# Fabrication and Characterization of n-$Zn_{1-x}Al_xO$ /p-Si Heterojunction Nanocrystalline Thin Films

Ankit Gupta, Namrata Hada, Praveen K. Jain
Department of Electronics and Communication Engineering
Swami Keshvanand Institute of Technology Management & Gramothan, Jaipur
***Email- ankit6685@gmail.com***

Received 27 July 2015, received in revised form 24 August 2015, accepted 26 August 2015

*Abstract:* **ZnO (II-VI) semiconductor is currently in major use and is in rapid expansion mode for the preparation of thin film and other solar cell applications due to its wide availability in market, cheaper than other materials required for the same applications, other physical properties like transparency, piezoelectric (generates voltage on the application of pressure) ,high electron mobility, high thermal conductivity and pyroelectric (generates voltage on the application of heat). The main aim of the presented work is to synthesize a high quality nanocrystalline thin films with pure and Al doped ZnO ($Zn_{1-x}Al_xO$; x=0.0, 0.02, 0.05, 0.1) on the p type silicon (100) substrate at room temperature. The technique used for the deposition of thin films is Electron beam physical vapor deposition. Investigation of structural and optical properties has been done by using X-ray diffraction (XRD), Atomic Force Microscopy (AFM) and UV-VIS-NIR Spectrometer.**

## 1. INTRODUCTION

Zinc oxide (ZnO) thin films have been used as transparent conducting films for various opto electronic devices such as solar cells, liquid crystal display and heat mirrors [1-2]. However, there are limitations in the application of ZnO to the integrated optical devices because bandgap of ZnO being not wide enough. $Zn_{1-x}Al_xO$ thin films have emerged as one of the important compound semiconductor due to high exciton binding energy and its tunable band gap [3-6]. ZnO thin films are used in doped and undoped form in this work. ZnO has easy availability in nature and are cost effective. This unique property attracted our attention while choosing the raw material. This ZnO powder was doped with $Al_2O_3$ by varying the concentration of $Al_2O_3$ in the powder. ZnO is of "Fishe Scientific" make where as $Al_2O_3$ is of "CDH –Central Drug House".

## 2. EXPERIMENTAL DETAILS

Thin Film of aluminum doped zinc oxide was deposited on Silicon (Si) wafer through electron beam deposition. ZnO and $Al_2O_3$ were taken in proportion to their molecular weight for the required doping. Resultant powder is then obtained after grinding both the chemicals with the help of Mortar and Pestle for about 10 hours. Before using the apparatus for grinding, it was properly washed with acetone and allowed to dry at STP (Standard Temperature and Pressure). After proper grinding, samples were sintered at 500 degree centigrade for 6 hrs in the presence of oxygen gas. In this way four samples ZnO, $Zn_{0.98}Al_{0.02}O$, $Zn_{0.95}Al_{0.05}O$ and $Zn_{0.9}Al_{0.1}O$ were prepared for the deposition on Si wafer. Cleaning of silicon substrate was done by a procedure which started with the ultrasonic cleaning of the substrate with acetone which was further followed by rinsing of substrate in DI water. Then the substrate was boiled in trichloroethylene (TCE) for 5 minutes at a temperature of 80ºC to 90ºC. Later it was cleaned by using methanol and was kept in 1:10 HF dip for 2 to 3 minutes. The substrate was again rinsed in DI water and blower was used for drying. The parameters used for EBPVD are shown in Table 1

| Parameter | Value |
|---|---|
| Pressure | $2.3\times10^{-5}$ mbar |
| Thickness of deposition | 60 nm |
| Rate of deposition | 0.7 Å/sec |
| Voltage | 5kV |
| Current | 13 mA |
| Temperature | Room temperature |

## 3. RESULTS AND DISCUSSION

### *3.1 Structural Properties*

The fig.1 the shows the XRD of the $Zn_{1-x}Al_xO$ with x = 0.00, 0.02, 0.05 and 0.1. XRD was performed with $CuK_\alpha$ as radiation source with a wave length of 1.54 Å at room temperature in the range of 15 – 75°. It can be seen from the graph that up to 5%, the mixture contains only a 002 peak denoting a single phase and hexagonal wurtzite structure of ZnO. However with the increase in concentration of trivalent aluminum, the 002 decreases. its peak value and the shoot shifts towards the lower

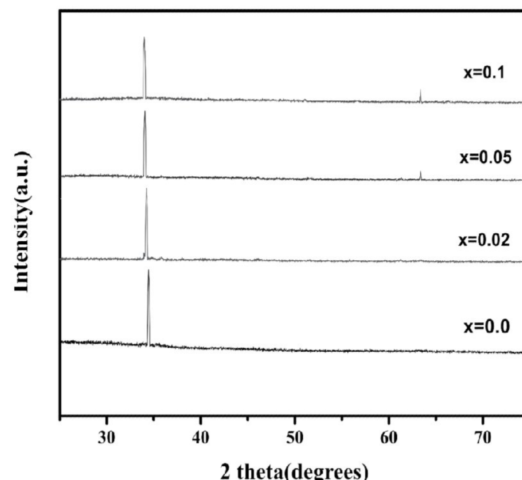



Fig.1 XRD pattern of the $Zn_{1-x}Al_xO$(x = 0.00, 0.02, 0.05, 0.1) thin films

angle (2 theta). The appearance of (0 0 2) peak with maximum intensity in undoped and Al-doped ZnO films indicates that the preferred orientation of the thin films is along the *c*-axis. Also with increase in aluminum concentration, the crystallinity of the structure decreases (Fig. 2) which may be due to the formation of stress induced by ion size difference between zinc and aluminum and the segregation of aluminum in grain boundaries for high doping concentrations. Also with increase in the value of x, decrease of film crystallinity reflected on lower peak intensity and crude peak broadening The peak of aluminum can be observed at x = 0.05 indicating that the segregation of the aluminum has started in the structure.

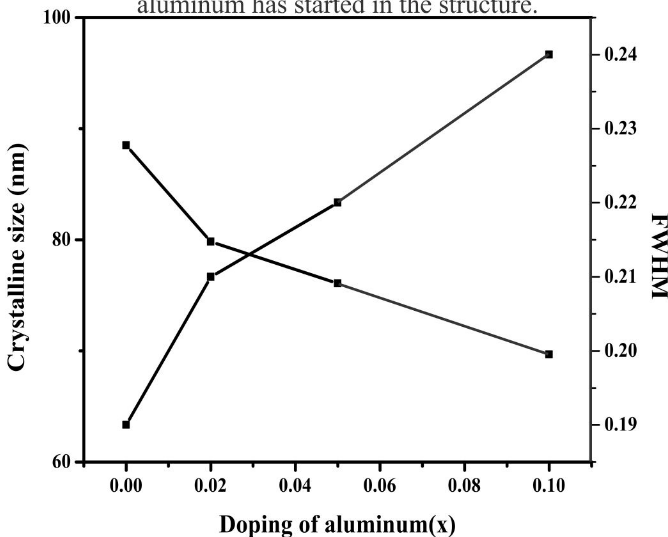



Fig.2 Effect on crystalline size and FWHM w.r.t. doping

The quality of the film is determined by many parameters such as strain, stress, crystallite size, etc. The crystallite size (t) has been calculated for various doping concentrations have been calculated by the Debye Scherrer's formulae.

$$t = \frac{0.91\lambda}{\beta \cos\theta}$$

where,

$\beta$ = FWHM (Full Width Half Maximum)

$\lambda$ = Wavelength of the source used (1.54 Å)

$\theta$ = Value of angle at which peak occurs (in degrees)

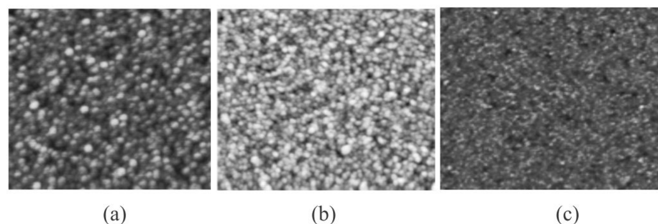



Fig. 3 AFM images of Zn1-xAlxO thin films for various Al concentrations (a) 0% (b) 2% (c) 5%

Fig. 3 revealed the morphology of aluminum doped zinc oxide. The uniform granular arrangement can be seen. With the increase in doping concentration, the grain size also decreases as seen from atomic force microscope. The grain size of pure ZnO is larger than doped ZnO.

### *3.2 OPTICAL PROPERTIES*

Fig.4 shows optical absorbance spectra at room temperature for undoped ZnO and ZAO films. All films showed a good absorbance when the incident wavelength ($\lambda$) < 380 nm. From fig.5 for 0%, 2%, 5% and 10% doping percentage of aluminum, the band gap ($E_g$) was found to be 3.24 eV, 3.14 eV, 2.95 eV and 2.87 eV respectively. The value of band gap is estimated from fundamental absorption edge of the films.

Band gap were found using the Tauc's equation:

$$(\alpha h\nu) = A(h\nu - Eg)^n$$

where,

A is the constant,

Eg is the energy gap,

$\nu$ is the frequency of the incident radiation,

$\alpha$ is the absorption coefficient,

h is Planck's constant and

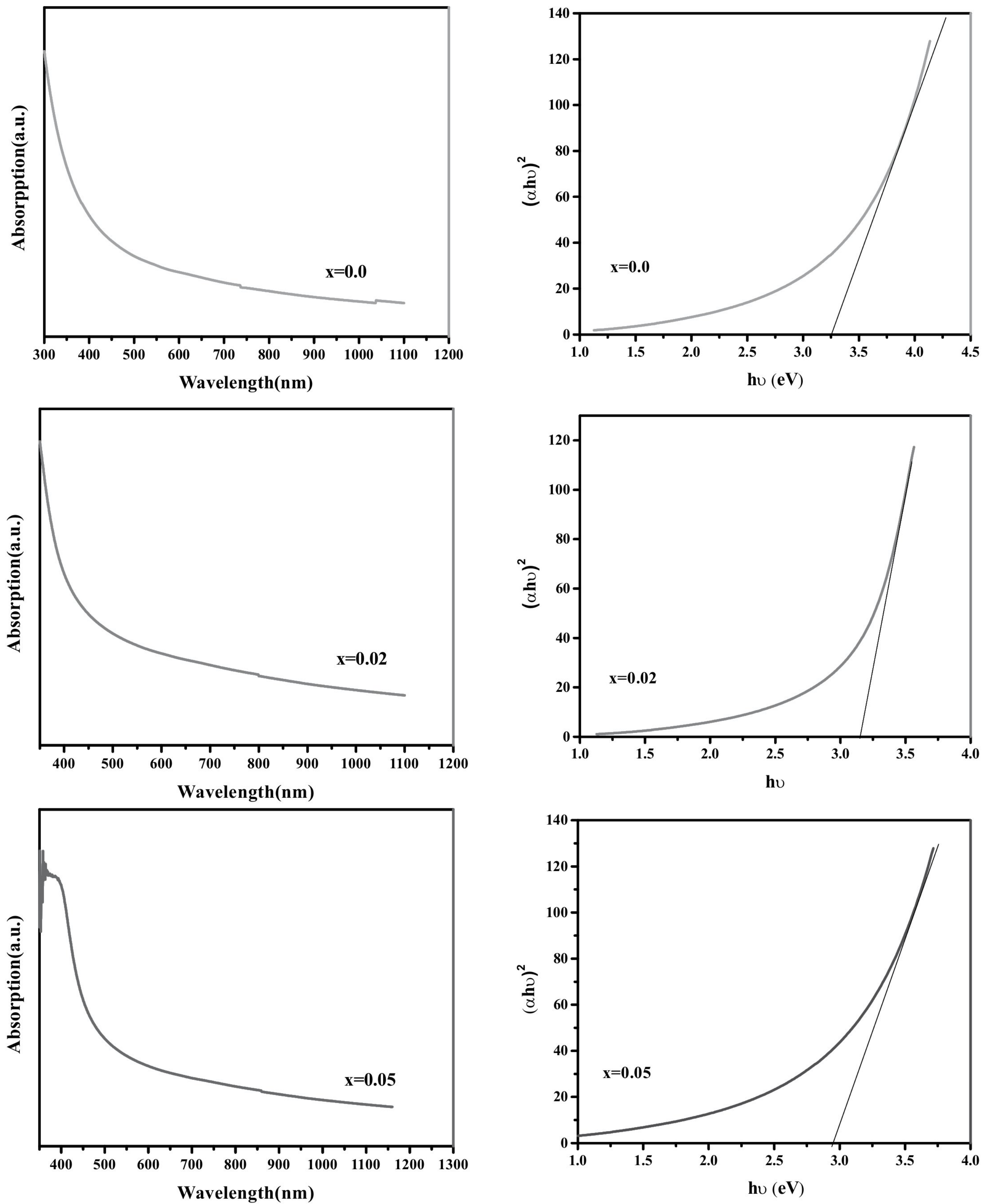
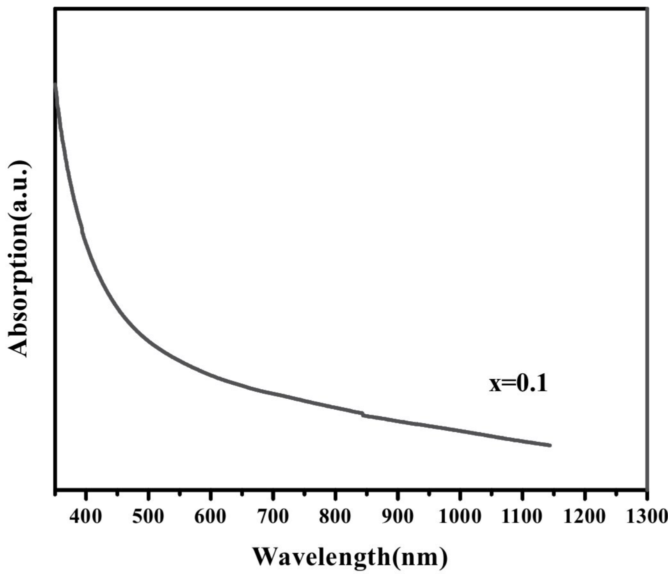



Fig. 4 Absorbance spectra of $Zn_{1-x}Al_xO$ with various concentrations of Al



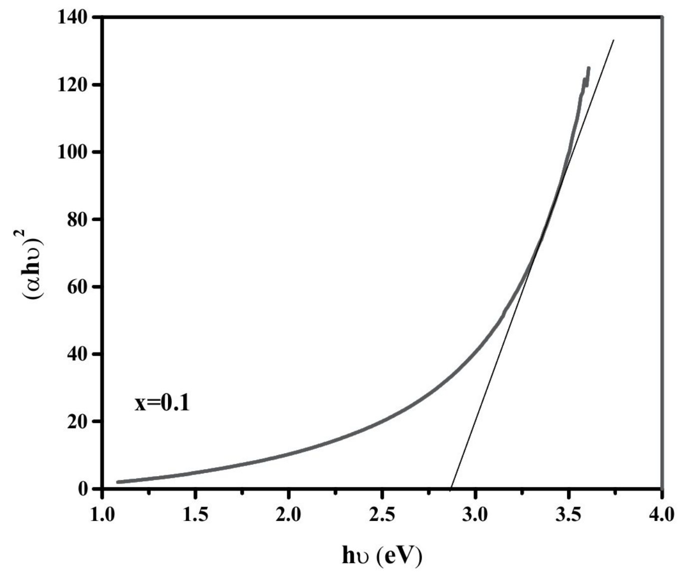




Fig.5 $(\alpha h\upsilon)^2$ vs. hυ plots of $Zn_{1-x}Al_xO$ films of various Al content

In our case value of "n" = ½ (direct allowed transitions).The presence of a single slope in the plot suggests that the films have direct and allowed transition. The band gap energy is obtained by extrapolating the straight line portion of the plot to zero absorption coefficient. We have found no net increase of the bandgap with Al concentration due to the Burstein–Moss effect in the prepared samples. The decrease in band gap can also be explained from the fact that as the concentration of doping material increases, the voids present in the structure are filled up and reduce the scattering (resulting in increase in absorbance).

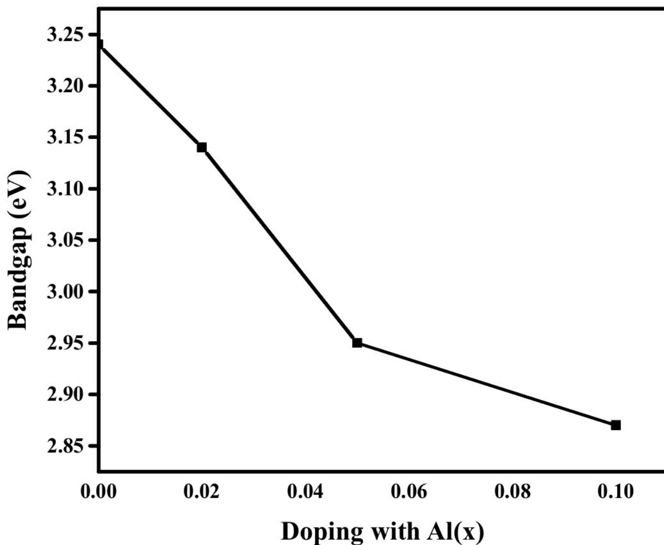



Fig. 6 Variation of Band gap with Al content

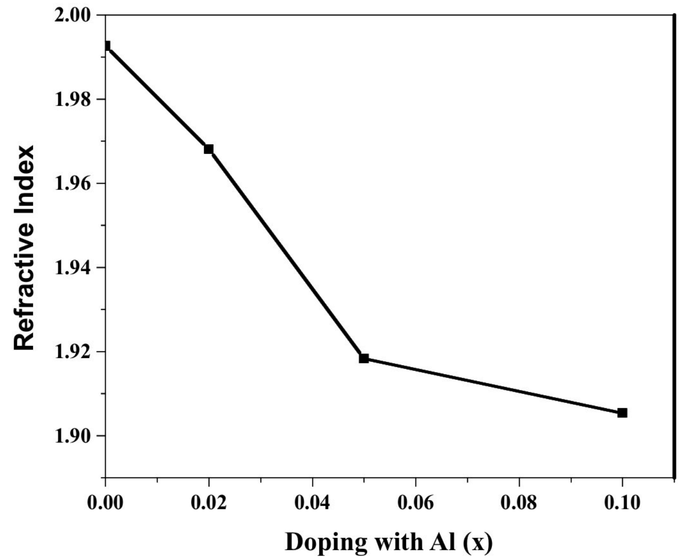



Fig. 7 Variation of Refractive Index with Al content

The refractive index (*n*) was estimated by using following expression:

$$n = \left[N + (N^2 - {n_0}^2{n_1}^2)^{1/2}\right]^{1/2},$$

where

$$N = \frac{{n_0}^2+{n_1}^2}{2} + 2n_0n_1\frac{T_{\max} - T_{min}}{T_{max}\,T_{min}}$$

and $n_0(1)$ and $n_1(3.42$ in our case) are the refractive index of air and substrate, respectively. $T_{max}$ and $T_{min}$ are maximum

and minimum transmittance values at the same wavelength. Figure 7 represents the derived values of the refractive index "n" as a function of Al content. Decrease in refractive index was found with the increase in doping concentration.

## 4. CONCLUSION

We have deposited high quality $Zn_{1-x}Al_xO$ (x=0.0, 0.02, 0.05, 0.1) thin films on n type silicon substrate by using Electron Beam Physical Vapor Deposition method. XRD patterns show the highly c-axis oriented hexagonal wurtzite structures of the thin films. It has been observed that as the doping of Al increases, the crystalline size decreased and FWHM increases substantially. AFM patterns revealed the decrease in grain size with an increase in the Al content. Continuous decrease in optical band gap i.e. from 3.24 eV to 2.87 eV is also observed with the increase in Al concentration due to absence of the Burstein–Moss effect. This reduction in band gap can also be understood from the fact that with the increase in doping concentration, voids are filled.

## REFERENCES

[1] Y.M. Hu, C.W. Lin, J.C.A. Huang, "Dependences of the Al thickness and annealing temperature on the structural, optical and electrical properties in ZnO/Al multilayers", *JOURNAL of Thin Solid Films*, vol-497, pp. 130 – 134, 2006

[2] Ramanathan S., "Thin film metal-oxides: fundamentals and applications in electronics and energy", *ISBN 1489984933*, Springer, 2014

[3] R. Al Asmar, J.P. Atanas, M. Ajaka, Y. Zaatar, G. Ferblantier, J.L. Sauvajol, J. Jabbour, S. Juillaget, A. Foucaran, "Characterization and Raman investigations on high-quality ZnO thin films fabricated by reactive electron beam evaporation technique", *JOURNAL of Crystal Growth*, vol- 279, pp. 394–402, 2005

[4] J Arbiol, Q Xiong, "Semiconductor Nanowires: Materials, Synthesis, Characterization and Applications", *ISBN 1782422536,* Woodhead Publishing Series in Electronic and Optical Materials, 2015

[5] S. Calnan, J. Hupkes, B. Rech, H. Siekmann, A.N. Tiwari, "High deposition rate aluminium-doped zinc oxide films with highly efficientlight trapping for silicon thin film solar cells", *JOURNAL of Thin Solid Films*, vol- 516, pp. 1242–1248, 2008

[6] K.L.Chopra, S.R.Das, "Thin Film Solar Cells", *ISBN 0306411415*, Springer, 1983.