Simulation, synthesis and band-gap engineering of 2nd group doped ZnO nanostructures

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Abstract
Nano-materials are considered as a fundamental constituent in almost every field of medical science to engineering. However, the field of application of nano-material largely depends on its structural, chemical and optical properties of nano-material. Doping of nano-materials results in changes their particle size and band-gap which affects its applications. In this work, the effect of change in band-gap and particle size has been studied for 2nd group element doped ZnO (Zinc Oxide) nanostructures synthesized on AAO (Anode Aluminum Oxide) template having a pore size of 180.5 nm fabricated using chemical bath deposition and Anodization respectively. Fuzzy logic rule based system is used to study the effect of 2nd group element doping in ZnO nano-structure fabricated on AAO template with a fix pore size on the band-gap and output nanostructure. With addition of 2nd group element in ZnO nano-structure, a variation in rod length and band-gap has been observed. A decrease of rod length and an increase in band-gap have been observed by the addition of 2nd group including Be, Mg, Ca and Sr elements in ZnO nano-crystal. The fuzzy logic results are in accordance with the experimental system which shows the effectiveness of the simulations.

1. Introduction
Advancement in the field of research based on material is gaining enormous attention owning to their excellent application [1, 2]. Materials are classified as an important aspect in electronics as well as medical and communication applications [3]. However, the application largely depends on the properties of the material. Materials are classified as bulk materials and micro and nano scale materials. Bulk materials give less surface area to volume ratio which makes them unsuitable for small scale application [4]. Micro and nano scale materials are getting huge attention in research domain owning to their superior electrical, structural, chemical and optical properties [5]. These materials provide excellent surface area to volume ratio which makes them suitable for small scale application including MEMS (Micro-Electromechanical System) and NEMS (Nanoelectromechanical Systems) application [6].

Nano-materials are classified in various structures which give them privilege for applications in different branches of science. Nano-particles, nano-rods, nano-wires, nano-fibers and nano-flowers are some structures which give applications in the field of energy, medical, communication, gas sensing, filtration and photocatalysis [7–9]. Energy applications including solar cell, fuel cell and energy harvesters utilize semi-conductor nanostructures materials including TiO₂ (Titanium Dioxide), SnO₂ (Stannic Oxide) and ZnO [10–12]. Among these materials, ZnO is categorized as an efficient material owning to its transparency, lead-free biocompatibility, nano-structural formability, chemical stability, and coupled piezoelectric and semiconductor
properties [13, 14]. The piezo-electric behavior of ZnO makes it an excellent choice for energy harvesting applications [15]. Various methods are been opt to make doped ZnO nanostructures, including, hydrothermal, spin-coating, PVD (Physical vapour deposition), CVD (Chemical vapour deposition), chemical bath deposition, electrophoresis and dip-coating. Among various chemical methods, chemical bath deposition is considered as an effective method for reproducibility of the sample.

However, doping ZnO with other material, results a change in the structural and optical properties of ZnO. As ZnO is classified as an n-type semi-conductor material, doping it with more conductive material results in the change and variation in its optical and structural properties. As per periodic table, 2nd group elements are considered excellent elements for doping due to their higher conductivity and easy in-corporation in the atomic structure. On the other hand, ZnO with elevated band gap is considered a good candidate for applications in photocatalytic applications and photonic devices [16]. Recently, various researchers have worked on band gap

Figure 1. Fis diagram of input and output (a) Mg concentration (b) Ca concentration (c) Ca concentration (d) Be concentration.
engineering for its applications in photonic devices including light emitting diode [17]. For example, Pearton et al [18] reported the tuning and engineering of ZnO band-gap by adding V group element for application in photonic devices.

In this work, an analysis and simulation based study is performed for the optical and structural properties of ZnO with the addition of 2nd group element including Mg, Ca, Sr and Be in the nano-crystal of ZnO. 2nd group elements have broad range of ionic radii: Mg\(^{2+}\) (0.57 Å), Sr\(^{2+}\) (1.18 Å) and Ba\(^{2+}\) (1.35 Å). The tuning of the lattice structure and the band gap for the ZnO semiconductor can be achieved by using 2nd group element. Fuzzy Logic tool is used to analyze the effect of 2nd group element doping in ZnO nano-structure fabricated on AAO template with a fixed pore size on the band-gap and output nanostructure. The material is fabricated on AAO template for use in piezo-electric MEMS energy harvester.

2. Fuzzy analysis

Fuzzy analysis provides a parametric estimation for two or more parameters and their effect on the multiple outputs using the rules defined based on real conditions. The Model used for the simulation is MAMDANI model owing to its ability to provide a value of output based on the variation in input. For fuzzy analysis to check the effect of 2nd group element doping on ZnO nano-structure, AAO pore size and process temperature and its effect on nano-rod length and band-gap. Three inputs and two outputs are taken in this work. 2nd group element doping concentration, chemical bath deposition temperature and AAO template pore size are taken as input while band-gap and Rod length is taken as output. The FIS figure for the input and output for all the simulations performed for Mg, Sr, Be and Ca doping is shown in figure 1.

Three membership functions and ranges of the input and output are defined in the next stage of the fuzzy analysis. The membership function of the inputs of 2nd group element doping in ZnO nano-structure, CBD temperature and AAO template pore size is taken as small, medium and large. The range for Mg, Ca, Sr and Be doping with ranges of 0%–10%, CBD Temperature in range of 75–95 °C and AAO template pore size in taken in range of 150–200. The membership function of the output Band gap and Rod length is taken as low, medium and high with ranges of 3.2–4 eV and 100–200 nm respectively. On the basis of real time data, 27 rules are set for the input and their effect on the corresponding outputs has been added. The 3D (Three-Dimensional) graphs in figure 2 shows the effect of Mg doping, CBD temperature and AAO template pore size on the output band-gap and rod length. Larger the Mg doping more is the rod length due to addition of Mg in ZnO nano-crystal and small atomic size of magnesium atom as compared to ZnO. However, Band-gap increases because of the high conductive nature of Mg. The AAO pore size provides more aligned Mg doped ZnO nano-rods with larger
length. More the pore size of the AAO membrane more will be the rod length and decreases in the band-gap. Larger the temperature of chemical bath deposition, more aligned nano-rods with larger length and low band-gap are seen. The investigated Eg results in the case of conventional CBD method were in well agreement with other previous works [19].
Similar trend is shown for Be, Ca and Sr doping in ZnO. The 3D graphs of input and output for Be doped ZnO nano-structures are shown in figure 3. No major effect on nano-rod length has been seen with Be doping. However, a slight change in Bandgap has been observed due to high conductive nature of Be. With increase in pore size of AAO membrane and CBD temperature, the nano-rod length increase because more aligned nano-rods is fabricated \[19\].

The 3D graphs of input and output for Ca doped ZnO nano-structures and Sr doped ZnO nanostructures are shown in figures 4 and 5 respectively.

Due to change in Ca concentration a change in band-gap is observed after 3% doping as shown in figure 4 (a). This abnormal behaviour can be attributed to themodification of structural defects caused by the presence of Ca in the ZnO matrix. Nano-rod length gradually increase with the addition of Calcium in the ZnO nano-crystal. Chemical bath time and AAO pore size shows similar trend as seen in figure 2.

With addition of Sr in ZnO nano-crystal the band-gap initially increase but then started decreasing after 6% doping of Sr in ZnO as shown in figure 5. This effect is due to the the substitution of Sr in Zn which generates a non-linear defects due to the large difference in atomic size between Zn and Sr and reduces oxygen vacancies. Chemical bath time and AAO pore size shows similar trend as seen in figures 2 and 3.

The calculated and simulated values of the fuzzy based model are then compared using MAMDANI model. The input of nano pore size is fixed at 180 nm, temperature of chemical bath deposition is set at 95 °C and Mg, Sr, Ca and Be doping is set at 2%. The MAMDANI model formula is used to calculate the calculated value using formula in equation (1),

\[
\text{MAMDANI Model} = \frac{\sum \text{Mi} \times \text{Si}}{\sum \text{Mi}} \times 100
\]

Where Mi is the minimum membership function value calculated from the crisp value from rule viewer and 3D graphs and Si is the singleton value of the output based on the input and rules selected.

Table 1 shows the simulated and calculated value of band-gap and rod length based on the simulations performed for 2nd group doped ZnO nano-structures.

The error is less than 2% which shows the accuracy of the system. The result provides a way to estimate the parameter of input concentration to get the required output. For the verification of the simulation results, it is compared with the experimentally synthesized 2nd group element doped ZnO nano-rods on AAO template.
3. Materials and methods

3.1. Preparation of anodic aluminum oxide template

The PAO (Porous Aluminum Oxide) template was prepared by using 2 steps anodization. 0.4 M solution of oxalic acid was used as an electrolyte and aluminum substrate was used as a cathode and lead rod was used as an anode. The two steps differ from each other on the basis of the applied voltage between the electrodes and the time for which the voltage has been applied. The 1st step of anodization also known as mild anodization utilizes 38 V for 20 min, which was gradually increased to 120 V. For 15 min it was kept at 120 V. The substrate after 1st step of anodization is etched using 4% Phosphoric Acid ($\text{H}_3\text{PO}_4$) and Chromic Acid ($\text{H}_2\text{CrO}_4$) for 20 min at 80°C. For 2nd step of anodization also known as hard anodization, 110 V is applied for 4 h. After the process of anodization, barrier layer is removed by changing the electrolyte to 0.3 M KCl solution and by applying a negative voltage for 6 min. The prepared substrate was then etched in Mercuric Chloride ($\text{Hg}_2\text{Cl}_2$) solution for 15 min. The prepared substrate was then used as a template to fabricate ZnO nanostructures and 2nd group element doped ZnO nanostructures.

3.2. Preparation of ZnO and 2nd group element doped ZnO Nanostructures

Dodecanthiol, Zinc Acetate di-hydrate, Hexamine, Magnesium Acetate, Calcium acetate, Strontium acetate, Beryllium acetate, ethanol and DI (Deionized) water was used for the preparation of ZnO and 2nd group element doped ZnO nanostructures. The prepared AAO template was initially pre-treated with Dodecanthiol which provide better sticking of nanostructures on AAO template. 1 ml of Dodecanthiol ($\text{C}_{12}\text{H}_{26}\text{S}$) was dissolved in 100 ml of Ethanol ($\text{C}_2\text{H}_5\text{OH}$) with continuous stirring for 15 min at room temperature. The AAO template was then dipped into the prepared solution for two hours. The pre-treated film was then subjected to drying at 60°C–70°C in air. 5 samples were prepared for ZnO and 2nd group element doped ZnO nanostructures using chemical bath deposition. For ZnO nanostructures, 20 mM solution of Zinc Acetate di-hydrate and Hexamine was prepared in DI water. The solution and the pre-treated AAO template were then inserted in Chemical bath deposition for 6 hours at 95°C and under continuous stirring. After the deposition process, the samples were washed using DI water, followed by annealing at 400°C. For the preparation of Mg doped ZnO nanostructures, 2% Magnesium Acetate solution was added in the 20 mM solution of Zinc Acetate di-hydrate and Hexamine prepared in DI water. For calcium doped ZnO, 2% of calcium acetate for strontium doped ZnO, 2% strontium acetate for beryllium doped ZnO, 2% beryllium acetate was added to the 20 mM solution of Zinc Acetate di-hydrate and Hexamine prepared in DI water for chemical bath deposition.

3.3. Characterization

The prepared AAO template, ZnO nanostructures on AAO template and 2nd group element doped ZnO nanostructures on AAO template was characterized using scanning electron micro-scopy, Energy Dispersive X-ray spectroscopy, X-ray diffraction and Ultra-violet-visible spectrophotometer. The SEM (Scanning Electron Microscope) was used to study the structure and morphology of the prepared substrates, X-ray Diffraction (XRD) for analysis of the crystallographic structure of a material, Energy Dispersive X-ray spectroscopy (EDX) to analyze the chemical composition and Ultra- violet-visible spectrophotometers provide an analysis on the variation of absorbance and band-gap of the prepared films.

### Table 1. Comparison between Simulated and Calculated Value.

|                          | Simulated Value | MAMDANI Calculated Value | Error |
|--------------------------|-----------------|--------------------------|-------|
| **Mg doped ZnO nano-structures** |                 |                          |       |
| Band-Gap (eV)            | 3.65            | 3.67                     | 0.54  |
| Rod length (nm)          | 181             | 183                      | 1.09  |
| **Be doped ZnO nano-structures** |               |                          |       |
| Band-Gap (eV)            | 3.71            | 3.74                     | 0.80  |
| Rod length (nm)          | 185             | 187                      | 1.06  |
| **Ca doped ZnO nano-structures** |             |                          |       |
| Band-Gap (eV)            | 3.49            | 3.51                     | 0.57  |
| Rod length (nm)          | 167             | 170                      | 1.76  |
| **Sr doped ZnO nano-structures** |             |                          |       |
| Band-Gap (eV)            | 3.41            | 3.44                     | 0.87  |
| Rod length (nm)          | 164             | 166                      | 1.20  |
4. Results and discussion

The structural analysis of the prepared nano-porous anodic aluminum oxide membrane is analyzed using scanning electron microscopy. The SEM images in figure 6 show ordered nano-porous membrane of AAO. Highly ordered, uniform and even layer of nano-pores membrane of anodic aluminum oxide is created after the two step of anodization. Average pore size of the prepared nano-porous film is approximately equals to 180.5 nm.

The Energy Dispersive X-ray spectroscopy (EDX) Spectrum in figure 7 shows that a highly pure nano-porous AAO template has been prepared with no impurity. Only oxygen and aluminum are present in the sample when depicts the purity of the material prepared.

Figure 6. Prepared nano-porous anodic aluminum oxide membrane at a magnification of (a) 500 nm (b) 500 nm with estimated pore size (c) 5 um (d) 2 um.

Figure 7. Energy dispersive X-ray spectroscopy (EDX) Spectrum of the nano-porous anodic aluminum oxide template.
The SEM micro-graph of the prepared ZnO nanostructures on AAO template is shown in figures 8(a)–(b). Highly ordered hexagonal shaped dense ZnO nano-rods are synthesized on anodic aluminum oxide with an average rod length of 192 nm. The average diameter of the nano-rod prepared is in range of 65–70 nm.

The SEM micro-graph of the prepared Mg doped ZnO nanostructures on AAO template is shown in figures 9(a)–(b). Highly symmetric hexagonal shaped Mg-ZnO nano-rods are synthesized on anodic aluminum oxide with an average rod length of 178 nm and rod diameter of 62 nm [20].

The SEM micro-graph of the prepared Be doped ZnO nanostructures on AAO template is shown in figures 10(a)–(b). Highly symmetric Be-ZnO nano-rods are synthesized on anodic aluminum oxide with an average rod length of 181 nm and a rod diameter of 61 nm.
The SEM micro-graph of the prepared Ca doped ZnO nanostructures on AAO template is shown in figures 11(a)–(b). Highly ordered Ca-ZnO nano-rods are synthesized on anodic aluminum oxide with an average rod length of 171 nm and a rod diameter of 58 nm [21].

The SEM micro-graph of the prepared Sr doped ZnO nanostructures on AAO template is shown in figures 12(a)–(b). Highly ordered Sr doped ZnO thread-like nanostructures are synthesized on anodic aluminum oxide, the average rod length of 168 nm and a rod diameter of 56 nm.

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**Figure 11.** SEM micrographs of Ca doped ZnO nanostructures on AAO template with magnification (a) 2 µm (b) 1 µm.

**Figure 12.** SEM micrographs of Sr doped ZnO nanostructures on AAO template with magnification (a) 5 µm (b) 1 µm.

**Figure 13.** X-ray diffraction results of (a) ZnO (B) Be doped ZnO (c) Mg-doped Zno (D) Ca doped Zno (e) Sr doped zno.

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9
The decrease in length and diameter of the rod is attributed to the addition of 2nd group element in the crystal structure of ZnO. The smaller the crystal size of the 2nd group element, more easily it can be added in ZnO nano-crystal to make wider length and diameter of nano-rods. The length of the ZnO and 2nd group element doped on AAO is in accordance with the fuzzy analysis results which a minimum error of 2%.

Figure 14. UV–vis Spectrophotometer results of 2nd group element doped ZnO nanostructures on AAO template.

Figure 15. Tauc plot for the prepared nanostructures on AAO template (a) Be doped ZnO (b) Mg doped ZnO (c) Sr doped ZnO (d) Ca doped ZnO.
The X-ray diffraction results of the prepared sample are shown in figure 13. Figure 13(a) shows ZnO hexagonal wurtzite structure which peak at (100), (002), (101), (102), (110) and (103) in accordance with JCPDS 89-1397 card. The (002) and (101) peak shows that the preferred direction of the ZnO nano-structured is in the direction along the c-axis perpendicular to the sample surface. Figure 13(b) shows X-ray diffraction results of Be doped ZnO nano-structure. No significant change is observed in the spectra due to the incorporation of small amount of Be. The ZnO structure dominates. However, a slight shift in (002) peak can be seen. Figure 13(c) shows X-ray diffraction results of Mg doped ZnO, No peak related to Mg, or MgO is observed. Similarly, figures 13(d), (e) shows X-ray diffraction results of Ca doped ZnO and Sr doped ZnO nanostructures. However, a small shift in (002) is observed after the incorporation of Be, Mg, Ca and Sr, suggesting that the prepared doped ZnO nanorods exhibit single hexagonal phase structure and preferential orientation along the c-axis. Similarly, with addition of larger atomic size material in ZnO nano-crystal, changes in the density of defects, induces stress, lattice distortion and reduction of oxygen vacancies has been observed in previous literature [22].

The absorbance spectrum of the prepared nanostructures on AAO template is studied using UV–vis spectrophotometer in the wavelength ranging from 250 to 650 nm. Figure 14 shows the UV–vis spectrophotometer result of the prepared 2nd group element doped ZnO nanostructures synthesized on AAO template. The least absorbance offset can be seen for Be-doped ZnO nanostructure. However with addition of element with higher ionic radius, including Mg, Ca nd Sr, a blue shift in absorbance off-set can be seen from figure. The estimated absorbance off-set for the prepared 2nd group element doped ZnO nanostructures on AAO template by drawing a tangential line is shown is table 2.

The band-gap of the prepared nanostructures is calculated by drawing the tauc plot. Figure 15 shows the tauc plot for the 2nd group element doped ZnO nanostructures. The prepared nanostructures show a change in band-gap owning to the addition of the 2nd group element in ZnO nanostructure [23]. A shift in Band-gap can be seen in figure 15(a) from Be doped ZnO nanostructures to Sr doped ZnO nanostructures. As shown in figures 14(c), (d), the band-gap decrease with addition of high atomic size element into ZnO nanostructures. The

| Table 2. Absorbance Offset for the Prepared Nanostructures. |
|-----------------|------------------|
| Material                | Absorbance Off-set |
| Sr Doped ZnO Nanostructure | 352 |
| Ca Doped ZnO Nanostructure | 344 |
| Mg Doped ZnO Nanostructure | 318 |
| Be Doped ZnO Nanostructure | 305 |

| Table 3. Band-Gap for the Prepared Nanostructures. |
|-----------------|------------------|
| Material                | Band-Gap (eV)   |
| Sr Doped ZnO Nanostructure | 3.48  |
| Ca Doped ZnO Nanostructure | 3.55  |
| Mg Doped ZnO nanostructure | 3.71  |
| Be Doped ZnO nanostructure | 3.76  |

| Table 4. Comparison between Simulated, Calculated and Experimental values of 2nd group doped ZnO nanostructures. |
|-----------------|------------------|
| Material                | Band-Gap (eV) | Rod Length (nm) |
| MATLAB Fuzzy Analysis  Mg doped ZnO nano-structures | Simulated 3.65 | 181 |
| Experimental Value Mg doped ZnO nano-structures | Experimental: MAMDANI Calculated 3.67 | 183 |
| MATLAB Fuzzy Analysis  Be doped ZnO nano-structures | Simulated 3.71 | 185 |
| Experimental Value Be doped ZnO nano-structures | Experimental: MAMDANI Calculated 3.74 | 187 |
| MATLAB Fuzzy Analysis  Ca doped ZnO nano-structures | Simulated 3.76 | 181 |
| Experimental Value Ca doped ZnO nano-structures | Experimental: MAMDANI Calculated 3.49 | 167 |
| MATLAB Fuzzy Analysis  Sr doped ZnO nano-structures | Simulated 3.51 | 164 |
| Experimental Value Sr doped ZnO nano-structures | Experimental: MAMDANI Calculated 3.44 | 166 |
| Experimental Value Sr doped ZnO nano-structures | Experimental 3.48 | 168 |
approximated band-gap from the tauc plot for Be, Mg, Ca and Sr doped ZnO nanostructure of AAO template is 3.76 eV, 3.71 eV, 3.55 eV and 3.48 eV respectively. The results are in accordance with the fuzzy simulated values as shown in table 1. The calculated band-gap of the prepared materials is shown in table 3.

Due to the addition of the 2nd group element, the widening of Eg is related to an increase in the transition tail width. The increase in the compressive strain alongside the c-axis and decreases with an increase in tensile strain causes an increase in Eg.

5. Comparison between simulation and experimental results

The simulated, MAMDANI calculated and experimental methods use for the preparation of 2nd group element is shown in table 4. Comparison shows that the simulated, calculated and experimental values are similar to each other with a very small difference.

Table 4 shows that the calculated and simulated values are similar to each other which small error. This shows the accuracy of the system.

6. Conclusion

The band-gap and structural variation is a key feature for nano-material owning to their properties. Variation in band-gap as well as particle size provides a broader window for nano-structural application in various fields. In this work, a fuzzy analysis study is performed to analyze the effect of doping, process temperature and substrate pore size and its effect on band-gap and rod length has been analyzed for ZnO nano-structures provided via chemical bath deposition. To compare the simulated with experimental results, a study is performed to analyze the effect of addition of 2nd group element in ZnO nanostructures. A highly porous AAO membrane is prepared by using an odization which shows a pore size of 180.5 nm. The AAO substrate is used as a template and substrate for the deposition of the 2nd group element doped ZnO shows nanostructures. The prepared 2nd group element doped ZnO by chemical bath deposition were characterized which shows a decrease in rod length with addition of 2nd group element from 192 nm to 167 nm. Similarly, the nano-rod results simulated, MAMDANI calculated and characterized results are similar to each other with minor errors. X-ray diffraction results validate the substitution of 2nd group element in ZnO nanostructure. Band-gap changes mainly due to the addition of conductive materials which results in the decrease in rod length. The approximated band-gap from the tauc plot for Be, Mg, Ca and Sr doped ZnO nanostructure of AAO template is 3.76 eV, 3.71 eV, 3.55 eV and 3.48 eV respectively. The use of chemical method reduce the reproducibility of the results however, Chemical bath deposition is considered a suitable method to reproduce the nano-material with better precision. In future, deposition of various 2nd group elements doping percentage in ZnO nano-crystal can been studied based on the simulation and experimental results.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflict of Interest

The Authors have no conflict of interest.

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