Preparation of Zinc Oxide (ZnO) Thin Film as Transparent Conductive Oxide (TCO) from Zinc Complex Compound on Thin Film Solar Cells: A Study of O₂ Effect on Annealing Process

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Abstract. Zinc oxide (ZnO) thin film as a transparent conductive oxide (TCO) for thin film solar cell application was successfully prepared through two step preparations which consisted of deposition by spin coating at 2000 rpm for 10 second and followed by annealing at 500 °C for 2 hours under O₂ and ambient atmosphere. Zinc acetate dehydrate was used as a precursor which dissolved in ethanol and acetone (1:1 mol) mixture in order to make a zinc complex compound. In this work, we reported the O₂ effect, reaction mechanism, structure, morphology, optical and electrical properties. ZnO thin film in this work shows a single phase of wurtzite, with n-type semiconductor and has band gap, carrier concentration, mobility, and resistivity as 3.18 eV, 1.21x10⁻¹⁹cm³, 11 cm²/Vs, 2.35 x 10⁻³ Ωcm respectively which is suitable for TCO at thin film solar cell.

1. Introduction
Zinc oxide (ZnO) thin film is the II-IV thin film semiconductor which is widely used in many important applications such as sensors, photodetectors, LEDs, transistors and also as a conductive layer in the solar cells [1,2,3]. As a conductive layer, ZnO thin film has band gap and resistivity of 3.35 eV and 4.4 x 10⁻³ Ωcm respectively [4]. ZnO can be fabricated by vacuum and non-vacuum processes and both methods have their own advantages. However to fabricate a simple, low cost and easy scalability of ZnO thin film, non-vacuum process is more preferable especially chemical or wet process [5]. Commonly, to fabricate thin film by chemical or wet process, organic solvents is used such as 2-propanol, methanol, ethanol, oleylamine, aminoalcohols, hexamethyldetraamine [6-10].

In this work, ZnO thin film successfully synthesized from zinc acetate dehydrate as starting material and using a mixture of acetylacetone and ethanol as solvents. Spin coating method is used to deposit the precursor solution and continued by annealing to get ZnO thin film layer. However, this work focuses on O₂ effects to optical and electrical properties of ZnO thin film layer to be applied as a transparent conductive oxide (TCO) in thin film solar cell.
2. Experimental

2.1. Materials and Methods

ZnO thin film layer was prepared from 0.1 M of zinc acetate dihydrate from Aldrich as starting material which dissolved in the mixture of ethanol and acetylacetone (both from Aldrich) in 1:1 mol ratio. This solution defines as a precursor solution and it was a clear and homogeneous solution and deposited on soda lime glass (SLG) which cleaned with acetone, ethanol, deionized water using ultrasonic for 15 minutes respectively and followed by nitrogen gas drying in order to eliminate further contaminants. Moreover, 0.2 mL of precursor solution was deposited by a homemade spin coating apparatus at 2000 rpm for 10 seconds and dried at room temperature for 3 minutes. This process was repeated for 5 times and continued by annealing at 500 °C for 2 hours under O2 and ambient atmosphere using a tube furnace from Best Made In Korea (BMIK, South Korea).

2.2. Characterization of ZnO Thin Film

The morphology of the thin film was characterized by scanning electron microscope (SEM; Hitachi S-4800, Japan) with an operating voltage 15 kV. The chemical composition of the thin films was analyzed by energy dispersive spectrometry (EDS; Horiba, Japan) attached to the SEM with an acceleration voltage, working distance and emission current of 15 kV, 15 mm, and 10 μA respectively. The phase of crystallographic information was obtained from the x-ray diffraction (XRD; PANanalitycal, Netherlands). The spectra absorption was recorded by UV-Vis-NIR Spectrophotometer in the wavelength range of 300-1500 nm (Carry 5000, Varian, USA). Electrical properties were determined using Hall-Effect measurement at 0.01 μA (HMS-300, Ecopia, USA).

3. Results and Discussion

In the preparation, the mixture of acetylacetone and ethanol with the same mol ratio could form a hemiketal compound which could dissolve and form a zinc complex compound with zinc acetate dihydrate simultaneously. Then, the zinc complex solution was deposited on the substrate and allowed to evaporate under room temperature. Moreover, ZnO thin film was fabricated by annealing the deposited zinc complex on the substrate under O2 atmosphere at 500 °C for 2 hours, the zinc complex compound was decomposed into ZnO and deposited on the substrate, meanwhile the organic compounds were decomposed into carbon dioxide and water vapor.

\[
C_2H_6O (l) + C_5H_8O_2 (l) \rightarrow C_7H_{14}O_3 (aq)
\]

\[
C_7H_{14}O_3 (aq) + Zn^{2+} (aq) \rightarrow Zn[C_7H_{14}O_3]_x (s)
\]

\[
Zn[C_7H_{14}O_3]_x (aq) + 11O_2 (g) \rightarrow ZnO (s) + 7CO_2 (g) + 7H_2O (g)
\]

After annealing at 500 °C under O2 atmosphere for 120 minutes, ZnO thin film had been formed with a single phase of hexagonal wurtzite. X-ray diffraction (XRD) pattern, showed identical XRD peaks with ZnO standard (ICDD: 01-089-7102). Meanwhile, ZnO thin film annealed under ambient atmosphere showed the existence of carbon residue as amorphous which identified as a broadened peak from 20 to 50°. However, although ZnO thin film also could be formed by annealing under ambient atmosphere, but there was carbon remained as a residue due less oxygen contained in the air. This condition makes the organic compounds were not decomposed completely and formed carbon compounds as residue which trapped inside the thin film.

\[
Zn[C_7H_{14}O_3]_x (aq) + 3O_2 (aq) \rightarrow ZnO (s) + CO (g) + 6C (s) + 7H_2O (g)
\]
Figure 1. XRD pattern of substrate before annealing (a), ZnO thin film after annealed under ambient atmosphere (b), and O$_2$ gas atmosphere (c).

From scanning electron microscope (SEM), ZnO thin film annealed under O$_2$ gas atmosphere showed a similar shape with solid ZnO [11] with uniform granular with grain size around 60 nm and from cross-sectional image could be seen a dense thin film with 507 nm of thickness. On the other hand, ZnO thin film annealed under ambient atmosphere showed carbon as residue surrounded by small granular of ZnO. Meanwhile, carbon in the thin film came from organic compounds left and trapped in the thin film due to every incomplete combustion reaction from organic compounds would leave carbon behind as residue was detected by energy dispersive spectrometry (EDS).
Figure 2. SEM images of ZnO thin film annealed under ambient atmosphere (a) and O$_2$ (c), and their cross-sectional image respectively (b and d).

From the EDS spectrum, it was clearly shown that ZnO thin film annealed under ambient atmosphere still contained carbon as residue whereas ZnO thin film annealed under O$_2$ gas atmosphere showed that no carbon spectrum was detected due to complete combustion reaction between O$_2$ with organic compounds in the thin film. Besides, O$_2$ from the atmosphere also helped oxidation of Zn became ZnO. However, Si and Ca from substrate (soda lime glass) containing Si and Ca were detected due to dispersion spectrum of Si and Ca could penetrate the ZnO thin film and were detected by detector as shown in Figure 3b.
Figure 3. EDS images and spectrums of ZnO thin film annealed under ambient atmosphere (a) and O₂ (b).

The optical properties of ZnO thin film annealed either under O₂ atmosphere or ambient atmospheres showed low transmittance at 300 nm to 400 nm and high transmittance at 400 nm to 1500 nm. However, the ZnO thin film annealed under O₂ atmosphere had higher transmittance and band gap energy due to no carbon residue which could absorb the light. The band gap energy of ZnO thin film annealed under air and O₂ atmosphere was 3.07 and 3.18 eV respectively. ZnO annealed under ambient atmosphere absorbed less light than annealed under O₂ atmosphere due to the existence of carbon as residue. However, ZnO annealed under O₂ atmosphere had similar transmittance and band gap energy with the reference [12].

Figure 4. Optical transmittance of ZnO annealed under O₂ and ambient atmosphere (a) and their energy band gap (b).

The electrical properties of ZnO thin films both showed n-type semiconductor with electrical properties such as carrier concentration and mobility as shown in Table 1. Carrier concentration and
mobility of ZnO annealed under O$_2$ and ambient atmosphere showed appropriate by reference. However, carrier concentration and mobility of ZnO annealed under an ambient atmosphere were lower than annealed under O$_2$ atmosphere. This phenomenon was also caused by carbon which left behind the thin film as a residue that could restrict the electrons movement in the ZnO thin film.

Table 1. Electrical properties of ZnO wurtzite thin film prepared under several conditions

| Electrical Properties | Under O$_2$ atmosphere | Under ambient atmosphere | Reference [13] |
|-----------------------|------------------------|--------------------------|----------------|
| Carrier Concentration | 1.21x10$^{-19}$ cm$^3$ | 2.35x10$^{-18}$ cm$^3$ | 10$^{-17}$ - 10$^{-20}$ cm$^3$ |
| Mobility              | 11 cm$^2$/Vs           | 9 cm$^2$/Vs              | 5 - 50 cm$^2$/Vs |

4. Conclusion
The ZnO thin film could be fabricated through zinc complex compound pathway which is made from zinc acetate dihydrate and hemiketal without pre heat treatment process. The amount of O$_2$ during annealing of ZnO thin film is critical due to acts as a reagent for eliminating the organic compounds and as an oxidant simultaneously. The ZnO thin film annealed under O$_2$ atmosphere shows better morphology, optical and electrical properties due to sufficient of O$_2$ during reactions. ZnO thin film has suitable properties as TCO for thin film solar cell application.

5. References
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