INTRODUCTION

Over the past decade, semiconductor devices are mostly based on advancement of coating in the form of thin or thick film technology. The thin film is a two-dimensional material coating of thickness in the order of nanometre range and deposited by either molecule-by-molecule or atom-by-atom condensation method. On the other hand, thick film coating is deposition of particles of thickness in the order of micron.\(^1,2\) Semiconductor oxide material has drawn tremendous attention due to wide range of optoelectronic device applications, from material emission and transistors to optical detection.\(^3\) In this context, zinc oxide (ZnO) possesses many desirable properties such as nontoxic, high electron mobility, direct wide bandgap (3.37 eV), and high exciton binding energy (60 meV), suggesting that the electron-hole pairs are stable even at room temperature.\(^4\) Therefore, it can be used in a wide range of applications in the blue/UV region of optoelectronic...
devices. Moreover, ZnO is a promising candidate for gas sensor, short wavelength optoelectronic devices, especially for ultraviolet light-emitting diodes (UV LEDs) and laser diodes (LDs).

So far, great effort has been made to improve the structural, optical, and electrical properties of ZnO films through a diversity of material synthesis methods, annealing, doping, substrate, and processing. Up to now, various researchers have prepared ZnO films of high quality of different techniques such as pulsed laser deposition (PLD), chemical vapor deposition (CVD), molecular beam epitaxy (MBE), magnetron sputtering, spray pyrolysis, screen printing, and sol-gel. Out of these, sol-gel syringe method has many advantages with respect to others. This method is well known for its simplicity, less time taking for fabrication, environment-friendly, operates at room temperature and possibility of producing cheap large-area films. According to our knowledge, there is no such detailed work except one report in Ref.15 With this purse in mind, we have prepared ZnO thin and micro-films by sol-gel syringe method followed by sintering at 450°C for 10 minutes and then reduced down to room temperature. These films were characterized by the use of XRD, SEM, UV-visible, PL, FTIR, and DC electrical measurements for photovoltaic devices applications.

2 | EXPERIMENTAL

2.1 | Materials

The material used was zinc acetate (Zn(CH₃COO)₂·2H₂O), sodium hydroxide (NaOH) was purchased from Sigma-Aldrich with purity (99%), and de-ionized water was used as solvent.

2.2 | Preparation of extract gel

We have synthesized ZnO powder by the following methodology, as a starting material, 2.2 g of zinc acetate was dissolved in 100 mL of de-ionized water and then stirred the solution vigorously by a magnetic stirrer. Next, 0.05 g of NaOH was dissolved in 100 mL of de-ionized water and was added dropwise to zinc acetate solution under vigorous stirring for 1 hour as shown in Figure 1A. By gradually mixing the solution of Zn(CH₃COO)₂·2H₂O, and NaOH, a white precipitate of Zn(OH)₂ gel was formed. The overall reaction for the synthesis of ZnO can be written as,

\[
\text{Zn} \left( \text{CH}_3\text{COO} \right)_2 \cdot \text{2H}_2\text{O} + \text{2NaOH} \rightarrow \text{2NaCH}_3\text{COO} + \text{2H}_2\text{O} + \text{Zn(OH)}_2
\]

The precipitate was collected and washed three times with distilled water, respectively. The washed precipitate was dried at 100°C for 2 hours to form the precursor ZnO.

\[
\text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O}
\]

The residue was then heat treated at 400°C for 1 hour, and a white powder is obtained.

2.3 | Preparation of micro and thin films

Half of the obtained dried powder was kept for micro-film preparation, and remaining powder was grinded to reduce the size of particles by the use of mortar and pestel for 1 hour. Then both bulk and nano-powders were dissolved in de-ionized water separately under vigorous stirring for 1 hour. Finally, both solutions were dropped on glass substrates by using a medical syringe as shown in Figure 1B. Further, the
films were inserted into an muffle furnace and kept at 450°C for 10 minutes in order to evaporate the organic material. Figure 1C depicts the required stable films.

3 | CHARACTERIZATION

X-ray diffraction pattern of the films was obtained by X-ray diffractometer (Bruker D8 Advance) using Cu Kα line ($\lambda = 1.54056$ Å). The surface morphology of the films with elemental composition is examined using scanning electron microscopy (JEOL JSM-7001F). Optical measurements of the films were carried by using Hitachi (UV-3400 PC) UV-VIS spectrophotometer device. FTIR spectra were recorded on a Perkin Elmer SpectrumRXI for determining bond position in the films. Photoluminescence spectra were scanned (Perkin Elmer spectrometer -JY800) by using a 325 nm He–Cd laser as the excitation source was used. The DC conductivity of the films was measured by using double probe method with (Keithley 6517A). The thickness of ZnO micro- and ZnO nano-thin films was calculated by the gravimetric weight difference method regarding deposited weight of a ZnO film on the glass substrate, per unit area (g/cm²). The thickness was calculated using formula (1).

$$T = \frac{M}{\rho A}$$

Where “$T$” is film thickness, “$M$” is the mass of the film material in g., “$A$” is the area of the film in cm², and $\rho$ is the density of the film material. The calculated values are 1 μm for ZnO micro-film and ~700 nm for ZnO nano-film, respectively. All the characteristic measurements were carried out at room temperature in air.

4 | RESULTS AND DISCUSSIONS

4.1 | Crystal structure and phase analysis

X-ray diffraction (XRD) is a multipurpose, nondestructive technique which gives direct information about the phase purity and crystal structure of material. Figure 2 shows the XRD patterns of micro- and nano-ZnO films. Diffraction peaks are identified at twice of angle (2θ) and given to (100), (002), (101), (102), (110), (103), (200), (112), and (201) planes one-to-one, although plane (101) has supreme diffraction intensity. For micro-ZnO film, no single peak for any other element or compound is perceived in the pattern, signifying the utmost phase purity, means only single-phase ZnO was formed. All the diffraction peaks are well matched with the standard XRD data of pure ZnO as per standard JCPDS card no (36-1451).

Likewise, meant for nano-ZnO film the intensity of peak decreases and shifted on the way to higher angle with increase in full width half maximum of corresponding peaks, suggesting decrease in grain size and hence signifies the formation of nano-material. Several parameters have been calculated for the most oriented diffraction peak (101) by means of different formulas and are listed in Table 1. It is clearly seen that the crystalline orientations are distributed among the planes; this is due to the changing of bond length that causes wurtzite structure of ZnO shift away from its original position habitually.

The grain size estimated using the classical Debye-Scherer formula (2):

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$

Where $\lambda$ is wavelength (Cu-Kα), $\beta$ is full width at half maximum (FWHM), and $\theta$ is diffraction angle.

The dislocation density and tensile strain were calculated using Equations (3) and (4).

| Sample   | Plane (hkl) | Peak angle (°) | FWHM (°) | Grain size (nm) | Inter-planar spacing (d) Å | Dislocation density (δ) lines/m | Strain ε |
|----------|-------------|----------------|----------|-----------------|----------------------------|---------------------------------|----------|
| Micro-ZnO | (101)       | 18.23          | 0.00314  | 48.57           | 2.461                      | 439 × 10^{-15}                  | 0.000784 |
| Nano-ZnO | (101)       | 18.34          | 0.00505  | 28.66           | 2.447                      | 1217.44 × 10^{-15}              | 0.0011021 |
In the present study, it is observed that the dislocation density and strain are increased with the decrease of grain size of ZnO, this is because in nano-regime surface to volume ratio increases.\textsuperscript{18}

### 4.2 | Scanning electron microscope (SEM) with EDX

Scanning electronic microscope (SEM) is one of the most useful characterization technique in the material science for the surface morphology examination. The surface image of micro- and nano-ZnO films is presented in Figure 3A,B with different scales, respectively. The surface morphology shown in figures specifies that the surface comprises with grains of crystallites almost have dissimilar shapes with different sizes. SEM micrographs clearly show the mixtures of grains in which some particles are in nano-size and some are in micro-size with high porosity. This would be useful to enhance the optical and electrical properties of films as the ZnO particles have high mobility.

The presence of ZnO is confirmed from the elemental study using EDX. The weight and atomic percentage (wt %) of the Zn and O as found in the EDX spectrum, and corresponding EDX results are shown at left side of Figure 4, respectively. It is observed that the O content (weight %) is decreased in nano-films as compared to micro-films. Thus, confirms the difference between micro- and nano-ZnO films.

### 4.3 | UV-Visible

The optical properties and the energy bandgap of nano- and micro-ZnO films were studied by UV-visible absorbance spectroscopy in the wavelength range 300-700 nm as shown in Figure 5A. These spectra show excitonic absorption edge at 387 and 363 nm for micro- and nano-ZnO films, respectively. The corresponding bandgap energy ($E_g$) for both the samples has been determined using Einstein’s Equations (5) and (6).\textsuperscript{19}

\[
E_g = \frac{hc}{\lambda_{\text{max}}}
\]

\[
E_g = \frac{1240}{\lambda_{\text{max}}} \text{eV}
\]

where $h$ is Planck’s constant, $c$ is the velocity of light, and $\lambda_{\text{max}}$ is the excitonic absorption edge. The bandgap energy calculated to be $\sim 3.21$ eV and $\sim 3.40$ eV for micro- and nano-ZnO films, respectively. This blue shift confirms occurrence of quantum confinement from micro- to nano-ZnO films.\textsuperscript{20}

The reflectance of the prepared micro- and nano-films is displayed in Figure 5B. The micro- and nano-ZnO films show the reflectance variation in the visible and near-IR region (300-700 nm). It can be observed that the micro-ZnO film shows the maximum reflectance than that of nano-ZnO film, and this is due to the changing of band gap.

\[
\text{Dislocation density } (\delta) = \frac{1}{D^2}
\]

\[
\text{Tensile strain } (\varepsilon) = \frac{\beta \cos \theta}{4}
\]
4.4 | Photoluminous study

PL spectroscopy technique is optical characterization technique measure the energy distribution of emitted photons after the optical excitation. Figure 6 shows the room temperature PL spectra of the ZnO as a function of photon energy for ZnO micro- and ZnO nano-films. These spectra have luminescence band having similar features, that is, the near band edge emission (NBE).

As observed in Figure 6, the PL spectra of the ZnO micro-films showed a near band edge at about 3.21 eV while it is 3.43 eV for ZnO nano-film, respectively. This can be attributed to the recombination of free electron via exciton collision process. The NBE emission is recognized as a result of direct recombination of electron-hole pairs. Here, our result support UV-visible study because blue shift occurs from micro- to nano-ZnO films, called quantum confinement effect, and this has been observed from the change of color of solution in which nano-solution is more transparent as compared to bulk is shown along with Figure 6. The intensities of peak are not in certain order because the number of defects depends on the amount of oxygen present in the atmosphere during annealing of samples in the furnace.
Fourier Transform Infrared Spectroscopy (FTIR)

FT-IR spectroscopic is a vibrational technique that allows us to obtain chemical information on molecules within the sample, as infrared radiation is used to vibrate molecular bonds within the sample that absorbs it. FTIR spectrum of the ZnO films synthesized by sol-gel syringe method in the range of 400-3000 cm\(^{-1}\) at 4 cm\(^{-1}\) resolution is shown in Figure 7. Usually, metal oxides exhibit absorption bands well below 1200 cm\(^{-1}\) arising due to interatomic vibrations and confirming the purity of ZnO structure. From these spectra, it is observed that micro-sample shows the sharpness of the characteristic peaks and shifts higher wave number, suggesting that the crystalline nature of ZnO increases on increasing thickness. The transmission peaks appear in the range of 1200-1400 cm\(^{-1}\) pertaining to C=O and O–H bending vibrations, respectively. The shift in band position can be related to the change in the bond length that takes place as surface volume ratio increase with decreasing particle size in nano-ZnO film with respect to micro-film.

Temperature dependence of conductivity

The electrical transport property plays a major role to understand the material to be used for device applications. As evidenced in Figure 8A, the current \(I\) raises exponentially as the temperature \(T\) increases from 90 to 180°C. This rise in current is due to increase in thermally generated carriers. The thermal dependence conductivity is calculated from the well-known Arrhenius Equation (7).

\[
\sigma = \sigma_0 \exp\left(\frac{-\Delta E}{kT}\right)
\]

Where \(\sigma\) is conductivity, \(\sigma_0\) is the pre-exponential factor, \(E\) is the thermal activation energy for generation process, \(K\) is Boltzmann’s constant, and \(T\) is the temperature (in Kelvin). The thermal conductivity of curve is shown in Figure 8B reveals semiconducting nature of the material as conductivity increases with the increase in temperature. The activation energy has been calculated from the slopes of curve and that come to be 0.39 eV for nano-ZnO films and 0.29 eV for micro-ZnO films. As per to the reported value when the thickness increases, gradient increases, hence emphasis fall of resistance.
because when the grain size is large then more atoms are in order and there is less grain boundaries. Therefore, atoms easily move from grain to grain, and electrical properties are improved. These conduction paths can operate in parallel through the grain boundary region and weakness the potential barriers of ZnO varistors, in agreement with the present data.27

5 | CONCLUSION

Micro- and nano-ZnO films were prepared by simple sol-gel syringe spray method followed by sintering at 450°C. XRD and SEM show formation of pure ZnO phase with different particle sizes supported by EDX study. The energy gap values for optical study through PL and UV-visible show particle size dependence indicating blue shift with respect to bulk. FTIR spectrum showing strong absorption band between 700 and 450 cm⁻¹ can be attributed to the stretching modes of ZnO. The semiconductor behavior has been identified from temperature dependence of resistivity measurement. Therefore, based on the study presented here, it is concluded that the simple and inexpensive sol-gel syringe technique discussed here can be used to fabricate semiconductor micro- and nano-ZnO films and the results obtained may be suitable for large-scale applications of optoelectronics.

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