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**Submission date:** 12-May-2022 08:47AM (UTC+0700)
**Submission ID:** 1834251258
**File name:** C14.pdf (1.17M)
**Word count:** 2692
**Character count:** 13581

*Solid State Phenomena*
*ISSN: 1662-9779, Vol. 266, pp 141-147*
*doi:10.4028/www.scientific.net/SSP.266.141*

*Submitted: 2017-06-07*
*Accepted: 2017-06-26*
*Online: 2017-10-02*

# The Influence of Nitrogen Doping Concentration on the Strain and Band Gap Energy of N-Doped Zinc Oxide Prepared Using Spray Coating Technique

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**Keywords:** Strain, N-ZnO, microstructure, spray coating, band gap.

**Abstract.** N-ZnO thin layer is widely used in application of wastewater photo catalyst. N-ZnO thin films have been successfully deposited on glass substrate using spray coating technique at 450 $^{o}$C with varying concentrations of N from Urea source. XRD test results showed that the N-ZnO has a polycrystalline structure with diffraction field (100), (002), (101) and (110). The presence of nitrogen atoms in the lattice of ZnO causes a shift in diffraction angle between 0.08$^{o}$ - 0.18$^{o}$. N-ZnO thin layer showed the occurrence of tensile strain. Surface morphology of N-ZnO is shaped like mine (like root). All samples have band gap energies lower than that of ZnO and the smallest is sample N6 with Eg = 3.249 eV. The presence of nitrogen atom increases surface roughness and decreases band gap energy.

## Introduction

Water is vital for all living beings. Nowadays, fulfilling the needs for clean water is a challenge as water quality declines. Industrial development makes it worse by increasing organic and inorganic liquid waste in both land and waters. This results in water pollution. Textile industry, with batik being one of them is a source of wastewater colorant [1-2].

Waste treatment technologies in textile dye and batik is now less effective due to its high cost and cumbersome maintenance and monitoring. Therefore, a new cheap, practical and low cost technology is required [3]. There are currently some methods of color and organic compound removal available. These include semiconductor photo catalyst, which is one of Advanced Oxidation Processes (AOP) technologies [4]. This method is very interesting because of its great potential to solve environmental issues, especially waste [5].

Zinc oxide (ZnO) is a type of catalyst widely used because it has chemical stability, and high optical properties, and is widely used in gas sensor device applications, UV-resistant coatings, and surface acoustic wave devices [6-7]. ZnO is widely reported to have high effectiveness in degrading dye solution [8-10], but it has not been widely used for organic pollutants.

There are two methods that have been developed to improve photo catalyst performance. The first one is changing the physical properties such as morphology and particle size. The second is the use of sensitized colorant, the addition of semiconductors with narrow energy gap, metal and non-metal (N, C, S) doping, and metal transition. Increasing the concentration of non-metal doping in ZnO will change the energy level. This in turn improves its physical and optical properties [11-13]. Among the non-metallic elements, nitrogen (N) has the advantage of being non-toxic, abundant in nature, has a low electronegativity and ionic radii similar to that of ZnO [14]. In addition, N doping in ZnO will improve its photo catalytic activity [15-16].

The influence of nitrogen doping on the microstructure of N-ZnO includes crystalline grain size, strain and optical properties. Sample of N-ZnO deposited on amorphous glass substrates by sol-gel method of spray coating technique will be reported in this paper.

## Experimental Method

ZnO-N made using Zinc Acetate was dissolved in 2-propanol and urea was added as impurities. A solution of ZnO-N was then deposited on a glass substrate at a temperature of 450 $^{o}$C. Zinc Acetate dehydrate was then dissolved in 26 ml of 2-propanol and then stirred for 15 minutes at room temperature using a magnetic stirrer. The solution was spilled by MEA with mole ratio of 1: 1 to Zinc Acetate and re-stirred using a magnetic stirrer for further 15 minutes. After 15 minutes, the urea as a nitrogen source in the ZnO solution was added with 4%, 6%, 8% and 10% percentages. Doping percentage is calculated using Eq. 1:

$$\%N = \left( \frac{nU}{nU + nZnAc} \right) x100\% \quad (1)$$

where $\%N$ is doping concentration of Nitrogen, $nU$ is Urea mole, and $nZnAc$ is Zinc Acetate Dehydrate mole. N doping was varied by 4%, 6%, 8%, 10%, and were labeled N4, N6, N8 and N10, respectively. Solutions mixed with urea were then stirred for 15 minutes as to make them homogeneous. After 15 minutes, the solution was deposited on a glass substrate using spray coating technique.

Glasses to be used as the substrate were first cleaned with methanol, acetone, and distilled water to remove impurities from its surface. ZnO thin layer deposition-N was carried out using a spray gun connected to the compressor with a pressure of 40 psi, the solution was sprayed at distance of 30 cm perpendicular to the glass substrate heated to a deposition temperature of 450 °C on a hot plate. The thin layer deposition equipment for N-ZnO is shown in Fig. 1.

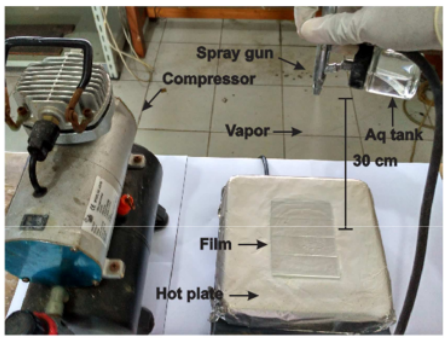


Fig. 1. N-ZnO thin film deposition on a glass substrate at 450 $^{o}$C by spray coating technique.

## Result and Discussion

**Microstructure Analyses.** The microstructure of ZnO-N thin layer was analyzed using XRD and the result is shown in Fig. 2. Test results of N-ZnO thin layer show it has poly crystal structure with h k l diffraction peaks at (100), (002), (101) and (110), which correspond to COD database #96-901-1663. The dominant peak of (002) from all samples of ZnO doped with N shows that diffraction angle 2θ shifted to 0.08$^{o}$-0.18$^{o}$ from the diffraction peak angle of ZnO (002) at 34.42$^{o}$. Meanwhile, crystallite size ($L$) can be known using Scherer equation.

The complete results of XRD test include position of peak diffraction, FWHM and crystallite size (L), as shown in Table 1. Shifted angle of 2θ shows that N atom is naturally led to the strain. From the calculations, the value of L consecutive samples N4, N6, N8 and N10 are 239.36 nm, 102.54 nm, 201.48 nm and 178.98 nm respectively. The presence of nitrogen atom (N) affects crystal growth and a new orientation is formed at (110), (013) and (112).

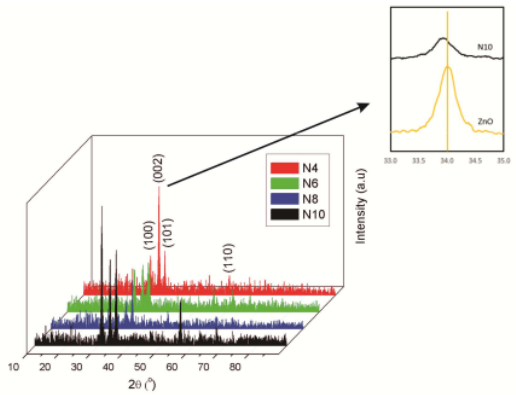


Fig. 2. XRD spectra of N-ZnO thin films deposition with varied N percentage.

Table 1. Peak angle diffraction ($2\theta$), FWHM, hkl and crystallite size of samples.

| %N | 2θ (°) | FWHM (°) | h | k | l | $L$ (nm) | $\overline{L}$ (nm) |
|---|---|---|---|---|---|---|---|
| 4 | 31.95 | 0.2903 | 1 | 0 | 0 | 284.65 | 239.36 |
| | 34.59 | 0.3336 | 0 | 0 | 2 | 249.41 | |
| | 36.43 | 0.3587 | 1 | 0 | 1 | 233.16 | |
| | 56.79 | 0.4151 | 1 | 1 | 0 | 217.56 | |
| | 63.23 | 0.44 | 0 | 1 | 3 | 212.02 | |
| 6 | 31.48 | 0.6465 | 1 | 0 | 0 | 127.67 | 102.54 |
| | 34.24 | 0.5049 | 0 | 0 | 2 | 164.64 | |
| | 36.1 | 0.8188 | 1 | 0 | 1 | 102.05 | |
| | 47.4 | 1.6235 | 0 | 1 | 2 | 53.44 | |
| | 56.56 | 0.8509 | 1 | 1 | 0 | 106.02 | |
| | 67.98 | 1.5593 | 1 | 1 | 2 | 61.45 | |
| 8 | 34.53 | 0.3639 | 0 | 0 | 2 | 228.61 | 201.48 |
| | 36.39 | 0.3331 | 1 | 0 | 1 | 251.05 | |
| | 47.61 | 0.4186 | 0 | 1 | 2 | 207.43 | |
| | 62.97 | 0.7839 | 0 | 1 | 3 | 118.84 | |
| 10 | 31.74 | 0.3444 | 1 | 0 | 0 | 239.81 | 178.98 |
| | 34.34 | 0.3662 | 0 | 0 | 2 | 227.06 | |
| | 36.18 | 0.4363 | 1 | 0 | 1 | 191.55 | |
| | 56.54 | 0.4263 | 1 | 1 | 0 | 211.59 | |
| | 62.7 | 1.3127 | 0 | 1 | 3 | 70.86 | |
| | 67.9 | 0.7202 | 1 | 1 | 2 | 132.98 | |

The strain on the lattice is calculated using Williamson-Hall equation that states the relationship between widening diffraction peaks and crystallite size (L) and lattice strain ($\eta$) [17]:

$$\frac{\beta_{1/2}\cos\theta}{\lambda} = \frac{0.9}{L} + 2\eta\left(\frac{2\sin\theta}{\lambda}\right) \quad (2)$$

where $\beta_{1/2}$ is FWHM (rad), 0.9 is Scherer constant, θ is angle of diffraction peaks, and $\eta$ is lattice strain from the sample. Strain value calculation of the samples is determined from the value of gradient line extrapolation plotted for graphs K versus $\Delta$K, as shown in Fig. 3. The values of K and $\Delta$K are expressed by the following equation:

$$K = \left( \frac{2 \sin \theta}{\lambda} \right) \tag{3}$$

$$\Delta K = \frac{\beta_{1/2} \cos \theta}{\lambda} \tag{4}$$

Results of plotted graph of Williamson-Hall equation are shown in Fig. 3. Results of lattice strain calculation from N-ZnO samples are ηN4 = 0.0013, ηN6 = 0.0096, ηN8 = 0.0064 and ηN10 = 0.0068 respectively. The fourth variation of the N doping generated positive strain value (η), this indicates that the samples produced using spray coating technique experienced tensile strain. These results also indicate the presence of nitrogen with atomic size larger than that of oxygen (atomic radius N = 65 pm and O = 60 pm), which causes the lattice of ZnO to become larger and hence, the lattice strain.

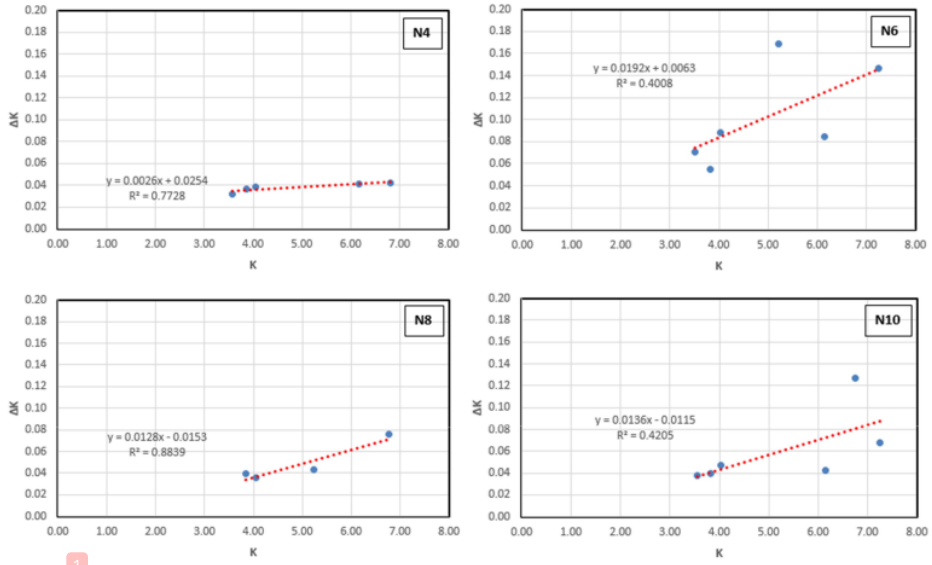


Fig. 3. Williamson–Hall plot of N-ZnO thin films with varied N percentage.

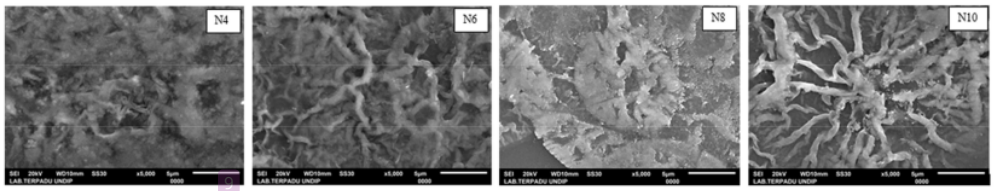


Fig. 4. SEM images of N-ZnO thin films with varied N percentage.

**SEM Analyses.** Morphology analysis by SEM in Fig. 4 shows that N-ZnO thin layer has a surface morphology that looks like a rod. The number of patterns increases along with the addition of N doping, but there is a difference in the percentage of N8 that forms a ring-shaped colony. These resulting morphological patterns correlate with the XRD diffraction patterns of samples. The sample of N-ZnO with 8% N doping (N8) has a poor pattern, but the one with 10% N doping has a good pattern. Different concentrations of added nitrogen promote a competition between nitrogen and oxygen when nucleation occurs. The root-like morphological pattern was made possible as pattern formation follows the pace and direction of the sprayed precursor vapor on the substrate. The regular rod-like pattern also shows crystallization process from the vapor phase to the solid phase. These results were confirmed with XRD test results.

**Optical Properties.** Absorbance test using UV-Vis spectrophotometer was used to analyze the band gap energy of N-ZnO samples using the Tauc equation as follows:

$$\alpha h\nu = A\left(h\nu - E_g\right)^{1/2} \quad (5)$$

where h is Planck's constant, v is light velocity, and Eg is energy gap. Fig. 5 shows the resulting plot equation (4) obtained from sample energies N4 = 3255 eV, N6 = 3249 eV, N8 = 3311 eV and N10 = 3278 eV. All nitrogen-doped ZnO samples have values of band gap energy smaller than those of ZnO without doping, which equals 3.352 eV. Narrowing band gap energies detected in samples show that nitrogen atom in the crystal matrix affects ZnO crystal growth [18]. In addition, the presence of N atoms forms an area between conduction band and valence band. This is because N atoms have valence atoms in the 2s orbital that act as acceptors. This is how band gap energy narrowing made possible. Results of band gap energy calculation also relate to morphology roughness of thin layers of N-ZnO, as confirmed with results of morphological SEM imaging (Fig. 4). This rough surface morphology leads to decreasing band gap energy.

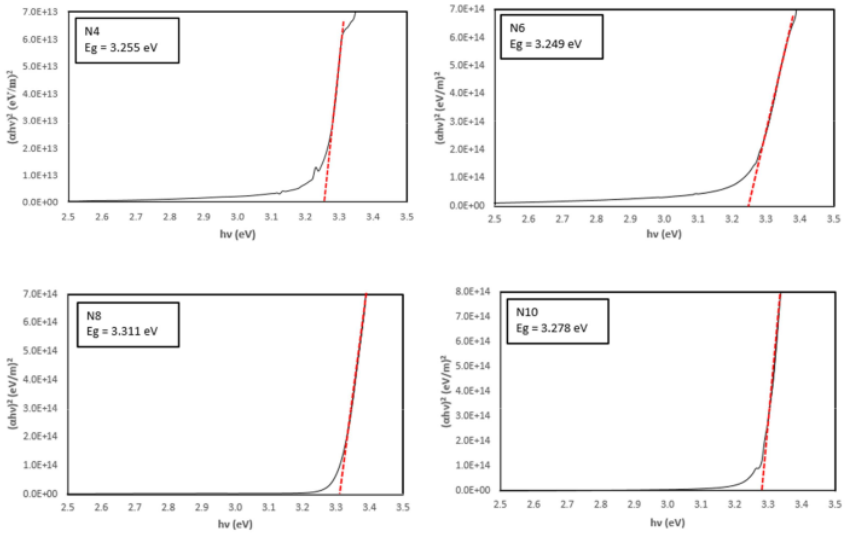


Fig. 5. Band gap energies of -ZnO thin films with varied N percentage.

## Summary

Deposition of a thin layer of N-ZnO has been successfully carried out by spray coating technique and showed polycrystalline structure with a dominant diffraction field (002). The entry of nitrogen atoms in the lattice of ZnO caused shifts in diffraction angle that range from 0.08° to 0.18°. The N10 sample showed better crystalline quality compared to the other samples of N-ZnO. A thin layer of N-ZnO deposition indicates the occurrence of tensile strain and the greatest value was observed in sample N6 with ηN6 = 0.0096. Surface morphology of thin layers of N-ZnO shows that the pattern formed is root-like, which is associated with the direction of deposition by spray coating technique. All samples have band gap energies lower than pure ZnO and the smallest was detected in sample N6 with Eg = 3.249 eV. The presence of nitrogen atom increases surface roughness and decreases band gap energy.

## Acknowledgment

The authors would like to thank the Ministry of Research and Higher Education of the Republic of Indonesia for funding this fundamental research with its grant scheme in 2017.

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