INVESTIGATION ON THE DOPING EFFECT OF ZINC (Zn) DOPED IRON OXIDE THIN FILMS

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Abstract-This Zn doped Fe3O4 was prepared by hydrolyzing FeCl3•6H2O on glass substrate using Vacuum spin coater. Naturally Fe3O4 is n-type. To make p-type Fe3O4 solution, Zn2+ dopant from Zinc acetate salt [Zn(O2CCH3)2] used into the solution. Carrier concentration of Zn doped Fe3O4 was investigated by Hall measurement and also type of Fe3O4 were determined. Zn-doped Fe3O4 was found as p-type semiconductor. The films are annealed at 450°C and 550°C temperatures. Carrier concentration of the films are varied from 2.90×1013 Ns to 2.31×1014 Ns in different molar concentration, different layer with different temperature. The surface morphology of the annealed film on glass substrate is measured by Atomic Force Microscopy (AFM). The average roughness of the annealed surface was varied from 60nm to 98nm and the thickness was 160nm to 540nm.

Keywords: Thin films, Zn doped Fe3O4, Carrier concentration, AFM

1. INTRODUCTION

“Energy Crisis” became a word we hear on daily life. The price of fossil fuel has gone up so high in the last decade that the development of poor countries has become at risk. To overcome this apparent and predictable crisis, there are intense researches on alternative energies. Therefore, naturally harvested energies are the preferred forms such as solar, wind and geothermal energies. Solar energy is a good solution for these energy crises [1]. One of the fundamental aim of this research to make p-type Zn doped Iron(III) Oxide thin films and analyzing their properties, which can be used in future as a solar cell or homojunction material for any kinds of semiconductor device. The present communication describes the PEC study on Zn-doped α-Fe3O4 thin films prepared by spray pyrolytic method [2] [3] at different doping concentrations (0.1, 0.005 and 0.0025 at %).

2. SOLUTION PREPARATION FOR DOPING

0.11 M FeCl2 Solution Preparation:

<table>
<thead>
<tr>
<th>Ethanol</th>
<th>100 ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl2</td>
<td>1.3943 g</td>
</tr>
</tbody>
</table>

0.01 M (CH3COO)2Zn.2H2O (Zinc acetate) Solution Preparation:

<table>
<thead>
<tr>
<th>Ethanol</th>
<th>100 ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH3COO)2Zn.2H2O</td>
<td>219.527 milligram</td>
</tr>
</tbody>
</table>

Then the two solutions were mixed and stirred at 10 minutes. After that Zn doped Iron(III) oxide solution had prepared. Like this way, 0.005M and 0.0025M Zn doped Iron (III) oxide solution had prepared.

3. DEPOSITION METHODORD

For thin film deposition there are various kinds of deposition methods like [4], [5]
- Chemical vapor deposition
- Spin coating
- Thermal evaporation
- Dip coating
- Spray pyrolysisetc

Among these methods spin coating is one of the easiest techniques for preparing thin films [6]. In this research Zn doped Iron(III) oxide thin films with different doping concentrations were prepared by spin coating method and doping effects of these films after annealing were also studied. After synthesis Zn doped Iron(III) oxide solution is taken by micropipette and drop cast on glass surface then spin coated. For making thin layer on glass surface the rotational speed and time is given below:

<table>
<thead>
<tr>
<th>SP1</th>
<th>T1</th>
<th>SP2</th>
<th>T2</th>
</tr>
</thead>
<tbody>
<tr>
<td>500rpm</td>
<td>3s</td>
<td>7000 rpm</td>
<td>30s</td>
</tr>
</tbody>
</table>

3.1 ANNEALING

The After the deposition, the samples were annealed in a thermal annealing furnace (Carbolite CWF-1200) in air. One of the set of Zn doped Fe2O3 samples were annealed first at 4500C temperature for 4 hours and another set samples were annealed at 5500C temperature for 4 hours. After annealing they were left to be cooled naturally to the room temperature before being used.
3.2 Studies with Atomic Force Microscope (AFM)

Atomic force microscope (AFM) [7] of model (XE 70) park system was used to study the roughness (nm) [8] of the film surface of different layer at different temperature.

4. RESULT

The result of this research can be taken in several ways. Here this research result is taken on the basis of carrier type & concentration measurement and surface morphology measurement by using AFM.

4.1 Carrier type & concentration measurement

The carrier type and concentration of the film has been determined by Hall Effect measurement [9], [10]. The carrier concentration of differ layer at temperature 450˚C & 550˚C of Zn doped α-Fe$_2$O$_3$ are shown in following table.

Table 1: Carrier concentration (Ns) of Zn doped α-Fe$_2$O$_3$ at temperature 450˚C.

<table>
<thead>
<tr>
<th>No of Layer</th>
<th>Ns at 0.01M</th>
<th>Ns at 0.005M</th>
<th>Ns at 0.0025M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer 1</td>
<td>2.90×10$^{13}$</td>
<td>3.88×10$^{13}$</td>
<td>4.10×10$^{13}$</td>
</tr>
<tr>
<td>Layer 3</td>
<td>3.15×10$^{13}$</td>
<td>5.04×10$^{13}$</td>
<td>5.17×10$^{13}$</td>
</tr>
<tr>
<td>Layer 5</td>
<td>1.01×10$^{14}$</td>
<td>2.97×10$^{14}$</td>
<td>1.22×10$^{14}$</td>
</tr>
</tbody>
</table>

Table 2: Carrier concentration (Ns) of Zn doped α-Fe$_2$O$_3$ at temperature 550˚C.

<table>
<thead>
<tr>
<th>No of Layer</th>
<th>Ns at 0.01M</th>
<th>Ns at 0.005M</th>
<th>Ns at 0.0025M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer 1</td>
<td>1.08×10$^{14}$</td>
<td>1.39×10$^{14}$</td>
<td>1.38×10$^{14}$</td>
</tr>
<tr>
<td>Layer 3</td>
<td>1.51×10$^{14}$</td>
<td>1.70×10$^{14}$</td>
<td>1.67×10$^{14}$</td>
</tr>
<tr>
<td>Layer 5</td>
<td>1.72×10$^{14}$</td>
<td>2.31×10$^{14}$</td>
<td>1.7×10$^{14}$</td>
</tr>
</tbody>
</table>

Naturally α-Iron(III) oxide is an n-type semiconductor. But when Zn dopant was applied on α-Fe$_2$O$_3$, it became p-type semiconductor. P-type charier concentration has been founded from the entire sample in this experiment.

Variation of carrier concentration (Ns) of Zn doped Iron(III) oxide with the variation of different layer, molar concentration and different temperature are shown in Fig.1 & Fig.2.

Fig. 2: variation of Carrier concentration (Ns) of different layer and different molar concentration of the thin films at temperature 450˚C.

4.1 Surface morphology measurement using AFM

The When the annealing temperature was increased the roughness of the thin film surface was decreased. Variation of average value of Roughness of Zn doped α-Fe$_2$O$_3$ at 450˚C, 550˚C & AFM images are following:

Fig.3: Average value of Roughness (nm) of the film surface of different layer at different temperature of the thin film

(a)

(b)

Fig. 4: Surface morphology of Zn doped α-Fe$_2$O$_3$ Layer 5 at 450˚C near to the Edge (a) & middle of the surface (b)
5. CONCLUSION
The effect of different parameters (temperature, thickness and molar concentration) on Carrier concentration of spin-coated thin film of Zn doped Iron(III) oxide on glass substrate has been investigated in this research. Carrier concentrations of the films are varied from $2.90 \times 10^{13}$ Ns to $2.31 \times 10^{14}$ Ns. It was observed that the Carrier concentration of annealed films increases with temperature. The increase in Carrier concentration was not linear. Surface of Zn:Fe$_2$O$_3$ was investigated with atomic force microscope (AFM) to see the effect of annealing on surface roughness. It was observed that the surface roughness was reduced after increasing the annealing temperature. This was due to the fact that increasing of annealing temperature reduces various types of defects like voids, crystal defects [11] and dislocation density [12]. So the film become smoother this was expected for thin film.

7. REFERENCES
[7] Jeffrey L. Hutter and John Bechhoefer “Calibration of atomic - force microscope tips”. Department of Physics, Simon Fraser University, Burnaby, British Columbia, V5A IS6, Canada