Systematic Variations in Structural and Photoluminescence Properties Produced in Zn Oxide Nanostructures by Cu (0-5)% Substitution

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Abstract:
Effects of Cu addition (0-5)% in ZnO are studied for structural and optical properties. The structural, photoluminescence properties and vibrational modes are strongly influenced with the Cu incorporation. Detailed investigations of the structural features of Cu doped ZnO nanostructures are reported. Our results show the systematic decrease in crystallite size (50.40 - 37.56 nm), lattice strain (1.82 - 1.49 micro), lattice stress (216.33 - 177.64 MPa) and energy density (196.78 - 132.69 KJ/m3) in the limit of small dopant concentration (0 < Cu ≤ 0.02). Decreasing trends are attributed to the smaller ionic size of Cu in comparison of Zn. Beyond Cu= 0.02 an increasing trend was noticed in crystallite size (41.67 - 70.67 nm), lattice strain (1.90 – 3.11 micro), lattice stress (226.32 – 369.35 MPa) and energy density (215.40 – 573.67 KJ/m3). This increase in structural parameters is attributed to segregation of secondary phases for Cu content increase beyond 0.02. Two prominent regions in PL spectra were observed and the deconvolution of these regions show a strong correlation with the structural changes observed within the limit of high and low dopant concentration. The FTIR spectra show shift of Zn-O vibrational mode toward higher frequency with increasing Cu concentration.

Keywords: Cu induced effect, Morphologies, Nanostructures, Photoluminescence, Structural variations, Vibrational modes.

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Introduction

There are several studies have been reported for pure and metal doped zinc oxide (ZnO) because of its unique and fascinating properties. This material has a prime technological significance due
to several applications: including optoelectronic devices, spintronic and piezoelectric devices, solar cells, LEDs, photodetectors and gas sensors. These features have been a continuous source of motivation for researchers to explore the possible use of these materials in industrial applications. ZnO is normally considered to be a wide band gap semiconducting oxide (3.40 eV) and it has a large exciton binding energy (60 meV). Due to the larger exciton binding energy, it can emit more ultraviolet phosphor than GaN (21-25 meV), which in turn leads to lower ultraviolet lasing threshold and higher ultraviolet emitting efficiency. Therefore, it is important to study that how the structure of this material can be modified according to the need for manufacturing devices, which is the interest of this research. It has been reported that the physical and chemical properties of ZnO can be tailored with the transition metals (Fe, Mn, Co, Ni and Cu) doping. But Cu is very significant dopant in ZnO because of the similar ionic radii and high electrical conductivity. The doping of Cu in ZnO can enhance its chemical and physical properties. So, it is very important to study more deeply the structure related properties such as crystallite size, strain, stress and energy density. Scherrer approach is very simple to calculate the crystallite size of nanomaterials from the peak width of the XRD spectrum. Beside this, the peak broadening of XRD is the convolution of two factors (crystallite size and lattice strain) and it could be due to several effects such as defects, grain boundaries and instrumental broadening. Williamson-Hal (W–H) consider these effects and this approach gives more realistic estimations for crystallite size and micro-strain. There are several analytical methods to calculate the crystallite size and micro-strain of the materials. The curve fitting on diffraction data of the samples is complicated, according to the Warren–Averbach approach the intensity of the XRD beam is estimated in Fourier space which is based on the combine effect of crystallite size and strain. But the intensity of the peaks can vary with the quantity of the sample placed in the sample holder. On the other hand, W–H approach is simple in which the crystallite size and strain can be estimated from XRD peak as the function of $2\theta$. The overall peak broadening is due to convolution of these two effects (crystallite size and strain) and is given as.

$$\beta = \beta_s + \beta_D$$

where $\beta_s = 0.89\lambda/DCos \theta$ represent the broadening due to crystallite size and $\beta_D = 4 \epsilon tan \theta$ represent the broadening due to strain induced.
In this work we accurately estimate the structure related properties by considering above mentioned effects in the peak broadening. The modified W–H method like Uniform Deformation Model (UDM), Uniform Deformation Stress Model (UDSM) and Uniform Deformation Energy Density Model energy density (UDEDM) were employed to study the strain, stress and energy density of the samples. Interestingly, the structural variations are in correlation with optical properties and morphological changes in Cu doped ZnO samples.

Materials and Method:

In the present study, Zinc nitrate hexahydrate \([Zn(NO_3)_2 \cdot 6H_2O]\), Copper nitrate trihydrate \([Cu(NO_3)_2 \cdot 3H_2O]\), Sodium hydroxides \([NaOH]\) and double distilled deionized water were used for the synthesis of pure and Cu doped ZnO nanostructures. All chemicals were of analytical grade and used here without any further purification. The values of molecular weights for the metal precursor and NaOH are given in Table 1.

Table 1: The molecular weight of the samples taken during the reaction.

| Samples               | Sample codes | \(Zn(NO_3)_2 \cdot 6H_2O\) (g/mol) | \(Cu(NO_3)_2 \cdot 3H_2O\) (g/mol) | \(NaOH\) (g/mol) |
|-----------------------|--------------|----------------------------------|-----------------------------------|------------------|
| Pure ZnO              | C0Z          | 14.8745                          | 0.00                              | 4.00             |
| 1% Cu doped ZnO       | C1Z          | 14.7258                          | 0.1208                            | 4.00             |
| 2% Cu doped ZnO       | C2Z          | 14.5770                          | 0.2416                            | 4.00             |
| 3% Cu doped ZnO       | C3Z          | 14.4283                          | 0.3624                            | 4.00             |
| 4% Cu doped ZnO       | C4Z          | 14.2795                          | 0.4832                            | 4.00             |
| 5% Cu doped ZnO       | C5Z          | 14.1308                          | 0.604                             | 4.00             |

The 0.1M solution for the metal precursor and the 0.2M solution for NaOH were prepared in 400 ml and 100 ml of double distilled deionized water respectively. The synthesis process for the growth of the samples comprises of five steps. First, the desired amounts of precursor (Zinc nitrate and Copper nitrate) were taken in a flask. Thereafter sodium hydroxides (precipitating agent) was added drop wise with heating and the continuous stirring for 5 hours until a precipitate was formed. The precipitate was washed several times with deionized water and dried at 80 °C for 24 hours. Finally, the nanoparticle samples were annealed at 300 °C for 3 hours.

Results and Discussion:

Figure 1(a) shows the SEM image of C1Z sample indicating its rod-like morphology. This morphology is more clearly visible in the TEM image of the sample as depicted in Fig. 1(b). Similar rod-like morphology was also observed for other samples in the limit of low concentrations (Cu = 0.02) in ZnO (all images not shown). The morphology of Cu doped ZnO samples remains
largely un-altered up to 2% Cu. This we attribute to the Cu substitution at the Zn lattice sites without significantly affecting ZnO crystal structure. This is further supported by the XRD results and which confirmed the phase purity of the sample in the low concentration regime (see Fig.2). It is also clear from electron microscopy images that the observed rod-like nanostructures are homogeneous and uniformly distributed. We have noticed that with increasing Cu concentration, the morphology of the sample changes from rod-like to flower-like. This transformation of the morphology was observed in the concentration range (3-5)% Cu in ZnO. Figure 1(d) and Fig. 1(e) show SEM and TEM images for C4Z sample respectively. The high-resolution transmission electron microscopy (HRTEM) images of C1Z and C2Z samples are shown in Fig.1 (c) and Fig. 1(f), respectively. Clearly the nano-rods and nano-flowers are largely single crystalline. The values of lattice spacing for C1Z sample is found to be 0.25 nm, which corresponds to the $d_{101}$ spacing of ZnO. While the obtained values of lattice spacing for C4Z sample is about 0.28 nm, which corresponds to the $d_{100}$ value of the samples. The crystallinity of the samples is also confirmed from the XRD results and the results exhibited the sharp peaks in accordance with the standard XRD pattern of ZnO (see Fig.2). In a previous work, we proposed a model to explain the dopant induced morphological changes in ZnO nanoparticles. In this picture, the hexagonal morphology is due to selective nucleation of ZnO crystallites in certain crystallographic directions. The nucleation along [0001] direction from rod-like and [01$\bar{1}$0] directions form flower-like nanostructures.
Figure 1. The right panel shows the SEM image (a), the TEM image (b) and the HRTEM image (c) for C1Z sample and the left panel shows the SEM image (d), the TEM image (e) and (f) the HRTEM image for C4Z sample.

The elemental and percentage mass compositions of the samples were examined by using the EDX technique. The findings are summarized in table 2. No trace of impurity could be identified in the samples within the detection limit of the EDX. The observed composition ratios are fairly consistent with the nominal compositions of the samples. EDX results showed that the stoichiometry of the samples during co-precipitation remain close to the desired composition.
Table 2: The elemental and percentage mass compositions of (0-5)% Cu doped ZnO.

| Sample codes | Expected Zn | Expected Cu | Observed Zn | Observed Cu | Observed O |
|--------------|-------------|-------------|-------------|-------------|------------|
| C0Z          | 1.0000      | 0.00        | 0.7938      | 0.00        | 0.2062     |
| C1Z          | 0.9900      | 0.0100      | 0.7860      | 0.111       | 0.2029     |
| C2Z          | 0.9800      | 0.0200      | 0.7562      | 0.209       | 0.2229     |
| C3Z          | 0.9700      | 0.0300      | 0.7641      | 0.298       | 0.2061     |
| C4Z          | 0.9600      | 0.0400      | 0.7760      | 0.406       | 0.1834     |
| C5Z          | 0.9500      | 0.0500      | 0.7390      | 0.512       | 0.2098     |

Figure 2 shows the XRD patterns of all the samples. The crystallite size of the samples was calculated from the peak (101) using Scherrer formula. The crystallite sizes of the samples were found to be decreasing from 28 nm to 19 nm for C0Z and C2Z samples respectively. Beyond this, the particle size gradually increases up to 24 nm for the C5Z sample. The intense and sharp peaks indicate the high crystalline quality of our samples. These peaks revealed the hexagonal wurtzite structure having the space group P63mc. The XRD data confirm high phase purity up to 2% of Cu concentration in ZnO. No traces of Cu related phase have been detected below 2% Cu doping. Beyond 2%, an additional small peak is observed (near $2\theta = 37^\circ$) which slightly increases in intensity with increasing Cu concentration. This peak was identified as secondary CuO phase which forms due to unreacted of Cu$^{+2}$ ions present in the samples.

Figure 2: The XRD spectra of (0-5)% Cu doped ZnO samples. The phase purity is disturbed with the higher dopant concentration which confirmed the solubility limit of the dopant.
It has been shown that the peak positions of Cu doped samples exhibit the slight shift towards lower $2\theta$ values with increasing the Cu concentration in the ZnO samples. Peak broadening and shifting with Cu doping in ZnO has been shown to be a signature of the successful Cu$^{+2}$ substitution at the Zn$^{+2}$ sites in the ZnO host structure. Similar behavior is observed in our Cu doped ZnO samples. In a next step, we systematically investigate the peak broadening and peak shifting observed in our samples using W–H methods viz., UD, UDS and UDED models. In our approach, the observed variations in peak width as a function of $2\theta$ are used to differentiate between the strain and size induced broadening.

In an isotropic crystal, lattice strain is assumed to be uniform in all crystallographic directions. In UD-model, the strain produced in the samples due to crystal defects is calculated from the equation

$$\beta \cos \theta = \frac{K\lambda}{D} + 4 \epsilon \sin \theta \quad (2),$$

where $\beta$ is the full width of the Bragg peak at the half maximum (FWHM), $\theta$ is peak angle, $D$ is mean crystallite size and $\epsilon$ is strain. The values of crystallite size and strain were estimated from the linear fitting of the $\beta \cos \theta$ vs $4 \sin \theta$ plot for our Cu (0-5 %) doped ZnO nanostructures (Figure 3 (left panel)). The strain is produced due to Cu as a dopant as well as oxygen vacancies, was not considered in the Scherrer estimation. The values of lattice strain and particle size of the samples as estimated using the UD model are given in table 3.

In the US model, the anisotropic nature of the crystal, i.e., variations in the strain in different crystallographic directions is taken into account. The small value of stress and strain produce in the samples are estimated using Hook’s Law: $\sigma = Y_{hkl} \epsilon$, where $\sigma$ is stress and $Y_{hkl}$ is Young’s modulus. Hence, according to the US model equation (2) is modified as:

$$\beta \cos \theta = \frac{K\lambda}{D} + 4 \frac{\sigma}{Y_{hkl}} \sin \theta \quad (4)$$

The following relation is used to estimate Young’s modulus for the hexagonal crystal.

$$Y_{hkl} = \frac{(h^2 + \frac{(h + 2k)^2}{3} + \frac{(al)^2}{c^2})^2}{S_{11}(h^2 + \frac{(h + 2k)^2}{3})^2 + S_{33}(\frac{al}{c})^4 + (2S_{13} + S_{44})(h^2 + \frac{(h + 2k)^2}{3})(\frac{al}{c})^2} \quad (5),$$
where $S_{11}$, $S_{13}$, $S_{33}$ and $S_{44}$ are the elastic compliances for the hexagonal lattice (ZnO) with the values of $7.858 \times 10^{-12}$, $-2.206 \times 10^{-12}$, $6.940 \times 10^{-12}$ and $23.57 \times 10^{-12}$ m$^2$ N$^{-1}$, respectively. The estimated value of $Y_{hkl}$ for our samples is found to be $1.189 \times 10^{11}$ N/m$^2$. The values of stress, strain and size were calculated from the plot of $4 \frac{\sin{\theta}}{Y_{hkl}}$ vs $\beta \cos{\theta}$ are tabulated in table 2. The USD plot of Cu (0-5 %) doped ZnO nanostructures are shown in Fig. 3 (middle panel).

The values of energy density ($U$) and the strain for an elastic system is estimated from the equation,

$$U = \frac{\varepsilon^2 Y_{hkl}}{2}.$$  

Using this relation in the equation (2) leads to the equation for the UDE model:

$$\beta \cos{\theta} = \frac{K \lambda}{D} + 4 \sin{\theta} \left(\frac{2U}{Y_{hkl}}\right)^{1/2} \quad (7).$$

The crystallite size and energy density were determined from the plot between $\beta \cos{\theta}$ and $4 \sin{\theta} \left(\frac{2U}{Y_{hkl}}\right)^{1/2}$ as shown in Figure 3 (the right panel). The values calculated for strain, stress, size and energy density are tabulated in table 3.
**Figure 3:** The UDM plot (see the left panel), the USDM plot (see the middle panel) and the UDEDM plot (see the right panel) for (0-5)% Cu doped ZnO samples.

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Calculated values of crystallite size from W-H models are found to be larger than the one estimated from the Scherrer equation. However, the variations in the values of crystallite size estimated from both methods are in good correlation. A number of factors, such as lattice strain, stress, crystalline imperfections, grain boundaries and dislocations are responsible for the variations in crystallite size. These effects give rise to the observed broadening of the XRD peaks as were also reported in other studies. In Scherrer procedure only the peak broadening due to crystallite size is considered. This greatly oversimplified view results in low values of crystallite size as compared to the one we have estimated from W-H method. Furthermore, it has been shown that in W-H method, the crystallite size estimation may also depend on the number of experimental data points taken for the linear fit. This explains the observed quantitative differences between the crystallite size as estimated from WH-method and Scherer formula. We believe that WH-method provides better estimate of the crystallite size and because of its realistic approach it should be preferred over the simplified Scherer formula. The values of crystallite size and lattice strain were found to be decreasing with increasing Cu concentration up to 2% and then show the increase with increasing Cu concentration up to 5% (see Fig. 4). Similar variations in the energy density and lattice stress are also observed with increasing Cu concentration in ZnO samples (See table 2). As we have mentioned previously the morphology of the samples also exhibit a change from rod-like {for (0-2)% Cu} to flower-like {for (3-5)% Cu doped} due to the structural changes in the ZnO nanostructures with the incorporation of metallic Cu additive. Therefore, the interesting correlation is found between the morphological transformations and structural variations with increasing Cu concentration in ZnO samples.

Table 3: The estimated values of strain, stress, energy density and crystallite size from UDM, USDM and UDEDM are presented.

| W-H Models | UDM | USDM | UDEDM |
|------------|-----|------|-------|
| Sample codes | $\varepsilon \times 10^{-3}$ | $\sigma$ (MPa) | $\varepsilon \times 10^{-3}$ | $\sigma$ (MPa) | $\varepsilon \times 10^{-3}$ | $\sigma$ (MPa) |
| $\text{C}_0\text{Z}$ | 1.82 | 216.33 | 1.82 | 216.33 | 1.82 | 216.33 |
| $\text{C}_1\text{Z}$ | 1.77 | 210.29 | 1.77 | 210.29 | 1.77 | 210.29 |
| $\text{C}_2\text{Z}$ | 1.49 | 177.64 | 1.49 | 177.64 | 1.49 | 177.64 |
| $\text{C}_3\text{Z}$ | 1.90 | 226.32 | 1.90 | 226.32 | 1.90 | 226.32 |
| $\text{C}_4\text{Z}$ | 2.86 | 339.55 | 2.86 | 339.55 | 2.86 | 339.55 |
| $\text{C}_5\text{Z}$ | 3.11 | 369.35 | 3.11 | 369.35 | 3.11 | 369.35 |

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Figure 4: The plot for the crystallite size and the strain vs Cu concentration.

The photoluminescence spectra of (0-5) % Cu doped ZnO samples are shown in Fig. 5. Two prominent peaks were observed in the photoluminescence spectra of all samples indicating emission in two regions: one region is ranging from 350 to 500 nm and the other is from 500 to 700 nm. In the first region, the values of wavelength are found to be 380 nm, 386 nm, 400 nm, 392 nm, 388 nm and 384 nm for all samples with respect to dopant concentration. The corresponding values of band gap energies for these samples are 3.23 eV, 3.21 eV, 3.10 eV, 3.16 eV, 3.19 eV and 3.22 eV. The observed peaks in the spectrum arise due to the superposition of multiple peaks originating from different factors. In the case of pure ZnO, the first peak was observed at 380 nm (3.23 eV) and it is deconvoluted with two possible Gaussian peaks G1 and G2. The G1 and G2 peaks reveal two emission bands at 368 nm and 414 nm respectively. Similarly, the deconvolution of the second peak yields three Gaussian peaks G3, G4 and G5 corresponding to three emission bands at 518 nm, 589 nm and 645 nm respectively. These variations in photoluminescence intensity are attributed to the Auger recombination process of non-radiative transitions. In this process, the released energy of one electron is absorbed by the other during the interaction and the
excess amount of energy losses transferred to the thermal vibration (phonons). These results revealed that the photoluminescence intensity, crystallite size, strain and the optical band gap undergoes a transition near 2% Cu doped ZnO sample.

![Figure 5](http://jn.wum.edu.pk)

**Figure 5:** PL spectra of (0-5)% Cu doped ZnO samples along with Gaussian fitting within the two prominent peaks from experimental data.

Different types of transmission bands in C0Z sample were described with the help of the proposed energy band diagram as shown in **Fig.6**. In the first region, G1 at 368 nm (3.37 eV) attributes to the weak UV emission band which indicates the band-to-band transition. The G2 at 414 nm (3.00 eV) indicates blue emission due to trapped electron recombination at the shallow levels of the \(Zn_i\) interstitials. According to linear muffin-tin orbital method, such type of transition from \(Zn_i\) level to the valence band in ZnO has been reported near 3.1 eV. In the second region, the G3 at 518 nm (2.39 eV) corresponds to the green emission band. There are two possible reasons for this emission: (i) the green emission at 518 nm is due to the recombination of trapped holes to singly ionized Zn vacancy acceptor-level (\(V_{Zn}^-\)) with trapped electrons at the donor \(Zn_i\) level, (ii) this emission is due to the singly ionized oxygen vacancy in ZnO samples such as the transition between singly ionized
oxygen vacancy ($V_{O}^+$) and the holes (photo generated). The G4 fitting at 589 nm (2.11 eV) shows the orange emission which is due to the transition between the free electron and the hole at $O_i$ level. The peak G5 at 645 nm (1.92 eV) shows the red emission line which is due to the transition of the trapped electron at $Zn_i$ level to hole at $O_i$ level. Similarly, photoluminescence spectra of pure and Cu doped ZnO samples show different types of transition bands as listed in Table 4.

**Figure 6:** Proposed energy level diagram of the C0Z sample with possible transition level.

**Table 4:** The photoluminescence (PL) analysis of pure and Cu doped ZnO samples. The first PL peak is deconvoluted with two Gaussian peaks G1 and G2 and the second PL peak is also deconvoluted with the three Gaussian peaks G3, G4 and G5. These transitions are responsible for the different emission bands in the samples.
The variations in the PL intensity originate due to the presence of Cu additives in the host material. In order to further elucidate this, a graph of the crystallite size and PL intensity (the second peak) verses dopant concentration is shown in Fig. 7. Clearly, a good correlation is visible for both crystallite size and PL intensity. This correlation is well supported to the structural and morphological transition near 2% Cu.

![Graph showing correlation between crystallite size, PL peak II, and Cu concentration.](image)

**Figure 7:** The plot for the crystallite size and PL intensity versus Cu concentration.

The FTIR spectra of (0-5) % Cu doped ZnO samples are shown in Fig. 8. The peaks in FTIR spectra ranging from 400 to 700 cm$^{-1}$ indicate the stretching modes of metal and oxygen. The FTIR spectra of the samples indicate stretching modes at 490 and 493 cm$^{-1}$ of Zn-O bonds. The observed vibrational frequencies of metal and oxygen bonds for (2-5%) Cu doped ZnO samples are 496 cm$^{-1}$.

| Sample codes | Gaussian fitting | Region I (350-500nm) | Region II (500-700nm) |
|--------------|------------------|----------------------|-----------------------|
|              |                  | Weak UV Emission Band (nm)-(eV) | Near UV Emission Band (nm)-(eV) | Green Emission Band (nm)-(eV) | Orange Emission Band (nm)-(eV) | Red Emission Band (nm)-(eV) |
| C0Z          |                  | (368)-(3.37)         | (414)-(3.00)          | (518)-(2.39)         | (589)-(2.11)         | (645)-(1.92)         |
| C1Z          |                  | (377)-(3.29)         | (405)-(3.06)          | (535)-(2.32)         | (584)-(2.12)         | (638)-(1.94)         |
| C2Z          |                  | (378)-(3.28)         | (406)-(3.05)          | (540)-(2.29)         | (605)-(2.05)         | (639)-(1.94)         |
| C3Z          |                  | (378)-(3.28)         | (406)-(3.05)          | (527)-(2.35)         | (573)-(2.16)         | (636)-(1.94)         |
| C4Z          |                  | (378)-(3.28)         | (406)-(3.05)          | (514)-(2.41)         | (573)-(2.16)         | (637)-(1.95)         |
| C5Z          |                  | (368)-(3.37)         | (405)-(3.06)          | (506)-(2.45)         | (566)-(2.19)         | (630)-(1.96)         |
1, 496 cm\(^{-1}\), 500 cm\(^{-1}\) and 513 cm\(^{-1}\). It was observed that, incorporation of Cu results in the slight shift of the Zn-O stretching modes toward the higher frequency as compared to the pure ZnO sample. The shift towards higher frequency is due to the substitution of a lighter atom Cu at Zn sites. Hence, the observed shift in the stretching modes is in excellent agreement with our structural analysis. The vibration frequencies from 679 – 697 cm\(^{-1}\) correspond to the weak bonds which were due to the variation in microstructure of Zn-O samples with increasing Cu contents in the samples. The two major peaks in FTIR spectra viz., one varying from 1172–1195 cm\(^{-1}\) and other from 3206–3292 cm\(^{-1}\) of pure and Cu doped ZnO samples indicate the O-H stretching vibration of water molecules. This we attribute to the atmospheric moisture. The peak corresponds to the vibrational frequencies ranging from 1306 to 1448 cm\(^{-1}\) show Zn-OH bending vibration modes.
Figure 8: The plot of transmittance vs the wave number for (0-5)% Cu doped ZnO samples.

Conclusion:
To summarize, several interesting correlations between optical, morphological and structural features of Cu doped ZnO nanoparticles were observed. In particular, doping of Cu triggers an interesting morphological transition from rod-like to flower-like nanostructures. X-ray diffraction revealed that the hexagonal wurtzite crystal of our ZnO samples. The crystallite size was estimated from Scherer formula (e.g., 28 nm for C0Z sample) found different significantly from the one estimated by the W-H procedure (e.g., 50.40 nm for C0Z sample). However, both yields
qualitatively similar trends for the crystallite size vs. Cu concentration. Crystallite size was found to be decreasing with increasing Cu concentration up to 2%. Beyond 2%, the further addition of Cu results in a slight increase in crystallite size. Three models of W-H method were employed to estimate the micro strain, stress and energy density of the samples. The values of these results were found to vary in similar manner as observed for the crystallite size of the samples. FTIR spectra of the samples reveal that the presence of Cu is responsible for slight shifts in the Zn-O stretching modes toward higher frequencies such as 490 cm\(^{-1}\) for pure ZnO and 513 cm\(^{-1}\) for 5% Cu doing. The optical results revealed that the band gap decreases for low dopant concentration up to 2% and it is slightly increases with further the Cu addition. Structural and optical studies revealed a strong correlation between the band gap energy and sample morphology. These Cu induced effects in the sample suggest that this systematically variation in structural and optical properties of ZnO can be used for opto-electronic applications.

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