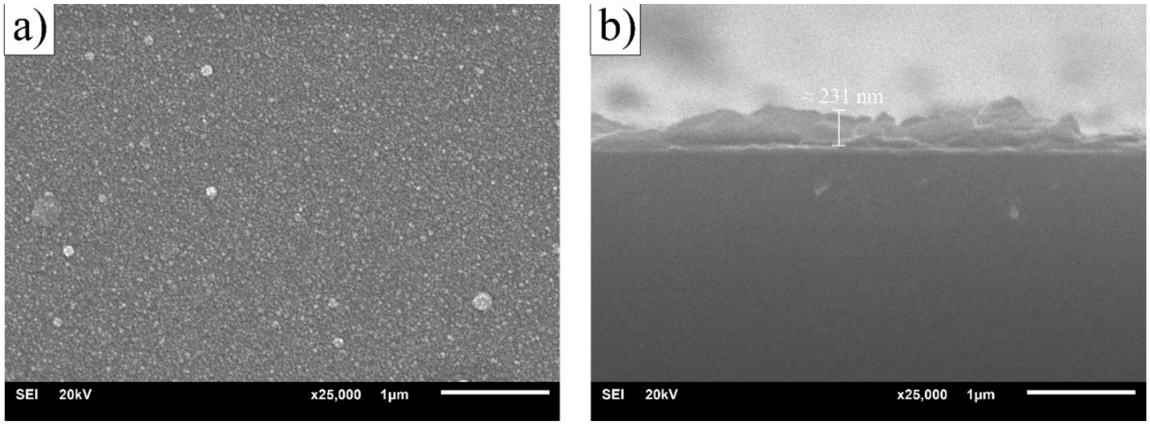

Fig. 5 SEM images (a) surface area and (b) Cross-section of $ZnZrO_3$ thin film.

The surface morphology in Fig. 5(a) are also observed the distribution of nano-granular around ~1 – 63 nm throughout on surface film, the nano-granular was demonstrated to the interconnect grain structure at a temperature lower than phase formation of materials, grain can give to a larger size with annealing using temperature higher 400 ˚C [38]. The average thickness of film was observed on the cross-section image in Fig. 5(b) about 231 nm, in agreement with Lv, M. *et al.* [24]. However, the uneven thickness may be caused by a non-reactive DC magnetron sputtering process and a short time for the deposition.

The optical properties of $ZnZrO_3$ film were studied on transmission spectra scan on the wavelength range from 350 – 1,100 nm as shown in Fig. 6. The film samples also showed high transparency 95.46% demonstrating a good transparent film in the visible region on the solar spectrum.

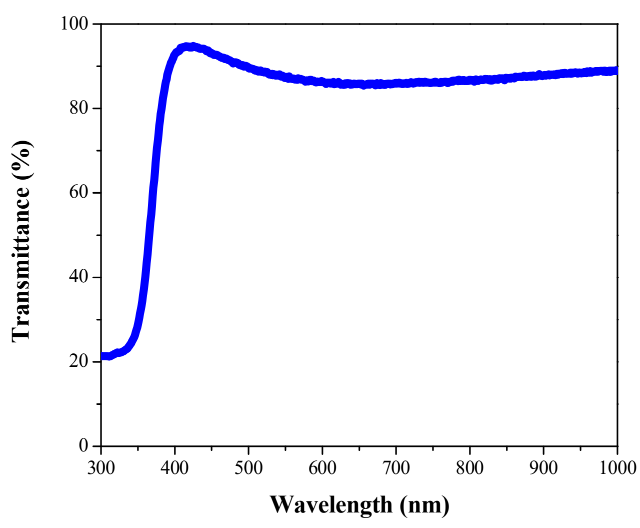

Fig. 6 Transmission spectra of $ZnZrO_3$ thin film.

The absorption coefficient (α) of $ZnZrO_3$ thin film was illustrated in Fig. 7. The sample film was observed a high absorption in an ultraviolet wavelength range of <400 nm which is caused by the absorption of light on the semiconductor basis of ZnO materials (bandgap about ~3 eV) and low absorption visible. The absorption coefficient can be considered with the Beer-Lambert's relation in eq. (2) [39];

$$\alpha = \frac{2.303A}{t} \tag{2}$$

Where A is absorbance and t is the thickness of the thin film. The absorbance can be considered with the logarithmic function of transmittance value (T) determine by eq. (3) [39];

$$A = \log\left(\frac{1}{T}\right) \tag{3}$$

Moreover, the absorption coefficient can be calculation the optical energy gap (E_g) can be determined using the Tauc's plot relation in eq. (4) [40];

$$\alpha h\upsilon = B(h\nu - E_g)^n \tag{4}$$

Where B is the constant, E_g is the energy gap, n is 1/2 for direct gap allowed transition h is Planck's constant and ν is the frequency of the incident radiation. The optical bandgap of $ZnZrO_3$ thin film was estimated by the extrapolating the linear portion of the $(\alpha h\nu)^2$ versus $h\nu$ plot, as shown in Fig. 8. The $ZnZrO_3$ showed bandgap about 3.27 eV.

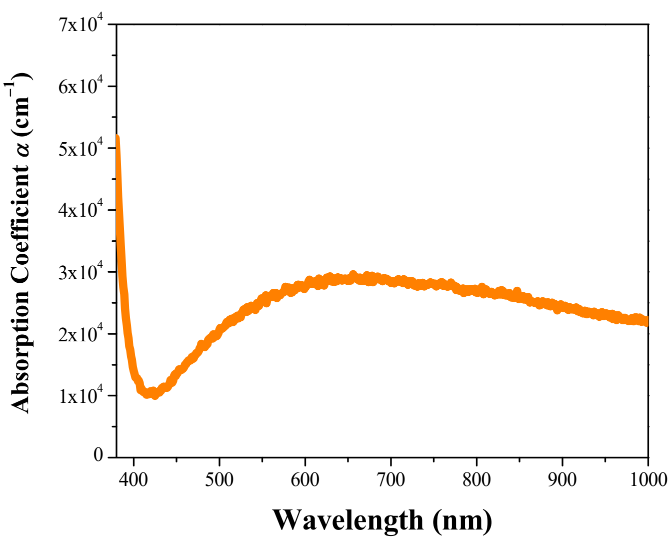

Fig. 7 Absorption coefficient of $ZnZrO_3$ thin film.

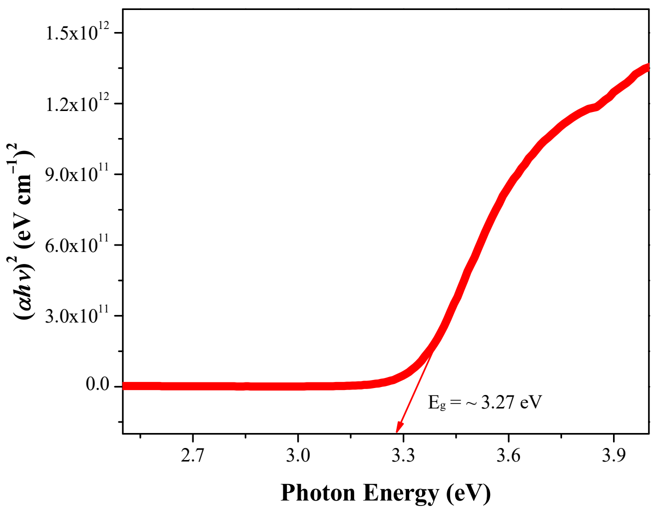

Fig. 8 Plot of Tuac's function $(\alpha h\nu)^2$ vs $h\nu$ of $ZnZrO_3$ thin film.

4. Conclusion

$ZnZrO_3$ thin film could be deposited on the glass substrate by a non-reactive DC magnetron sputtering method. The crystal structure of the sample film was corresponded with literature reviews suggestions to the cubic phase with crystallite size of approximately 9.69 nm. The surface morphology shows distribution of nanogranular around ~ 1 – 63 nm, and average thickness about 231 nm. The optical properties show the good value of high transparency 95.46% and the optical bandgap was about ~3.27 eV. These results were proved that the film cab be developed into a transparent thin film for solar cell applications.

5. Acknowledgement

The authors are thankful to Optic Research Laboratory (ORL), Thin Film Research Laboratory (TFRL), Center of Excellence on Alternative Energy (CEAE), Research and Development Institution (RDI), Sakon Nakhon Rajabhat University SNRU), Thailand.

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