Published in AJSE, Vol:21, Issue: 1
Received on 10th January 2022
Revised on 11th May 2022
Accepted on 12th May 2022

AIUB JOURNAL OF SCIENCE AND ENGINEERING
**ISSN: 1608 – 3679 (print) 2520 – 4890 (Online)**

# Effect of N Doping on the Optical and Electrical Properties of Thermal Spray Pyrolyzed ZnO Thin Films

Rahimuddim, M. Rahman, M. S. Islam, M. A. Sattar, M. A. Halim, M. E. Haque, M. N. I.Khan, and S. Tabassum

*Abstract* – **This paper considers the experimental study of Nitrogen doped ZnO (ZnO:N) thin films deposited on a glass substrate at 350ºC using low cost homemade thermal spray pyrolysis technique in a typical environmental condition. In this study the average reflectance, transmittance, and absorbance were experimentally measured 20%, 35%, and 45%, respectively. Absorption coefficient is obtained $3.5x10^4$ $cm^{-1}$ for N doped ZnO sample. However, direct bandgap energy varies from 3.08 to 2.99 eV and indirect band gap energy varies from 2.86 to 2.67 eV. XRD analysis shows that the (002) plane is present in the experimental sample and the average grain size decreases with the increasing N concentration. Surface morphology of the sample is studied by Scanning Electron Microscopy. It is seen that few voids are present in the hexagonal crystal grains. The surface exhibits more or less uniform surface morphology with some clusters on the whole surface. Hall Effect study confirms that Nitrogen doped ZnO (ZnO:N) thin films using Vander Pauws method were made at room temperature at a constant field of 9.75 KG. Experimentally (1, 2, 3, and 4) % N doped ZnO thin films have shown negative Hall Constant ($R_H$), which exhibits N-type characteristics. $R_H$ and Hall concentration (n) increase with increasing N doping concentration. Initially Hall mobility, increases linearly for (1-2) % N doping concentration and then it decreases for the rest of the doping concentration. We also found that the resistivity decreases, and the conductivity increases with increasing N doping concentration, which exhibits the semiconducting nature.**

***Index Terms - Optical study, XRD, SEM, Hall Effect measurement, N doped ZnO thin film.***

**Md. Rahimuddin** is a master's student of Department of Material Science & Engineering (MSE), University of Rajshahi, Rajshahi-6205, Bangladesh. E-mail: rahimuddin204060 @gmail.com
**Md. Mizanur Rahman** is a master's student of Department of Material Science & Engineering (MSE), University of Rajshahi, Rajshahi-6205, Bangladesh. E-mail: mizanmse11ru@gmail.com
**Md. Shoriful Islam** is a master's student of Department of Material Science & Engineering (MSE), University of Rajshahi, Rajshahi-6205, Bangladesh. E-mail: shorifru14@gmail.com
**Md. Abdul. Halim** is an Associate Professor of Department of Material Science& Engineering (MSE), University of Rajshahi, Rajshahi-6205, Bangladesh. E-mail: halimtsukuba2012@gmail.com
**Md. Abdus. Sattar** is an Associate Professor of Department of Material Science& Engineering (MSE), University of Rajshahi, Rajshahi-6205, Bangladesh. E-mail: sattarjaist@gmail.com
**Md. Ehasanul Haque** is a Senior Assistant Professor of the Department of Industrial & Production Engineering, American International University-Bangladesh (AIUB), Dhaka-1229, Bangladesh. E-mail: ehasanul@aiub.edu
**Md. Nazrul Islam Khan** is a Chief Scientific Officer, Material Science Division, Bangladesh Atomic Energy Commission Dhaka, Bangladesh. E-mail: ni_khan77@yahoo.com
**Mst. Samia Tabassum** is a Senior Scientific Officer, Bangladesh Council of Scientific and Industrial Research (BCSIR), New Elephant Rd, Dhaka 1205, Bangladesh. E-mail: shawon14@gmail.com

## I. INTRODUCTION

Wide band gap materials are attractive for optical devices. ZnO is one of the wide band gap materials and was studied as a short-wavelength light-emitting material, because it has a direct band gap of 3.37 eV at 300K compared with other wide band gap materials, ZnO has larger exciton binding energy (59meV), which assures more efficient excitonic emission at higher temperatures [1,2]. Many important properties of ZnO are related with its optical behavior, such as bandgap reflectance and transmittance of ZnO film can be exploited for improving the performance of various optoelectronic devices. There are some potential advantages of Zinc oxide which have non-toxicity, low cost and abundance in nature [3**].** These attractive properties privileged to make this material suitable for many applications, such as solar cells, optical coatings, photo-catalysts, antibacterial activities, electrical devices, active medium in UV semiconductor lasers and in gas sensors [4,5]. After realizing the versatile applications of ZnO, it is very essential to fabricate both the *p*-type and *n*-type semiconductors. Usually, undoped ZnO shows *n*-type conductivity due to the presence of native point defects [6]. Although, fabricating *p*-type ZnO by high conductivity and stability is the big chalenge, but hot topic for the researchers during the last decades. By fabricating *p*-type ZnO, it may solve be the bipolarity problem and consequently increase the homojunction ZnO based applications of light emiting diodes, photo diodes and transperant thin film transistors [7]. For solving this problem preparing *p*-type ZnO, suitable dopent is more important. Among the candedate dopent nitrogen has attractive attention due to its small defect energy level and less probability to produceing dopent related defects [8]. Several research groups have used ZnO thin films using various growth techniques, including RF/DC magnetron sputtering [9], chemical bath deposition [10], reactive thermal vacuum evaporation [11], pulsed laser

deposition [12], sol-gel method [13]. However, there are very limited studies have been found on the fabrication of ZnO:N thin films by using thermal spray pyrolysis method. Therefore, the aim of the present work is to fabricate the ZnO:N thin films by low cost thermal spray pyrolysis method and to study its optical and electrical properties.

## II. EXPERIMENTAL PROCEDURE

### *a. Materials:*

Hydrated zinc acetate, deionized alcohol, acetic acid, Zn salt, ammonium acetate, cupric acetate.

### *b. Procedure for sample preparation*

In this experiment, we used glass substrate for the film deposition. Substrate cleaning is one of the most important factors for the fabrication of thin films. The optical and electrical properties of films are great affected by substrate surface. So, we carefully cleaned the substrates.

Present experiment web follows this step-

1. Firstly, the glass slides are cut into desire shape. For the UV measurement, substrate dimension was about 10 cm x 1-1.5 cm x 0.1 cm.
2. The slides are then immerged in water with detergent.
3. Warm it up to 1000ºC temperature for 15 minutes. Care would take when boiling solvents.
4. After cooling, substrates are immerged in acetone and taken few minutes.
5. And finally dry it in the atmospheric environment. But it is not appropriate drying procedure. For our liability it was done.

### *c. Solution preparation*

ZnO:N thin films were deposited on glass substrate by spray pyrolysis (SP) technique at 350°C at an ambient atmosphere. The details of spray pyrolysis are given elsewhere [11]. Three kinds of aqueous solutions, zinc acetate, ammonium acetate and copper chloride are chosen as the source of Zn, N respectively. The films were produced at constant atomic ratio (3 at % N).

The possible chemical reactions that occurred on the heated substrate to produce ZnO N doped ZnO films are as follows:

$$Zn(CH_3COO)_2.2H_2O \xrightarrow[\text{Decomposed to}]{350^\circ C} ZnO + CO_2(g) + CH_4(g) + Steam(g)$$

$$Zn(CH_3COO)_2.2H_2O + CH_3COONH_4 \xrightarrow[\text{Decomposed to}]{350^\circ C} N{:}ZnO + CO_2(g) + CH_4(g) + Steam(g)$$

## III. RESULT AND DISCUSSION

## XRD analysis

X-ray diffraction is a non-destructive analytical technique which reveals information about the crystallographic structure, chemical composition, and physical properties of materials thin films. X-ray diffraction yields the atomic structure of materials and is based on the elastic scattering of X-rays from the electron clouds of the individual atoms in the system. The structural properties of Cu doped ZnO films fabricated on glass substrates at 350˚C temperature was investigated by X-ray diffraction (XRD) patterns. XRD pattern clearly shows that ZnO thin film deposited by Spray pyrolysis method is polycrystalline in nature.

| Type of Samples | No of peak | Peak position, 2θ, (deg) | Observed Rel. Intensity (%) | Miller Indices (hkl) | θ (deg) | FWHM (deg) | Grain size (nm) | Average Grain size (nm) |
|---|---|---|---|---|---|---|---|---|
| 1% N | 1 | 36.65 | 214 | 002 | 18.32 | 0.253 | 34.56 | 34.56 |
| 2% N | 1 | 32.07 | 265 | 100 | 16.03 | 0.4270 | 20.23 | |
| | 2 | 34.73 | 296 | 002 | 17.36 | 0.2669 | 32.59 | |
| | 3 | 36.55 | 446 | 101 | 18.27 | 0.3391 | 25.78 | 25.06 |
| | 4 | 47.81 | 106 | 102 | 23.90 | 0.3628 | 25.03 | |
| | 5 | 56.87 | 151 | 110 | 28.43 | 0.4351 | 21.69 | |
| 3% N | 1 | 36.55 | 31 | 002 | 18.27 | 1.244 | 7.03 | |
| | 2 | 44.25 | 34 | 101 | 22.12 | 0.408 | 7.20 | 5.70 |
| | 3 | 48.33 | 28 | 102 | 24.16 | 1.295 | 1.881 | |
| 4% N | 1 | 32.07 | 265 | 100 | 16.03 | 0.4270 | 20.23 | |
| | 2 | 34.73 | 296 | 002 | 17.36 | 0.2669 | 32.59 | |
| | 3 | 36.55 | 446 | 101 | 18.27 | 0.3391 | 25.78 | 25.06 |
| | 4 | 47.81 | 106 | 102 | 23.90 | 0.3628 | 25.03 | |
| | 5 | 56.87 | 151 | 110 | 28.43 | 0.4351 | 21.69 | |

Table- 1. XRD peak positions and possible phase for N doped ZnO films.

| B Concentration (%) | D (nm) | δ (×10$^{15}$ m$^{-2}$) | ε | a (Å) | c (Å) | V(×10$^{-30}$ m$^{3}$) | u | Bl(Å) |
|---|---|---|---|---|---|---|---|---|
| 1% N | 34.56 | 83.72 | | | 4.89 | | | |
| 2% N | 20.23<br>32.59<br>25.78<br>25.03<br>21.69 | 2.44<br>94.15<br>1.50<br>1.59<br>2.12 | 0.371<br>0.213<br>0.256<br>0.204<br>0.200 | 3.24 | 5.64 | 51.27 | 0.360 | 2.030 |
| 3% N | 7.03<br>7.20<br>1.881 | 0.202<br>0.192<br>0.028 | 0.941<br>0.250<br>0.721 | <br><br>3.46 | 4.92 | 51.00 | 0.414 | 2.036 |
| 4% N | 20.23<br>32.59<br>25.78<br>25.03<br>21.69 | 2.44<br>94.15<br>1.50<br>1.59<br>2.12 | 0.371<br>0.213<br>0.256<br>0.204<br>0.200 | 3.24 | 5.64 | 51.27 | 0.360 | 2.030 |

Table-2. Structural parameters including crystallite size (D), dislocation density (δ), micro-strain (ε), lattice parameters (a and c), unit cell volume (V), internal relaxation parameter (u) and bond length (bl) of N doped thin films with various concentrations.

The observed reflection planes (100), (002), (101), (102) and (110) could be indexed with hexagonal ZnO structure which was identified by comparing with standard JCPDS card (Card no. 2100100).

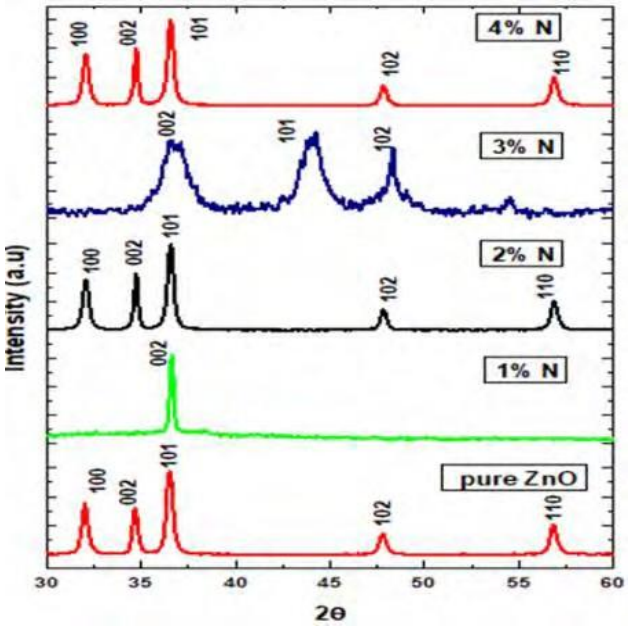


Fig: 1. XRD pattern of un-doped ZnO and N doped ZnO thin films for different composition of N deposited on glass substrate.

Fig 1. shows that the peak intensity of (100), (002), (101), (102) and (110) planes are dominating both for un-doped and doped samples. For 1% N doped ZnO sample of only (002) peak. For 2 and 4% N doped ZnO sample the peak intensity of (002) plane is higher than other plane. However, the intensity of (002) plane for N doped ZnO samples is found lower compared to (101) planes andhigher than others plane. For 3% N doped ZnO sample thepeak intensity of (002) plane is found lower compared to (101) planes and higher than others plane.

These results suggest that the preferential orientation of un-doped sample is in the (002) plane. As a result, crystal grains are oriented along (002) plane for doped samples. It seems that the microstructure of the ZnO lattice changes due to the doping effect that inevitably perturbed the thermodynamic energy in the system that may create probability to change the preferable orientation.

## Determination of crystallite sizes:

The average size of crystallites was estimated by using the Debye-Scherrer's formula:

$$\xi = 0.94\lambda/\beta\cos\theta \text{ ---------- (1)}$$

Where, ξ is the crystallite size, λ is the wavelength of the X-ray used, θ is the diffraction angle and β is the full width at half maximum (FWHM) measured in radians. The calculated crystallite size or grain size for N doped ZnO films are also included in Table 1 it is observed that the average grain size along the c-axis slightly affected by N doping in ZnO.

## Determination of micro-strain (ε)

The micro-strain developed in the film was evaluated using the relation [11].

$$\varepsilon = \frac{\beta}{4tan\theta} \text{ ----------(2)}$$

Calculated values of strain are presented in Table 2 and show a negative correlation with the crystalline size.

## Determination of unit cell volume (V)

Unit cell volume (V) for the hexagonal structure can be determined using the relations [12].

$$V = \frac{\sqrt{3}}{2}a^2c \text{ ----------(3)}$$

The calculated values of a, c and V are summarized Table-2 the (2 and 4) % N doped ZnO of unit cell volume remain same, (21.27) but decrease for 3% N (51.00).

## Determination of internal relaxation parameter (u)

The internal relaxation parameter (u) was calculated using the following relations [13].

$$u = \frac{1}{3}\left(\frac{a^2}{c^2}\right) + \frac{1}{4} \quad \text{----------(4)}$$

The internal relaxation parameter is a measure of the amount by which each atom is displaced with respect to the next along the c-axis. From the table we can conclude that in the deposited films, the atoms are displaced from the ideal configuration due to the addition of impurities. Nitrogen doped ZnO (N:ZnO) doping resulted of internal relaxation in almost same.

## Determination of the bond length ($b_l$)

The bond length ($b_l$) was calculated using the following relations [14].

$$b_l = cu \quad \text{.....(5)}$$

The calculated values of bond lengths are a little longer than the ideal value (1.93Å) which could be due to the strain suffered by the lattice. We can see from the table that the Nitrogen doped ZnO (N:ZnO), resulted in (2, 3 and 4) % N doped ZnO bond length almost same.

## Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) has been used to characterize the surface morphology of Cu doped ZnO thin films deposited on glass substrate under low magnification. Usually to take SEM micrograph an additional metallic layer is required to deposit on the film surface for insulator films though the additional layer sometimes damage the film surface and produced distorted image. In the present work, additional metallic layer is not necessary because of the good electrical conductivity of our samples. Surface morphology of N doped ZnO films is studied by Scanning Electron Microscopy (SEM), and the SEM images are shown in Fig. 2.

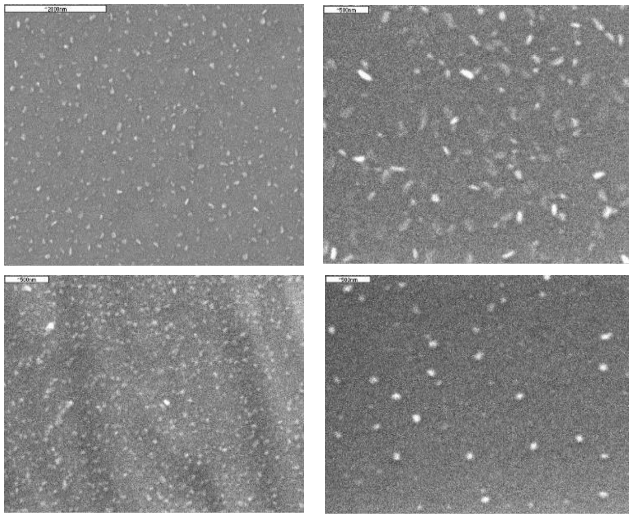

Fig: 2. (a) SEM images of 1% N- doped ZnO and low magnification. (b) SEM images of 2% N- doped ZnO and low magnification. (c) SEM images of 3% N- doped ZnO and low magnification. (d) SEM images of 4% N- doped ZnO and low magnification. Fig. 2: show the SEM images of (1, 2, 3 and 4) % N doped ZnO films surfaces at low magnification respectively. It is seen that hexagonal crystal grains few voids are evident for N doped ZnO samples. The surface exhibits more or less uniform surface morphology with some clusters on the whole surface. Crystal grains are almost equal in size while a few bigger agglomeratedcrystal grains are distributed over the whole surface along with smaller one for N doped ZnO samples.

## Optical Study

### *a. Reflectance*

Reflectance behavior for the N doped ZnO films are revealed in figure 3 respectively with the wavelength range 380-800nm. The reflectance varies 12-25%. The reflectance varies 12-25%. Reflectance is nearly constant upto 800-400nm wavelength and sharply decreases in below 400nm wavelength. But in case individual doping of N, reflectance decreases with the increasing doping concentration. If we compare these values to the undoped ZnO thin film, reflectance makes a change with doping concentration. It should be remembered that in present work, nitrogen concentration was constant at 3%.

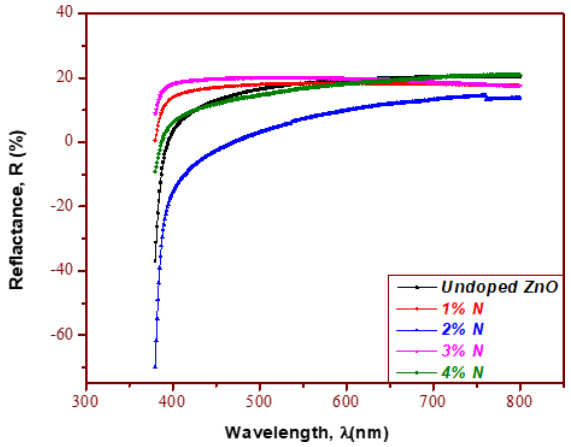


Fig: 3. Reflectance of N doped ZnO films with various concentration.

### *b. Transmittance*

Transmittance behavior for the N-doped ZnO films are shown in figure 4 respectively with the wavelength range 380-800 nm. The value of transmittance varies 10-60%. Transmittance is increased with increasing the wavelength. But in case of N doping, decreases in transmittance with the increasing doping concentration. The maximum transmittance is viewed in 1% N and minimum for 2% N doped film.

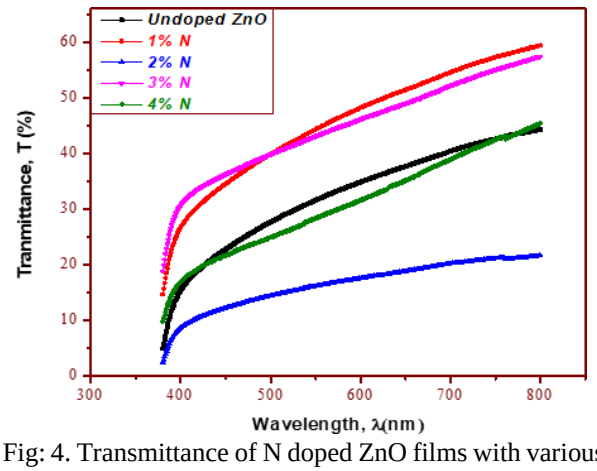


Fig: 4. Transmittance of N doped ZnO films with various concentration.

### *c. Absorbance*

When a light beam in impinged on a material surface, portion of the incident beam that is not reflected by the material is either absorbed or transmitted through the material [4]. Bouguer's law: The fraction of beam that is absorbed is related to the thickness of the materials and the manner in which the photons interact with the material's structure [5,6].

$$I = I_0\, exp(-\alpha.x) \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Absorption behavior for the N-doped ZnO films is revealed in figure 5, respectively with the wavelength range 380-800 nm. The absorbance varies 12-70%. Absorption is increased with decreasing the wavelength. Itis gradually increase in range 800-400 nm wavelength and sharply increased in 400-380 nm for all films. But individualdoping of N, absorption decreases with increasing doping concentration except 4% N. The maximum absorption is viewed from 4% N doping film. However, the absorbance is not so significantly changed with changing the concentrations of N doping in ZnO film.

.

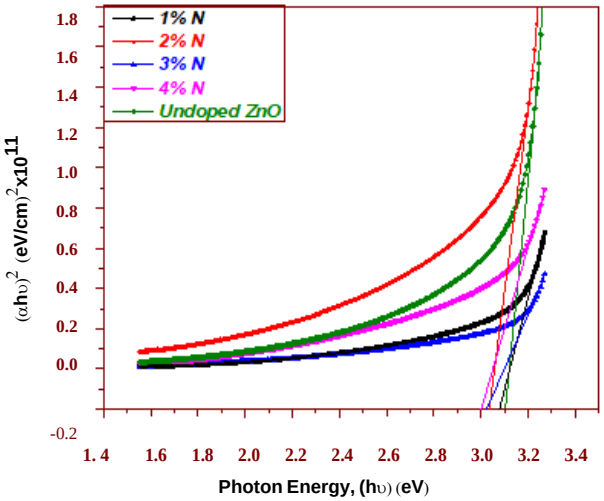


Fig: 5. Absorbance of N doped ZnO films with various concentration.

### *d. Absorption co-efficient*

The value of the absorption coefficient was calculated according to the following relation [7]

$$\alpha = \frac{2.303 * A}{t} \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

where t is the film thickness and A is absorbance. The variation of absorption coefficient of N doped ZnO films are present in Fig. 6, respectively. Initially the absorption coefficient increases slowly with the increasing the photon energy. But this value is rapidly increased after photon energy 3.00eV. For all films, absorption coefficient increased with increasing doping concentration. But these values are lower the undoped ZnO. This absorption coefficient value is greater than $10^5$ times.

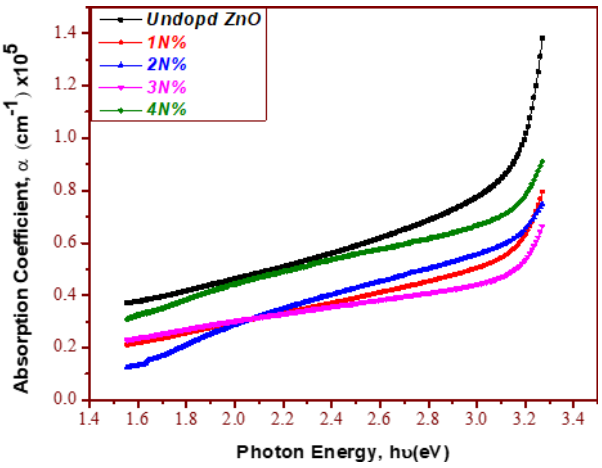


Fig: 6. Absorption coefficient of N doped ZnO films with various concentration.

### *Optical Band gap*

From the equation (3) we can calculate direct bandgap of these films. The direct transition involved in the absorption process, n = ½, by the plotting the value of 〖(αhϑ)〗 ^2 with the photon energy hϑ. This direct bandgap variations of N doped films are shown in figure 7. The bandgap of the film was obtained from the intersects on horizontal axis after drawing the straight line from the curve. In our investigation, the direct bandgap of the ZnO was funded 3.138eV instead of 3.37 eV. The values of band gap energy are 3.085-2.995 eV for N doped ZnO thin films respectively. For case of N doping, the bandgap decreases with increasing of doping concentration. These variations are shown in table 1

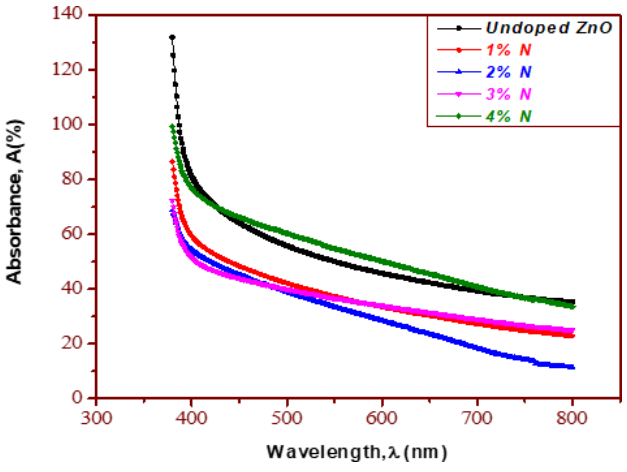


Fig: 7. direct band gap of N doped ZnO films with various concentration.

### *Indirect Band gap*

From the equation (3) we can evaluate indirect bandgap of these films. The indirect transition involved in the absorption process, n = 2, by the plotting the value of 〖(αhϑ)〗 ^(1/2) with the photon energy hϑ. The indirect bandgap variations of N doped films are shown in figure 8.

In our investigation, the indirect bandgap of the ZnO was found 2.903 eV. The bandgap of the film was obtained from the intersects on horizontal axis after drawing the straight line from the curve. The range of the bandgap energy was varied from 2.86-2.67 eV for different concentration of N doping. In case ofN doping, the bandgap energy decreases with increasing ofdoping concentration. The maximum and minimum indirect bandgap energy were observed from the undoped ZnO and 4 % of N doped ZnO samples respectively. These variations are shown in table 3.

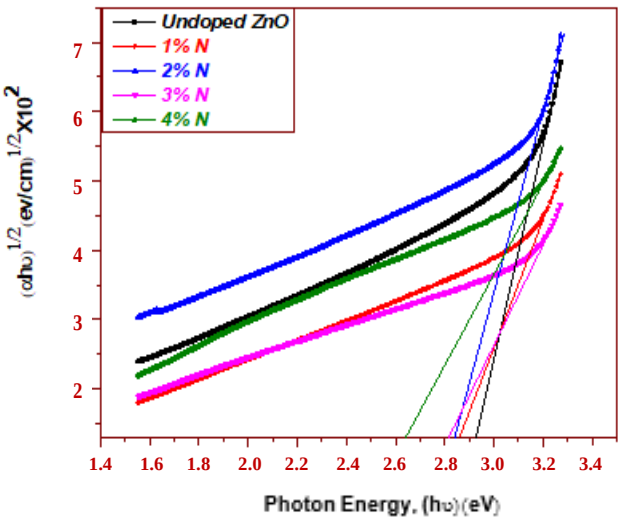


Fig: 8. Indirect band gap of N doped ZnO films with various concentration.

| Percent of N on ZnO | Direct BG of N ZnO (eV) | Indirect BG of N doped ZnO (eV) |
|---|---|---|
| 1% N | 3.085 | 2.86 |
| 2% N | 3.065 | 2.83 |
| 3% N | 3.025 | 2.82 |
| 4% N | 2.995 | 2.67 |

Table: 3 Direct and indirect band gaps of N doped ZnO film.

## Electrical Study

### Hall Effect

Hall Effect measurement was performed to characteristics the electrical properties of the ZnO:N films with various Nitrogen doping concentration. The results indicates that ZnO:N films were n-type, this goes in agreement with the previous work. The square samples were prepared according to Van der Pauw method with Ag paste contacts at the corners. The measurement was repeated several times to conform the carrier types of the samples.

| **Doping conc. (X)** | **Hall constant, $R_H$ ($cm^3$/coul)** | **Hall mobility, µH ($cm^2$/Vsec)** | **Hall conc. n, ($cm^{-3}$)** | **Resistivity ρ, (Ω-cm)** | **Con-ductivity σ, ($\Omega cm^{-}$)** | **Semi-conductor type** |
|---|---|---|---|---|---|---|
| 1% N | $-161.94\times10^{6}$ | $8.151\times10^{1}$ | $3.855\times10^{10}$ | $198.7\times10^{4}$ | $0.00503\times10^{-5}$ | n |
| 2% N | $-70.26\times10^{6}$ | $20.85\times10^{1}$ | $8.884\times10^{10}$ | $33.70\times10^{4}$ | $0.296\times10^{-5}$ | n |
| 3%N | $-12.53\times10^{6}$ | $13.38\times10^{1}$ | $49.83\times10^{10}$ | $9.364\times10^{4}$ | $1.068\times10^{-5}$ | n |
| 4%N | $-2.180\times10^{6}$ | $12.42\times10^{1}$ | $221.4\times10^{10}$ | $2.271\times10^{4}$ | $4.404\times10^{-5}$ | n |

Table. 4. Values of Hall Constant ($R_H$), Hall mobility ($\mu_H$), Hall concentration (n), Resistivity (ρ), and Conductivity ( σ), for (1, 2, 3, and 4) % N doped ZnO.

Fig. 9 and 10 show the variation of Hall Constant ($R_H$), Hall mobility ($\mu_H$), Hall concentration (n), Resistivity ($\rho$), and Conductivity ( $\sigma$), with different N doping concentration. The values of Hall Constant ($R_H$), Hall mobility ($\mu_H$), Hall concentration (n), Resistivity ($\rho$), and Conductivity ( $\sigma$), with different N doping concentration are given in Table 4.

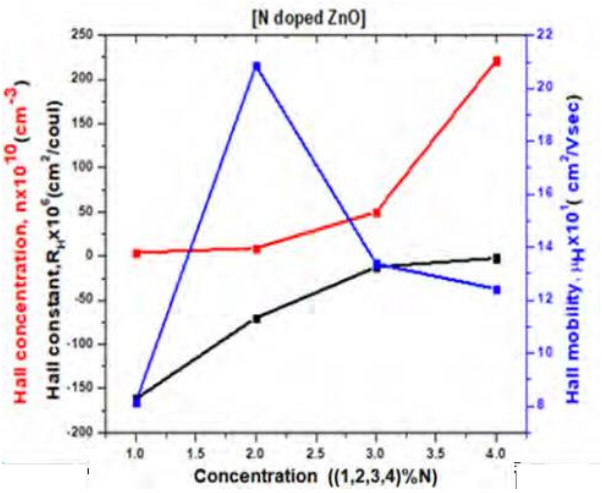


Fig: 9. Variation of Hall constant ($R_H$), Hall mobility ($\mu_H$), Hall concentration (n), with concentration (1, 2, 3 and 4) % N doped ZnO thin films.

Due to low level doping concentration the sample exhibit n-type characteristics but increasing doping concentration (5 at. % to 30 at. %) the possibility of turning the sample into p-type semiconductor [10]. At (1,2,3, and 4) % nitrogen-doping concentration, the substitution of N ions with O ions on O site produces $N_o$ in the ZnO crystal lattice sites, which resulted in sufficient holes that dominate the intrinsic n-type defects [10].

Hall Constant ($R_H$), and Hall concentration (n), increases with increasing N doping concentration. Initially Hall mobility ($\mu_H$), increases linearly for (1-2) % N doping concentration then it decreases for lest of the doping concentration. The decrease of mobility is due to the increases of ionized impurity scattering mobility. The ionized impurity scattering mobility is inversely proportional to the carrier concentration and hence the decreases in Hall mobility [11-12

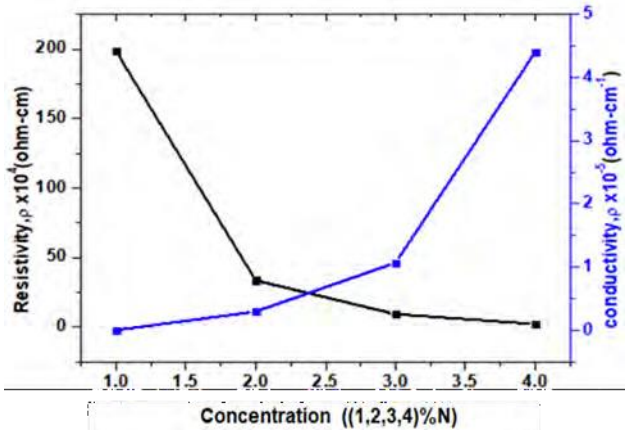


Fig: 10. Variation of Resistivity ($\rho$), and Conductivity ( $\sigma$), with concentration (1, 2, 3 and 4) % N doped ZnO thin films.

Resistivity ($\rho$), decreases with Cu doping concentration that's way conductivity ( $\sigma$), increases. At high nitrogen doping concentration, the compensation of $N_o$ occurs as the excess of N atoms may lead to the substitution of $N_2$ complexes, which behave as double shallow donor and single donor respectively [13].

## IV. Conclusion

Spray pyrolysis is a versatile and effective technique to deposit metal oxide films. The quality and properties of the films depend largely on the process parameters. The most important parameter is the substrate surface temperature. The higher the substrate temperature, the rougher and more porous are the films. If the temperatures are too low the films are cracked. The deposition temperature also influences the crystallinity, texture, and other physical properties of the deposited films. The precursor solution is the other important spray parameter, which affects the morphology and the properties of the deposited films. In addition, the film morphology and properties can be drastically changed by using various additives in the precursor solution. In this thesis undoped ZnO, N doped ZnO thin films were deposited by chemical spray pyrolysis technique. Substrate temperature was 2000C, deposition rate 1 ml/min. Films were deposited for 20-35 minutes. In this study the average Reflectance is 20%, Transmittance 35%, Absorbance is 45%. Absorption coefficient for N doped ZnO film is $3.5x10^4cm^{-1}$ ZnO film. Direct bandgap energy for undoped ZnO is measured 3.13eV, 3.08-2.99eV for N doped Indirect bandgap energy are 2.90eV, 2.86-2.67eV doped ZnO thin films respectively.

XRD analysis shows the (002) plane is present of samples and the average grain size decrease with increasing N concentration. Surface morphology of N doped ZnO films is studied by Scanning Electron Microscopy (SEM). It is seen that hexagonal crystal grains few voids are present for N doped ZnO samples. The surface exhibits more or less uniform surface morphology with some clusters on the whole surface. Hall Effect study confirms that Nitrogen doped ZnO (ZnO:N), thin films using Vander pauws method were made at room temperature at a constant field of 9.75 KG. Experimentally (1, 2, 3, and 4) % N doped ZnO thin films have shown in negative Hall Constant ($R_H$). Which exhibited n-type characteristics. Due to low level doping concentration the sample exhibit n-type characteristics but increasing doping concentration (5 at. % to 30 at. %) the possibility of turning the sample into p-type semiconductor. At (1,2,3, and 4) % nitrogen-doping concentration, the substitution of N ions with O ions on O site produces $N_o$ in the ZnO crystal lattice sites, which resulted in sufficient holes that dominate the intrinsic n-type defects. Hall Constant ($R_H$), and Hall concentration (n), increases with increasing N doping concentration. Initially Hall mobility ($\mu_H$), increases linearly for (1-2) % N doping concentration then it decreases for lest of the doping concentration. The decreases of mobility are due to the increases of ionized impurity scattering mobility. The ionized impurity scattering mobility is inversely proportional to the carrier concentration and hence the decreases in Hall mobility. Resistivity ($\rho$), decreases with Cu doping concentration that's way conductivity ( $\sigma$), increases. At high nitrogen doping concentration, the compensation of $N_o$ occurs as the excess of N atoms may lead to the substitution of $N_2$ complexes, which behave as double shallow donor and single donor respectively.

## Acknowledgments

This project is founded by the Ministry of Science and Information & Communication Technology (MOSICT) of Peoples Republic of Bangladesh for providing financial support. We gratefully acknowledge thin film, Photovoltaic Laboratory, Department of Materials Science and Engineering, University of Rajshahi, Rajshahi- 6205, Bangladesh. We gratefully acknowledge Bangladesh Atomic energy Commission (AEC) Dhaka Bangladesh for providing XRD, and SEM facilities. We also gratefully acknowledge Bangladesh Council of Scientific and Industrial Research (BCSIR). Institute of Fuel Research and Development (IFRD) for providing Hall measurement system.

## REFERENCES

[1]. V. Srikant and D.R. Clarke, J. Appl. Phys. **83**, 5447 (1998).
[2]. S. L. King and J. G. E. Gardeniers, Appl. Surf. Sci. **811**, 96 (1996).
[3] D. C. Look, Mater. Sci. Eng. B **80,** 383 (2001).
[4] D. Song, D.H. Neuhaus, J. Xia, A.G. Aberle, Thin Solid Films **422**, 180-185 (2002).
[5]. H. E. Bennett and J. M. Bennettin: Physics of thin films, Academic press, New York **4**,1, (1967).
[6]. J. Black, E.M.Conwell, L. Seigle, C.W.Spencei, J. Phys. Chem. Solids, **2,** 240 (1957).
[7]. A. Janotti, C. G. Van de Walle, Phys. Rev. B **76,** 165202 (2007).
[8]. E. Fortunato, P. Barquinha, A. Pimentel, and R. Martins, Thin Solid Films **487,** 205 (2005).
[9]. C.H. Park. S. B. Zhang and S. H. Wei, Phys. Rev. B: Condens. Matter.**66,** 073202 (2002).
[10]. D. Brida, E. Fortunato, I. Ferreira, H. Aguas, and R. Martins, J. Non-Cryst. Solids **1272**, 299 (2002).
[11]. T. Manami, H. Nanto, and S. Takata, Jpn. J. Appl. Phys. L **280**, 23 (1984).
[12]. E. Fortunato, V. Assuncao, A. Gonc alves, A. Marques, H. Aguas, L. Pereira, I. Ferreira, and R.. Martins, Thin Solid Films **443**, 451 (2004).
[13]. A. Dutta and S. Basu, Mater. Chem. Phys. **41**, 34 (1993).
[14]. P. Nunes, B. Frenandes, E. Fortunato, P. Vilarinho, and R. Martins, Thin Solid Films **337**, 176 (1999).

**Rahimuddin** received her B.Sc and M.Sc Degrees in Materials Science and Engineering,(MSE) from Rajshahi University in 2016 and 2017 respectively. He joined in BSRM, Zorargonj, Mirasarai, Chattrogram, Bangladesh. As an Assistant Executive Production-SMS, in 2020. His intense research areas are renewable energy especially, solar energy, thin films etc.

**Mizanur Rahman** received her B.Sc and M.Sc Degrees in Materials Science and Engineering, (MSE) from Rajshahi University in 2015 and 2016 respectively. He joined in Meghna Foil Packaging Ltd; Sister Concern of Meghna Group of Industries, (MGI), Meghna Industrial Economic Zone, Narayanganj, Bangladesh as a Senior Executive, Quality Control Officer in 2021. His intense research areas are renewable energy especially, solar energy, thin films etc.

**Md. Shoriful Islam** is a Ph.D. student at Ionics Laboratory in the department of Material science and Engineering, Chonnam National University, South Korea. His present research focuses on Mixed Potential Electrochemical Gas Sensors, Proton Storage Materials for Energy Conversion Devices, Nickel Metal Hydride Battery. He has achieved both his Master's degree and Bachelor's degree in Materials Science and Engineering, University of Rajshahi, Bangladesh. He has experienced in Materials synthesis by chemical routes and Materials Characterization, e.g., XRD, SEM, EDS, BET, XPS, TG-DTA, FTIR, Raman spectroscopy, WDXRF, Single crystal XRD etc. Additionally, he has three publications in international journal. He also has seven national and international conference paper and poster presentations where two of them awarded as best paper.

**Md. Abdus Sattar** received his B.Sc and M.Sc Degrees in the department of Physics from Rajshahi University in 2003 and 2004 respectively. He achieved Ph.D. degree from Japan Advanced Institute of Science & technology (JAIST), Japan in 2016 under Monbukagakusho (MEXT) scholarship. Before that, he joined in the department of Materials Science and Engineering, (MSE) Rajshahi University as a lecturer in 2010. Currently, he is working as an Associate professor in the same department. His interest in the research areas are renewable energy especially, solar energy, thin film and surface science etc. He has published a number of research papers in different journals in his research background. He is a member of BPS.

**Md. Abdul Halim** received his B.Sc and M.Sc Degrees in the department of Physics from Rajshahi University in 2007 and 2007 respectively. He achieved Ph.D. degree from the university of Tsukuba, Japan in 2016 under Monbukagakusho (MEXT) scholarship. Before that, he joined in the department of Materials Science and Engineering, (MSE) Rajshahi University as a lecturer in 2010. Currently, he is working as an Associate professor in the same department. His interest in the research areas are renewable energy especially, solar energy, thin film and photovoltaics etc. He has published a number of research papers in different journals in his research background. He is a member of BPS.

**Md. Ehasanul Haque** has completed his B.Sc. and Masters in Materials Science and Engineering from the University of Rajshahi, Bangladesh in 2008 and 2009 respectively. He received "Gold Medal Award" from the University of Rajshahi for securing top position in B.Sc. examination He received his PhD degree with one of the most prestigious MEXT Scholarship in 2018 and received "University President Award" for outstanding research output from Japan Advanced Institute of Science and Technology (JAIST). He joined American International University - Bangladesh (AIUB) in 2018 and currently working as a Senior Assistant Professor at the Department of Industrial and Production Engineering, Faculty of Engineering. His primary research areas are Nonlinear Optics, Electrodeposition, Corrosion Behavior Study, Nanofabrication, Alloy Formation, Study of Optical, Electrical and Mechanical Properties of Materials, Laser Technology, Microstructure Study, Properties of Carbon Nanotubes, Fabrication of Composite Materials and their properties and so on.

**Dr. Mohammad Nazrul Islam Khan** is working as Chief Scientific Officer at Materials Science Division, Atomic nergy Centre, Dhaka. He completed his doctoral program on Spintronics from Tohoku University, Japan. During his PhD, he used to fabricate thin films using Sputtering system and Microfabrication. Currently he is working on Magnetic Materials, Spintronics, Multiferroics, Ceramic Materials, Nanomaterials, Biomaterials, Thin film and so on. He has a patent and yet published a significant number of Journal papers and attended more than 100 conferences at home and abroad.

**Samia Tabassum** received her B.Sc and M.Sc Degrees in Applied Physics and Electronics from Rajshahi University in 2002 and 2003 respectively. She achieved Doctor of Energy Science Degree from Kyoto University, Japan in 2015 under Monbukagakusho scholarship. Before that, she joined in Bangladesh Council of Scientific and Industrial Research (BCSIR) as Scientific Officer in 2006. Currently, she is working as a Senior Scientific Officer in IFRD, BCSIR. She was a Post-Doctoral Research Fellow of IsDB Scholarship program 2020- 2021. Her intense research areas are renewable energy especially, solar energy, thin film and dye sensitized solar cell, photocatalyst material etc. She has published a number of research papers in different journals in her research background. She is a member of BPS.