The effect of Al Element on Electrochemical Impedance of ZnO Thin Films

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Abstract. We have grown no-doped and Al-doped ZnO thin films with different Al element composition by ultrasonic spray pyrolysis (USP). The deposition by USP was performed with the temperature of 450 °C, ultrasonic frequency of 1.7 MHz, and under atmosphere ambient for 15 minutes on top of Si substrate. Structurally, X-ray diffraction (XRD) pattern of non-doping and Al-doped ZnO (AZO) thin film have polycrystalline hexagonal wurtzite and amorphous. Optical absorbance confirmed that AZO thin films with polycrystalline phase have higher absorbance than amorphous. According to the frequency-dependent Nyquist plot of non-doping and AZO thin films at room temperature, we believed the proper concentration of Al in ZnO thin films can be used to improve electron transfer ability.

1. Introduction

To date, ZnO as a direct semiconductor material still become interesting research subject. As well known, ZnO has wide band gap (3.4 eV) and large exciton binding energy (60 meV) at room temperature [1]. Therefore, many researchers and engineers have demonstrated broad applications based on ZnO, such as photocatalyst [2], light emitting diodes (LEDs) [3,4], solar cell [5], sensor [6], etc.

Different methods have been demonstrated to growth ZnO thin films and nanostructures such as metal organic chemical vapor deposition (MOCVD) [7,8], ultrasonic spray pyrolysis (USP) [3], hydrothermal [9], spin coating [10], and sputtering [11]. The improvement of structures, optical, and electrical performance can be realized by post-growth thermal annealing and dopants [12,13].

As reported, some extrinsic doping such as Al, In, Ga, and Cu can be used to serve as donor in ZnO lattice and increase band-gap energy of ZnO [10]. Among these doping, aluminum (Al) as dopant have believed able to improve optical and electrical properties of ZnO thin films. A. Gahtar et. al. deposited Al doped ZnO thin films on glass substrate by ultrasonic spray method [14]. Their results confirmed the band gap energy and electrical conductivity increase by Al concentration. Meanwhile, Al-Ghamdi et. al. have deposited Al doped ZnO thin films by spin coating method on glass substrate [10]. They observed that Al doped ZnO thin films have a high transparency in the visible range.

In this paper, Al doped ZnO thin films were deposited on silicon (Si) substrate by ultrasonic spray pyrolysis for 15 minutes. We further investigated the structure, optical, and electrochemical impedance by X-ray diffraction (XRD) measurement (Phillips PW 3710 with CuKα radiation), UV-Vis spectrometer (Maya), and electrochemical impedance analyzer (EDAQ; ERZ100), respectively.
2. Experimental Methods

Non-doping and AZO thin films have been deposited on Si substrates by ultrasonic spray pyrolysis (USP) with the frequency of 1.7 MHz. Zinc acetate dehydrate [Zn(CH₃COO)₂·2H₂O] and aluminum hydroxide acetate hydrate [C₄H₉AlO₆] were chosen as host and dopant precursors, respectively. The zinc acetate (0.02 mol/ml) was mixed with the aluminum hydroxide acetate hydrate (1 wt.%, 3 wt.%, and 5 wt.%) and diluted in de-ionized (DI) water. The commercial ultrasonic spray pyrolysis was used to generate the aerosol of the precursor solution on top of a Si substrate heated at 450 °C.

3. Results and discussion

Figure 1 shows XRD pattern of non-doping and Al-doped ZnO (AZO) thin films with different Al concentration. It can be seen from the figure 2, XRD pattern of ZnO thin film with Al concentration of 1 wt.% exhibit seven (hkl) plane orientations i.e. (100), (002), (101), (102), (110), (103), (112). Meanwhile, by increasing Al concentration i.e. 3 wt.% and 5 wt.%, the XRD pattern deteriorate significantly with no diffraction peaks observed. Hence, by increasing Al concentration of 3 wt.% and 5 wt.% the crystalline phase change to amorphous. As others reported, the Al incorporation into ZnO site films have weaker crystallization [10].

![Figure 1. XRD pattern of non-doping and AZO thin films](image)

| Sample               | 2 theta  | a=b(Å) | c(Å) | d(hkl) | Vol. (Å³) | FWHM  | Micro-strain | Crystallite size (nm) |
|----------------------|----------|--------|------|--------|-----------|-------|--------------|-----------------------|
| ZnO (non-doping)     | 34.4156  | 3.2527 | 5.2107 | 2.6037 | 47.7451   | 0.4249| 0.8589       | 15.1563               |
| ZnO-Al (1%)          | 34.4076  | 3.2498 | 5.2111 | 2.6044 | 47.6625   | 0.3545| 0.7907       | 16.4681               |

According to Inorganic Crystal Structure Database (ICSD) number #98-006-7454, the non-doping and AZO thin film with an Al concentration of 1 wt.% possess polycrystalline hexagonal wurtzite structure. By texture of coefficient (TC) [15], we have determined that (002) peak is the most prefer orientation compared to another crystalline plane. In this phase, we further observed the full width at half maximum (FWHM) of (002) peak decrease from 0.4249° for non-doping to 0.3545° for ZnO thin films with Al concentration of 1 wt.% (table 1). It is indicated that the narrowing of FWHM is due to crystallinity improvement when Al concentration of 1wt.%.
Figure 2 shows the optical absorbance of non-doping and AZO thin films. It is seen that a non-doping ZnO thin film has absorbance in the range of 375 nm to 485 nm.

![Figure 2](image1.png)

**Figure 2.** UV-Vis absorbance spectra of non-doping and AZO thin films

Furthermore, for AZO thin film with Al concentration of 1wt.%, there are 375 nm, 395-410 nm, 450-500 nm, 715 nm. On the other hand, AZO thin films with Al concentration of 3wt.% has a peak at 375 nm, meanwhile, Al concentration of 5wt.% the absorbance of AZO thin film in the range of 400 nm to near infrared wavelength. We predict this peculiar property due to amorphous phase of AZO thin films when the Al concentration in ZnO film of 3wt.% and 5wt.%.

Figure 3 shows the real of the complex impedance as a function of frequency at room temperature of non-doping and AZO thin films.

![Figure 3](image2.png)

**Figure 3.** The real of the complex impedance as a function of frequency at room temperature of non-doping and AZO thin films
It can be seen from figure 3, in the range frequency of 1.2 kHz to 20 kHz, non-doping ZnO thin film has higher complex impedance. Meanwhile, in the range of 1 kHz to 1.2 kHz and 30 kHz to 100 kHz, the complex impedance of AZO thin films with Al concentration of 3wt.% is higher. We predict the real complex impedance influenced by the change of AZO structure. In this case, the change of the structure from polycrystalline to amorphous cause change in grain boundary resistance [15]. Hence, AZO thin film with Al concentration of 3 wt.% has various complex impedance. Meanwhile, AZO thin film with Al concentration of 5wt.% in the frequency of more than 30 kHz has higher complex impedance compared to AZO thin film with Al concentration of 1wt.%.

Figure 4 shows the frequency-dependent Nyquist plot of non-doping and AZO thin films at room temperature. The inset is Randle equivalent circuit corresponding to Nyquist plot. According to the Randle equivalent circuit, Rs is the electrolyte solution resistance, Rct the charge transfer resistance, Cdl the double-layer capacitance, and Zd the Warburg impedance [16].

![Nyquist Plot of Non-Doping and AZO Thin Films](image)

**Figure 4.** The frequency-dependent Nyquist plot of non-doping and AZO thin films at room temperature

The radii of the Nyquist plot curves of non-doping and AZO thin films is equal with the value of Rct. It is seen that the radii of amorphous AZO with Al concentration of 3wt.% is larger than non-doping and polycrystalline AZO thin film with Al 1wt.%. Hence, it indicates that proper Al incorporation into ZnO thin films improves electron transfer ability of AZO thin films. Meanwhile, amorphous AZO thin films with Al concentration of 5wt.% has the smallest radii than polycrystalline AZO thin film with Al 1wt.%. It is indicating that too much Al in ZnO site cause difficulties to form crystallization and improve electron transfer ability.

**4. Conclusions**

In conclusion, non-doping and AZO thin films have been deposited by ultrasonic spray pyrolysis. Non-doping and AZO thin film (Al 1wt.%) possess polycrystalline hexagonal wurtzite structure, meanwhile, AZO thin films (Al 3wt.% and 5wt.) have amorphous phase. Proper Al concentration in AZO with polycrystalline structure has higher absorbance compared to AZO in the amorphous phase. On the other hand, electrically, proper Al concentration can be used to improve electron transfer ability of AZO thin films.
Acknowledgment

Financial support from hibah penelitian kompetitif Universitas Negeri Jakarta no. 27/KOMP-UNJ/LPPM-UNJ/V/2019 is gratefully acknowledged.

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