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Al- & Al-Ca-doped ZnO Thin Films by Sol-Gel Method for Solar Cell Application

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Abstract. Zinc oxide (ZnO) thin films, due to their excellent photovoltaic properties, are gaining much attention to be used as n-type semiconductor material for modern day solar cell. The change in photoelectric properties of zinc oxide with doping is an area of much consideration. In this work, 1.17%Al, 1.17%Al-2%Ca and 1.17%Al-4%Ca doped ZnO thin films were produced on glass substrate by Sol-Gel spin coating technique. Zinc acetate dihydrate, triethanolamine and isopropanol were used for making precursor solution. For Al doped ZnO, aluminum nitrate nona hydrate was added to the precursor solution as source of Al. Aluminum nitrate nona hydrate and calcium chloride dihydrate were utilized as source of Al and Ca respectively for Al-Ca doped ZnO. The films were deposited from precursor solutions at 1300 rpm for 20 seconds. After deposition, annealing was done at 520°C for one hour. Properties of deposited films were characterized by X-ray Diffractometer (XRD), Scanning Electron Microscopy (SEM) and UV-Vis spectroscopy. From XRD spectra the theoretical grain size was measured which increased from 0.31 nm to 0.33 nm because of doping. From SEM micrograph the uniformity and homogeneity of thin film was observed. The band gap of deposited thin films was measured from absorbance spectra. The band gap decreased from 3.27 eV to 3.17 eV because of doping 4% Ca in addition to 1.17% Al. From transmittance spectra, it was found that all films were transparent with average percentage of transmittance of more than 86%.

1. Introduction

A solar cell or photovoltaic cell (previously termed "solar battery") is an electrical device that converts the energy of light directly into electricity by the photovoltaic effect, which is a physical and chemical phenomenon [1]. Photovoltaic (PV) systems provide the possibility to generate electricity with environmental advantages as zero carbon dioxide emission during operation as well as scale flexibility, simple operation, and low-cost maintenance [2]. Despite its numerous advantages, two principal problems are the intermittent nature of environmental conditions and the low energy yield in PV systems that increase area-relate costs [3].

Different strategies are proposed to address this low-efficiency problem. Of them thin film solar cells are the most promising ones because of their low materials cost and energy cost during manufacturing. The present PV industry is dominated by crystalline and multi-crystalline Si wafer based solar cells. Because of high production cost, threat to environment and low efficiency, its development is getting limited attention. In contrast, thin film solar cells, only need very small amount of semiconductor materials. Thin film solar cells can be deposited onto various kinds of substrates such as glass, stainless steel, polymer, which account for a large fraction of the materials cost and energy cost. The development of new materials, such as
polymer, may help reducing the thin film solar cells cost. For example: CZTS (Copper Zinc Tin Sulpher), Zinc Oxide (ZnO) and it’s doping, Perovskite materials etc.

In the past ten years we have witnessed a revival of, and subsequent rapid expansion in the research on zinc oxide (ZnO) as a semiconductor. The prospects of gaining control over its electrical conductivity have led a large number of groups to turn their research for electronic and photonic devices. While a number of research groups have reported achieving p-type ZnO, there are still problems concerning the reproducibility of the results and the stability of the p-type conductivity [4]. Even the cause of the commonly observed unintentional n-type conductivity in as-grown ZnO is still under debate [4]. Band-gap engineering of ZnO can be achieved by alloying like with MgO or CdO. Adding Mg to ZnO increases the band gap whereas Cd decreases the band gap, similar to the effects of Al and In in GaN [4].

Most of the current ZnO application have made use of polycrystalline films that are grown by a variety of deposition techniques, mostly on glass substrates. For optimized growth and processing, environments (partial pressures and temperature) are necessary. Current techniques that allow for this level of control include Pulsed Laser deposition (PLD), Chemical Vapor Deposition (CVD), Metal-Organic CVD (MOCVD) and Molecular-beam Epitaxy (MBE), and to a lesser extent sputtering [5]. But for making low cost thin film solar cells, the sol–gel method has emerged as one of the most promising processing route as it is particularly efficient in producing thin, transparent, homogeneous, multi component oxide films of many compositions on various substrates and it allows the tuning of the refractive index and thickness of the film by varying synthesis parameters [6]. The objective of this work is to find out the change in band gap of ZnO because of doping. The process, which is free from the requirement to use expensive equipment, minimum wastage generation, environment friendly and low temperature deposition method, is used.

2. Experimental

2.1 Making Precursor Solution

Three basic methods were adopted to make precursor solutions. In method-1, Zn(Ac)2.2H2O in Isopropanol, for Al doping Aluminum nitrate nona hydrate, was added. For increasing solubility of Isopropanol, TEA (Triethanolamine) was added at molar ratio of 1.5:1 with Zinc acetate dihydrate. After that the solution is stirred with magnetic stirrer at 60°C by using hot plate for 2 hours. Then the solution was not aged before thin film making process. For 1.17% Al-2% Ca-doped ZnO & for 1.17% Al-4% Ca-doped ZnO this procedure was not continued because Isopropanol has boiling point 82.6°C so isopropanol was boiling out from reaction place which was hindering the process of making thin films by increasing solutions viscosity because of lack of solvent.

In method-2, Zn(Ac)2.2H2O was mixed with 20% (v/v) Isopropanol to make 0.5M solution. In that, for Al doping Aluminum nitrate nona hydrate was added. For Ca doping Calcium chloride dihydrate was used. They were added as they were calculated. After mixing for some time TEA was added at molar ratio of 1.5:1 with Zinc acetate dihydrate. After that the solution is stirred with magnetic stirrer at 60°C by using hot plate for 2 hours. After that the Solution was aged for 0-24 hours before thin film making process.

In method-3 (Reflux method), Isopropanol was boiling out from reaction place which was hindering the process of making thin films by increasing solutions viscosity because of lack of solvent. So reflux method was applied to the boiled Isopropanol back to the reaction place to complete the thin film making process. Zn(Ac)2.2H2O was mixed with 20% (v/v) Isopropanol to make 0.5M solution. After that for Al doping Aluminum nitrate nona hydrate was added. After adding TEA at molar ratio of 1.5:1 with Zinc acetate dihydrate, the mixture was taken into round bottom flask. It was stirred with magnetic stirrer at 60°C by using hot plate for 2 hours. Then the Solution was aged for 3 days before thin film making process.

2.2 Spin Coating Process

Precursor Solution was used to make thin films. The coating was done by dynamic spin coating process. Each solution was dispersed onto the substrate surface, which was spinning at a 1300 rpm. The process
continued for 20 seconds. After that the film was dried at 200°C for 3-5 minutes. This whole process (from spin coating to drying) was continued for 2-6 times for making multiple layered thin film.

2.3 Annealing Process
After completing the whole thin film making process each films were annealed at 520°C. The heating rate was 10°C/min and the holding time was 1 hour. Annealing was done to evaporate the impurity and lowering the defects from films.

3. Results and discussion

3.1 Scanning Electron Microscopy (SEM)
Figure 1, shows non uniform nature of the thin film. This might cause from change in viscosity because of still evaporating isopropanol. This hinders the spin coating process. The micrograph could not be taken properly because of reflection from glass slides. In figure 2, homogeneous and uniform film is found. The
film is also defect free for one time coating. In figure 3, uniform films were found but there were some nano level defects found on the films much likely pores. In figure 4, shows cracks due to solidification shrinkage in film and nano level precipitation. In figure 5, shows some non-uniformity in film which can cause from any fault in spin coating.

3.2 X-Ray Diffractometry (XRD)

3.2.1 Phase identification. For Figure 6, the peak is at the position $\theta = 36.2^0$ which corresponds to the crystal plane (002). The standard position should be $36.06^0$. This slight deviation from standard position could be because of residual stress. Plane (002) indicated that prevailing direction of orientation of the AZO film growth, a preferential orientation of c-axis is perpendicular to the substrate [7]. No XRD peaks due to Al or $\text{Al}_2\text{O}_3$ phase could be observed, since Al had been doped [8]. The d-spacing is 2.474 $\text{Å}^0$.

![Figure 6: XRD analysis of AZO film (Coated 4 time) from method 1](image)

![Figure 7: XRD Analysis of 1.17% Al - 2% Ca doped ZnO film](image)

![Figure 8: XRD Analysis of 1.17% Al - 4% Ca doped ZnO film](image)

For Figure 7, film the XRD spectra did not show any specific peak. The reason could be having precipitation and not having continuous film from Figure 4.8. After observing closely weak peaks were found at the position $\theta = 31.5^0$, 34.3$^0$ and 36.1$^0$ which corresponds to planes (100), (002) and (101) respectively. These are the planes of ZnO. So, doping of Ca$^{2+}$ shows no additional peaks, which confirms no additional impurity phase formation [9].

For Figure 8, the peaks are found at $\theta = 31.8^0$, 34.3$^0$, 36.2$^0$, 47.5$^0$, 56.7$^0$, 62.9$^0$, 67.3$^0$ and 68.9$^0$ which corresponds to the planes ZnO: (100), (002), (101), (102), (110), (103), (112) and (201) respectively. Of them three peaks are pronounced. They are originated from (100), (101) and (110) planes. Other peaks are weaker. No secondary additional phase was detected which proves the importance of the used process [10]. The d-spacing is for strong peaks which are 2.81 $\text{Å}^0$, 2.47 $\text{Å}^0$, and 1.62 $\text{Å}^0$ for (100), (101) and (110) planes respectively.

3.2.2 Grain size measurement. If crystallites were in the form of elongated hexagonal cylinders, the average grain size can be calculated using the Debye-Sherrer's equation [10].
\[ G = \frac{0.9 \lambda}{B \cos \theta_b} \]  

(1)

Where \( \lambda \) is the X-ray wavelength (1.54060 \( \text{Å} \)), \( \theta_b \) is the maximum of the Bragg diffraction peak (in radians) and \( B \) is the line width at half maximum. From Figure 9, it is evident that, increased amount of doping has increased the grain size that consists of the film.

### Table 1: Grain sizes according to planes

| Composition                   | Strong Peaks at planes | Grain Size, nm | Average Grain Size |
|-------------------------------|------------------------|----------------|-------------------|
| AZO (4 times Coating)         | (002)                  | 0.25           | 0.25              |
|                               | (100)                  | 0.305          |                   |
| 1.17% Al - 4% Ca doped ZnO   | (01)                   | 0.308          | 0.316             |
|                               | (110)                  | 0.334          |                   |

**Figure 9:** Comparison between average grain sizes

### 3.3 Ultraviolet-Visible Spectrometer

#### 3.3.1 Absorbance. From absorbance spectra, pattern of spectra are same for all compositions. AZO film from method-1 shows the edge of absorbance is between 312-385 nm. The maximum absorbance is 0.064. For AZO films from method-3 (Reflux method) edge of absorbance is between 312-394nm. The maximum absorbance is 0.303. For 1.17% Al - 2% Ca doped ZnO film edge of absorbance is between 314-395nm.

**Figure 10:** Absorbance Spectra for samples

But the increasing slope is between 314-360nm. The maximum absorbance is 0.3. For 1.17% Al - 4% Ca doped ZnO film, edge of absorbance is between 312-393nmThe maximum absorbance is 0.34. The
3.3.2 Transmittance. The optical transmittance is an important optical parameter for transparent oxides. The average optical transmittance for thin films for AZO film of method 1, AZO film of Method 2(R), 1.17% Al - 2% Ca doped ZnO film and 1.17% Al - 4% Ca doped ZnO film are 97.3%, 94.04%, 88.94% and 86.19% respectively. Transmission is decreased with increased doping. All films have an average optical transparency over 86% in the visible range. This implies that the AZO thin films transparent are largely preserved.

3.3.3 Optical band gap. From the optical absorption spectra, the band-gap $E_g$ of four samples could be calculated using the formula:

$$(\alpha h\theta) = A(h\theta-E_g)^{1/2}$$  \hspace{1cm} (2)

Where $A$ is a constant, $\alpha$ is absorption coefficient and $h\theta$ is the photon energy. The absorption coefficient can be calculated from this formula:

$$\alpha = 2.303 \frac{A}{d}$$  \hspace{1cm} (3)

Where $A$ is Absorbance and $d$ is thickness of coating. Band gaps measured from graph $(\alpha h\theta)^2$ vs Binding energy,$(h\theta)$. From Figure 13, it is observed that 4% Ca doping in addition to 1.17% Al decreases the band gap. But AZO film from method 1 shows unusual behavior having lowest band gap.

![Transmittance spectra for samples](image)

**Figure 11:** Transmittance spectra for samples

![Band gap](image)

**Figure 12:** Band gap: (a) AZO film from method 1, (b) AZO film from method 3, (c) 1.17% Al - 2% Ca doped ZnO film and (d) 1.17% Al - 4% Ca doped ZnO film
4. Conclusion
In this work 1.17% Al-doped ZnO (AZO), 1.17% Al-2% Ca-doped ZnO and 1.17% Al-4% Ca-doped ZnO thin films were fabricated by using low cost Sol-Gel spin coating technique. The effect of Al and Al-Ca doping (with different concentration of Ca) in ZnO is observed. The visual inspection proved that Al-doped ZnO have higher quality of films than Ca doped ZnO. The reflux method also provided better films than normal method for producing AZO. XRD analysis showed the bigger grains for with increasing doping. The SEM result showed defects in multiple layer thin films. The defects were not present in the case of single layered thin film. The band gap also decreased with increasing doping. The increased doping element was Ca. The films have optical transmittance more than 86%. So these conditions of fabrication can be used for making transparent thin films on glass substrate for solar cell application.

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