Investigation of Structural and Optical Properties of $Zn_{1-x}Mg_xO$ thin films

Namrata Hada, Ankit Gupta, Praveen K. Jain
Department of Electronics and Communication Engineering
Swami Keshvanand Institute of Technology, Management & Gramothan, Jaipur
Email- namratahada91@gmail.com
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Abstract: **n-$Zn_{1-x}Mg_xO$/p-Si heterojunctions were successfully fabricated at room temperature in a vacuum chamber via electron beam physical vapor deposition (EBPVD) of n-type $Zn_{1-x}Mg_xO$ on a chemically cleaned p-type Si substrate. The $Zn_{1-x}Mg_xO$ target was prepared by conventional solid state reaction method. In this paper, structural and optical properties of $Zn_{1-x}Mg_xO$ thin films have been studied. X-ray diffraction with CuK_α radiation source showed a single peak of hexagonal wurtzite structure without any phase segregation. The grain size of the deposited film reduced in the samples due to the difference in the ionic radii. Results revealed the relation of crystalline size and FWHM with the increase in Mg content. Bandgap and Refractive Index were calculated and their effect on the Mg concentration was also reported.**

Keywords: **Zinc Oxide, thin films, AFM, XRD, e-beam physical vapor deposition, optical properties, Magnesium Oxide.**

1. INTRODUCTION

Zinc oxide (ZnO) has received increasing attention due to its abundance in nature, unique properties and cost effectiveness. ZnO thin films have been used as transparent conducting films for various optoelectronic 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 band gap of ZnO being not wide enough. Ternary $Zn_{1-x}Mg_xO$ with wider band gap than ZnO (E_g = 3.37 eV) has received much attention due to its potential applications in ultraviolet optoelectronic devices [3-4].

$Zn_{1-x}Mg_xO$ thin films have emerged as one of the important compound semiconductor due to high exciton binding energy and its tunable band gap from 3.37 to 6.7 eV depending upon the Mg content (x = 0.0, 0.02, 0.05, 0.1). According to Schmidt–Grund's theory, the Mg content in $Zn_{1-x}Mg_xO$ is advantageous for excitonic light emitters [5]. A crucial step in designing modern optoelectronic devices is the realization of band gap engineering to create barrier layers and quantum wells in device heterostructures. It is known that $Zn_{1-x}Mg_xO$ is the solid solution consisting of ZnO and MgO. ZnO has wurtzite (a = 3.24 Å and c = 5.522 Å) crystalline structure, while MgO has NaCl-type cubic (a = 5.424 Å) structure with wide band gap. Due to structural dissimilarity between ZnO and MgO, $Zn_{1-x}Mg_xO$ alloys are of either hexagonal or cubic crystals.

Various physical vapor deposition techniques such as magnetron sputtering [6-7], laser molecular beam epitaxy (MBE) [8], pulsed laser deposition (PLD) [9-10] and e-beam physical vapor deposition (EBPVD) [11] have been used to deposit ZnO and $Zn_{1-x}Mg_xO$ thin films. In this work, optimal EBPVD conditions for the deposition of $Zn_{1-x}Mg_xO$ were identified. Multilayer deposition of oxide semiconductor thin films has attracted considerable and growing interest for functional device applications. In most of the cases these thin films showed enhanced or new physical properties, and sometimes combine the functional properties of two different materials.

2. EXPERIMENTAL DETAILS

The target material for EBPVD was prepared by conventional solid state reaction using 99.99% pure ZnO (Fishe Scientific) and MgO (CDH-Central Drug House) powder in appropriate molar ratio. The starting materials were ground for 24 h and then calcined at 400°C for 6 h. The calcined powder was reground for 6 h. The materials were pressurized by kBr press and pellets were formed. Cleaning of silicon substrate was done by a procedure which started with the ultrasonication 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 dried in an oven at 150°C for 10 minutes. This technique allowed the deposition of $Zn_{1-x}Mg_xO$ over cleaned silicon substrate. The deposition occurred at the pressure of 2.3×10^{-5} mbar at 5kV and 13mA at room temperature. Further, the phase and orientation of the as-grown thin films were characterized by using X-ray diffractometer (XRD). The surface topology and microstructure were examined by atomic force microscope (AFM) and SEM. .Absorption spectra have been taken using UV-VIS spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Structural Properties

Fig. 1 shows the XRD pattern of $Zn_{1-x}Mg_xO$ (x = 0.0, 0.02, 0.05, 0.1) at room temperature at an XRD range of 25º to 75º. The radiation source of CuK_α was used with 1.5407Å wavelength. A highly intense single peak of hexagonal wurtzite structure of ZnO was found with the absence of any Mg or MgO peak. This suggests the presence of only one phase or the films do not have any phase segregation

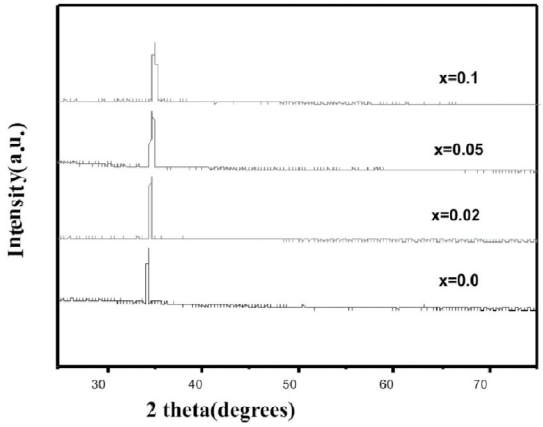


Fig. 1 XRD pattern of $Zn_{1-x}Mg_xO$ (x=0.0, 0.02, 0.05, 0.1) at room temperature

By observing the XRD data it was found that with the increase in the Mg content, the highest peak obtained at pure ZnO doped film shifted at higher angles as compared to the peak obtained at pure ZnO.

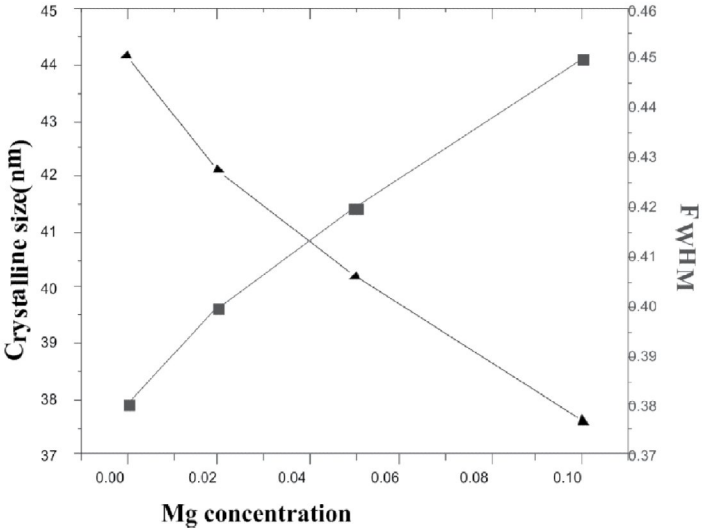


Fig. 2: Variation of crystalline size and FWHM parameter with Mg content

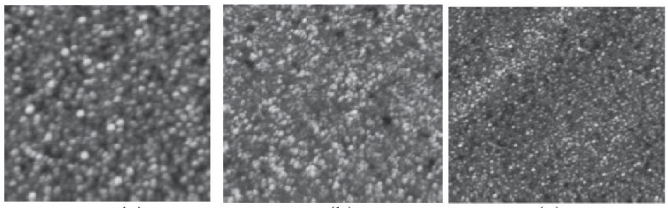
This shifting of angles was expected according to the Bragg's law as whenever the Mg2+ ions with a radius of 0.57Å replaces the Zn2+ ions which have a larger radius as compared to Mg2+, 0.60Å, the unit cell contracts. In the films of Zn1-xMgxO grain size is reduced when it is compared with the value of pure ZnO which is due to increase in the 2θ value when the FWHM value was simultaneously increased.

The crystallite size of these samples was calculated by using Scherrer's expression

$$t = \frac{0.91\lambda}{\beta \cos\theta} \quad (1)$$

Fig. 2 shows the effect of Mg content on crystalline size and FWHM. It was observed that crystalline size decreased while on the contrary FWHM increased with the increase in Mg concentration.

Fig. 3 revealed the morphology of Mg doped ZnO. 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.



(a) (b) (c)

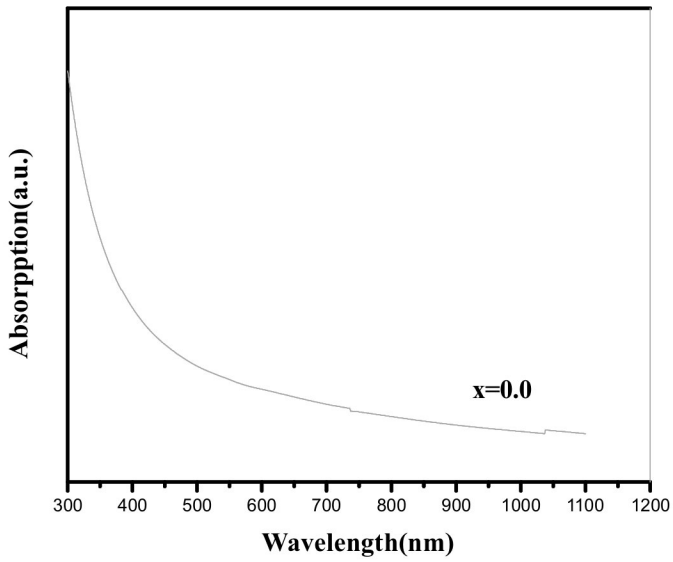
Fig. 3: AFM images of Zn1-xMgxO thin films for various Mg concentrations (a) 0% (b) 2% (c) 5%

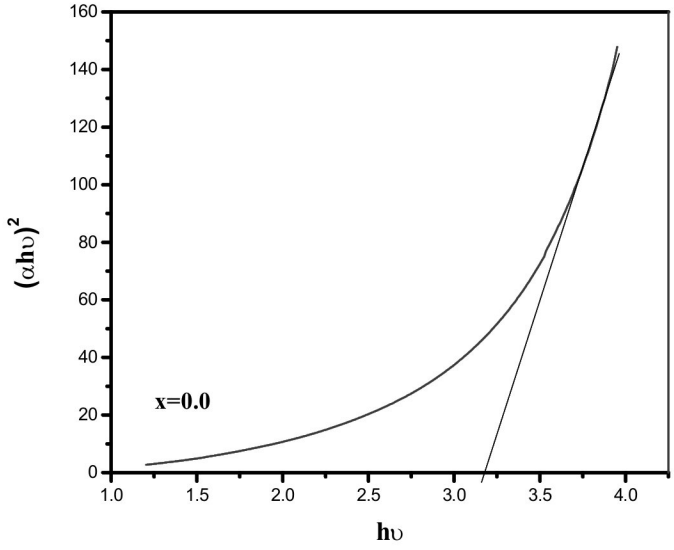
4. OPTICAL PROPERTIES

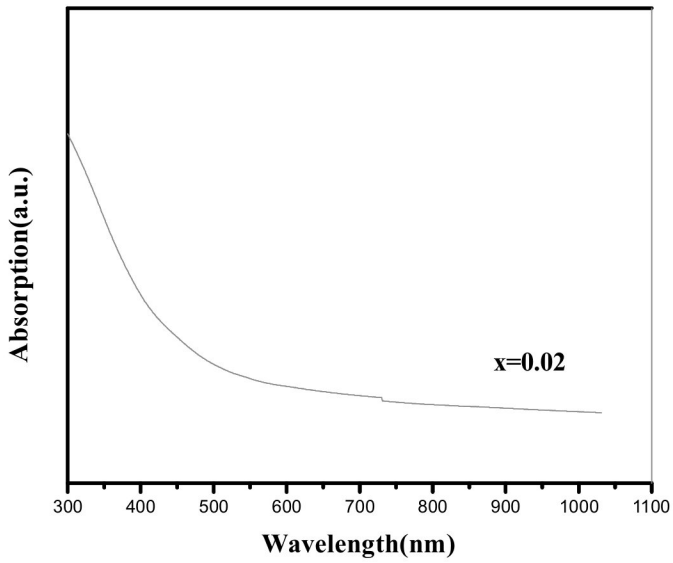
Fig. 4 shows optical absorbance spectra at room temperature for undoped ZnO and magnesium doped ZnO films. All films showed a good absorbance when the incident wavelength (λ) < 380 nm. For various doping concentrations of 0%, 2%, 5% 10% the band gap was found to be 3.24 eV, 3.2 eV, 3.98 eV, 3.89 eV respectively. Band gaps were calculated using the Tauc's equation:

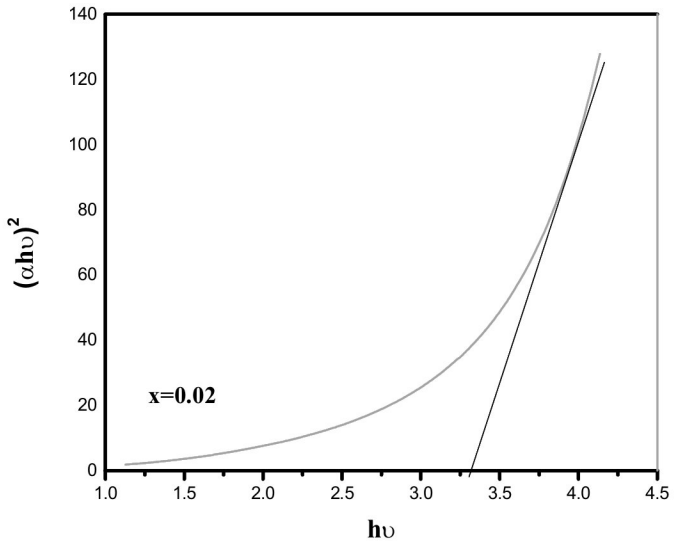
$$(\alpha h\nu) = A(h\nu - Eg)^n \quad (2)$$

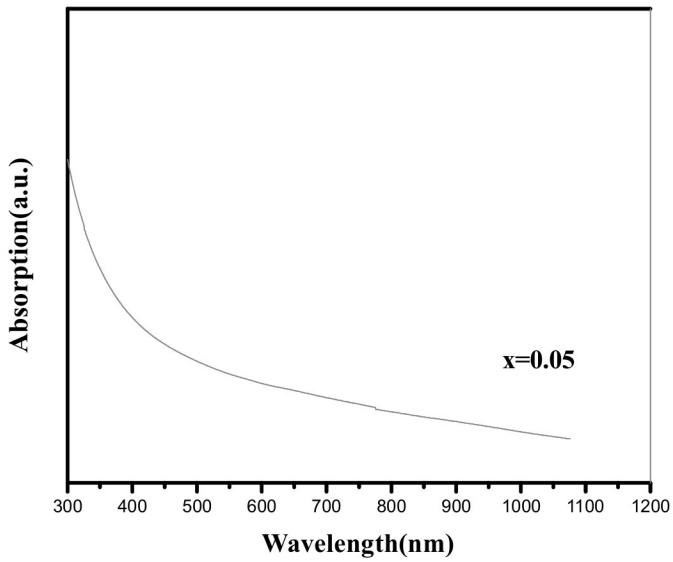
In our case value of n = ½. Band gap were calculated from the intercept of $(\alpha h\nu)^2$ v/s (hν) plot at α = 0 (fig. 5). From the graphs we found that there is increase in band gap as the doping concentration increases. This relation of band gap with Mg doping is shown in fig. 6. Substitution of Zn^{2+} by Mg^{2+} results in an increase in oxygen vacancies and electron concentration due to the electronegativity and ionic radius difference between Zn and Mg. This increase in carrier density results in the lifting of the Fermi-level towards the conduction.

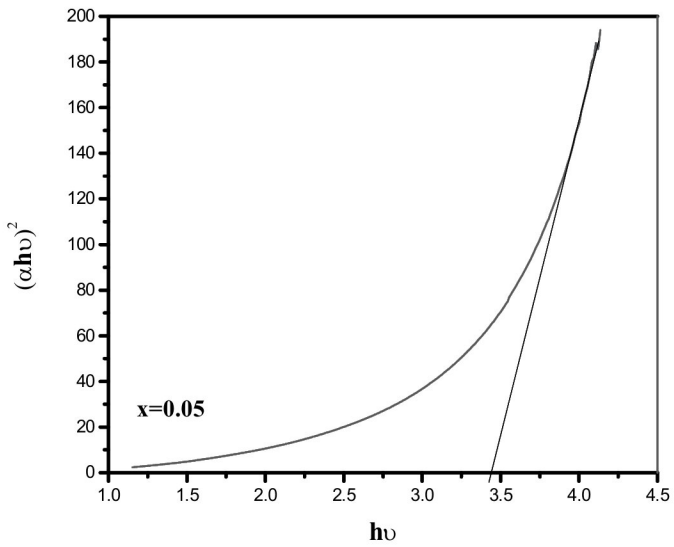

Absorption(a.u.)
x=0.0
300 400 500 600 700 800 900 1000 1100 1200
Wavelength(nm)


$(\alpha h\upsilon)^2$
x=0.0
0 20 40 60 80 100 120 140 160
1.0 1.5 2.0 2.5 3.0 3.5 4.0
$h\upsilon$


Absorption(a.u.)
x=0.02
300 400 500 600 700 800 900 1000 1100
Wavelength(nm)


$(\alpha h\upsilon)^2$
x=0.02
0 20 40 60 80 100 120 140
1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5
$h\upsilon$


Absorption(a.u.)
x=0.05
300 400 500 600 700 800 900 1000 1100 1200
Wavelength(nm)


$(\alpha h\upsilon)^2$
x=0.05
0 20 40 60 80 100 120 140 160 180 200
1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5
$h\upsilon$

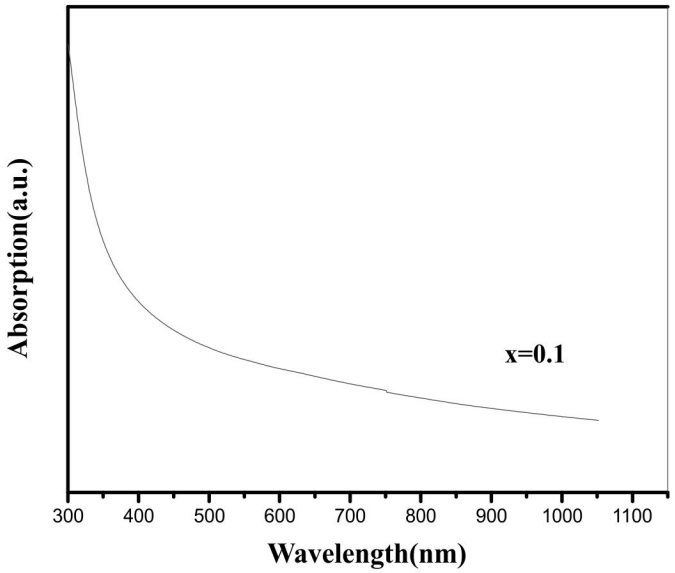


Fig. 4: Absorbance spectra of $Zn_{1-x}Mg_xO$ with various concentrations of Mg

band of the degenerate semiconductor and a consequent band gap widening. 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 $N = \frac{n_0{}^2 + n_1{}^2}{2} + 2n_0 n_1 \frac{T_{\max} - T_{min}}{T_{max} T_{min}}$

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. Fig. 7 represents the derived values of the refractive index "n" as a function of Mg content. Decrease in refractive index was found with the increase in doping concentration.

The refractive index was also calculated for the different values of Mg concentration and was plotted. Fig. 7 showed that the refractive index decreased with an increase in doping.

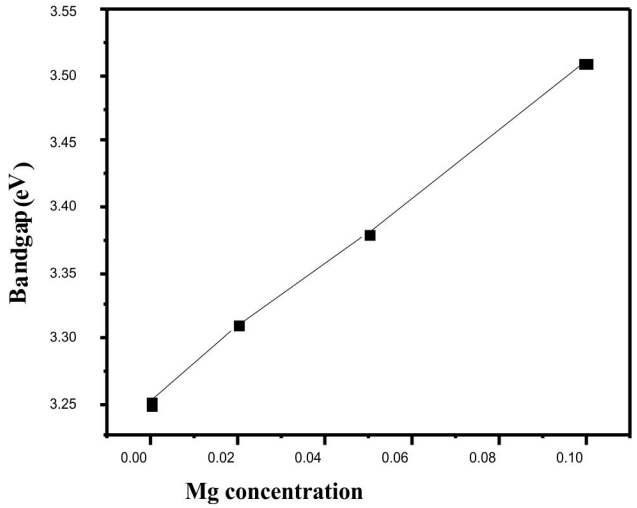


Fig. 6 Variation of Band gap with Mg content

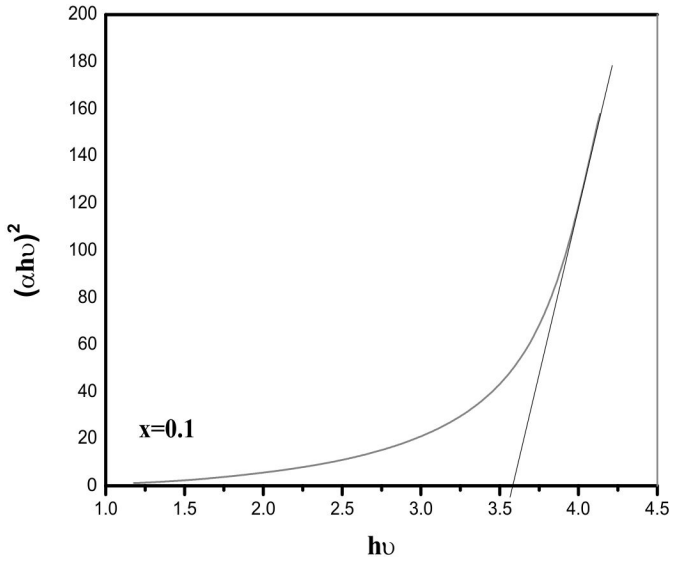


Fig.5 $(\alpha h\upsilon)^2$ vs. hυ plots of $Zn_{1-x}Mg_xO$ films of various Mg content

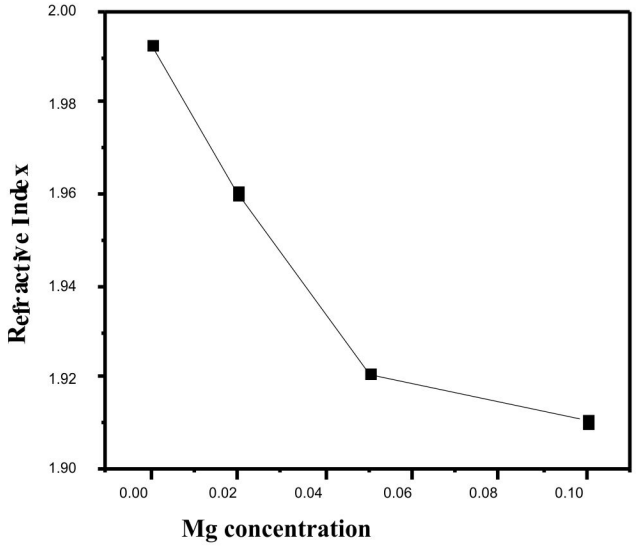


Fig. 7 Variation of Refractive Index with Mg content

5. CONCLUSION

Deposited $Zn_{1-x}Mg_xO$ (x=0.0, 0.02, 0.05, 0.1) thin films on a silicon substrate by using EBPVD (Electron Beam Physical Vapor Deposition) method. XRD patterns showed the presence of hexagonal wurtzite structures in the samples. It was found that as the doping of Mg was increased, the crystalline size decreased and FWHM increased with a high rate. AFM patterns revealed the decrease in grain size with an increase in the Mg content. Also, it was observed that with the increasing concentration of Mg, the resistivity increased. Bang gap was calculated by $(\alpha h\nu)^2$ v/s (hν) plot at α = 0 and it was concluded that band gap increased with the increase in doping concentration. Refractive Index was also determined and results showed that the Refractive Index decreased with increased Mg content.

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