CHAPTER 4

Investigations on Ru doped ZnO: Lattice Strain Calculations and Gas Sensing Studies
4.1. Introduction

Zinc oxide is a comprehensively studied post-transition metal oxide and explored as one of the prominent materials for gas sensing application. The conductivity changes in response to the adsorbed gases making it a potential sensor candidate. Point defects in the ZnO lattice are extremely important in gas sensing phenomenon as they create significant variations in the surface and bulk conductivity. The changes occur at the surface of the grains as a result of charge transfer and the band bending caused by the adsorbate species. Doped and undoped ZnO show response towards oxidizing gases like O₂, O₃, as well as reducing gases such as H₂, CO, NH₃, hydrocarbons depending up on the method of synthesis and the nature of dopants. Nevertheless, it suffers from long-term instability, sensitivity towards ambient humidity, and poor selectivity. To overcome these limitations, addition of certain impurities/dopants is reported to make it selective, lower the operating temperature and have fast response time [1-5].

Ruthenium (Ru) is primarily used as an alloying agent. Adding 0.1% ruthenium to titanium makes it 100 times more resistant to corrosion. Small amounts of Ru added to platinum and palladium strengthen them. These alloys are used in jewelry and in electrical contacts that must resist wear [6]. The Ru reduces NOₓ as well as supports the oxidation of CO and hydrocarbons (HC). However; its use was originally abandoned by the industry following research in the 1970's that showed its predilection to form volatile and toxic ruthenium oxide species that would be emitted into the environment. Therefore, exploiting ruthenium in three-way catalysts (TWC) for NOₓ destruction required stabilization of ruthenium under the high temperature and oxidizing conditions of the automotive exhaust system [7].

The structural and morphological properties of semiconductor oxides have a substantial effect on their optical [2], electrical [3], and gas sensing [4] properties. The controlled particle size and morphology facilitates the desired characteristics in the material. Several simple wet chemical routes like sol-gel [5], co-precipitation [8] and Pechini route [9] have been used to form nanostructures.

Synthesis of Ru doped ZnO nanoparticles using citrate gel method [10, 11], which involves complexation of metal ions by polyfunctional carboxyl acids having atleast one hydroxyl group (i.e. citric acid) is carried out. On heating this mixture, the solvent
evaporates resulting in increased viscosity. After complete removal of water, the mixture turns into a polymeric resin wherein all its constituents get mixed at the atomic level. This resin when heated at high temperature produces oxides. The only limitation of this method is possible carbon contamination.

In nanoscale dimensions the incorporation of Ru may produce strain in ZnO lattice. As a consequence of such changes due to the doping element, the nanomaterials possess region in the lattice with the state of tension or compression. The nanomaterial is then said to hold internal stress that vary from one grain to another. In this chapter, we report the study on the lattice strain and crystallite size calculations using Hall equation [12] and comparing these results with that obtained from Scherrer’s equation [13]. Such types of calculations were also reported earlier for Ru doped SnO$_2$ [14, 15]. In the present work, the observed gas response study of pristine ZnO is found to be highly sensitive towards liquefied petroleum gas (LPG) while Ru doped ZnO is highly selective towards ethanol (C$_2$H$_5$OH). The observed magnitude of sensing is also found to depend on Ru concentration. It can be measured in terms of change in various parameters like resistance, capacitance, pressure, etc. [16, 17]. The sensing parameter used in the present case is change in resistance. The influence of Ru doped SnO$_2$ with respect to its gas sensing study is reported in literature [14, 15] however the sensing studies for Ru doped ZnO as per our knowledge have not been carried out. Hence we have explored Ru doped ZnO as gas sensor at two different operating temperatures and varying the gas concentration.

### 4.2. Material Synthesis

All the reagents used in this work were obtained from Loba Chemie, India (AR grade). Pure and Ru doped ZnO has been synthesized using citrate gel method. The Ru content was varied from 0.3 to 3 wt%. Zinc nitrate (Zn(NO$_3$)$_2$.6H$_2$O) and ruthenium trichloride (RuCl$_3$.xH$_2$O) were used as starting reagents. Zinc nitrate (ZN) was first dissolved in distilled water to which citric acid (CA) (C$_6$H$_x$O$_y$) and ruthenium trichloride was added in the required ratio.

The ratio of ZN to CA was maintained at 1:1. The mixture was dissolved completely and kept on water bath having temperature in the range of 80 to 100 °C to form a gel, which was then transferred in the furnace and subsequently heated at 200, 300 and
$400^\circ$C for $3$ h. The XRD (X-ray diffraction), TEM (transmission electron microscope) and gas sensing studies were carried out for these samples. The XRD (PANalytical XPERT with an accelerating voltage $40$ kV) with a scan rate of $4^\circ$/min at room temperature was used to confirm the phase formation while for accurate lattice parameters calculation the scan speed employed was $0.5^\circ$/min and silicon was used as an internal standard.

The TEM and HRTEM (high resolution transmission electron microscope) images were recorded using Technai™ G² F30 with an accelerating voltage of $300$ kV. Initially powder was dispersed in acetone, sonicated and drop casted on the copper grid for these studies. The gas sensing studies were carried out by making pellets of the powder formed. The pellets of diameter $8$ mm and thickness $2$ mm were made under pressure of $2$ tons using hydraulic press. These pellets were sintered at $300^\circ$C for $2$ h to increase their mechanical strength. After providing ohmic contacts using silver paste the gas response was measured as described in earlier chapter 2. The gas response ($\%S$) has been calculated using following equation:

$$\%S = \frac{(R_a - R_g / R_g) \times 100}{\text{Eqn. (4.1)}}$$

where, $R_a$ = resistance in air

$R_g$ = resistance in presence of gas.

4. 3. Results and Discussion

4.3.1. XRD and TG/DTA Analyses

The calcination of the samples at $200^\circ$C resulted in the pinkish nanocrystalline powder, which may be due to the decomposition products of citric acid. The decomposition temperature of citric acid is $175^\circ$C and its melting point is $\sim 160^\circ$C. The formation of ZnO phase at $200^\circ$C was confirmed by XRD (Figure 4.1.).

It is interesting to find that the simple synthesis method used in the present study, is found to produce particles in the nanometer range at temperature as low as $200^\circ$C. The average particle size ($D_p$) for the most intense peak (101) was $3$-$5$ nm as estimated by Scherrer’s equation.
Figure 4.1. XRD pattern for 3% Ru calcined at 200 °C

Figure 4.2. DTA/TGA of 3 wt% Ru doped ZnO
Figure 4.2 shows DTA/TGA for 3 wt% Ru:ZnO ZnO sample. The weight loss begins at \( \sim 200 \, ^\circ\text{C} \) indicating formation of ZnO phase along with decomposition of carbonaceous matter. The ZnO phase formation at 200 \( \, ^\circ\text{C} \) is also supported by XRD analysis. However, the weight loss continues to 400 \( \, ^\circ\text{C} \) with endothermic peak indicating further loss of carbonaceous matter. The carbon content was found to be \( \sim 15 \% \) for samples calcined at 200 \( \, ^\circ\text{C} \) and less than 5\% for the samples calcined at 300 \( \, ^\circ\text{C} \).

![Figure 4.3. XRD patterns of pure and Ru doped ZnO calcined at 300 °C](image)

The XRD patterns of ZnO with various Ru contents (0 to 3 wt \%) calcined at 300 \( \, ^\circ\text{C} \) are shown in Figure 4.3. The XRD patterns also indicate decrease in FWHM of major peaks with increase in Ru content. The average crystallite size as calculated using Scherrer formula indicates increase in size with Ru concentration (Figure 4.4.). As the calcination temperature is increased to 400 \( \, ^\circ\text{C} \) the particles size increases further indicating high crystallinity as shown in XRD of Figure 4.5. The average particle size calculated using Scherrer’s formula is 130 nm and 125 nm for 1 and 3 wt \% Ru at 400 °C respectively.
Figure 4.4. Average particle size Vs Ru content using Scherrer’s equation for samples calcined at 300 °C

Figure 4.5. XRD patterns of 1 and 3 wt% Ru: ZnO calcined at 400 °C
The lattice strain and average crystalline size were calculated using Hall equation for the samples calcined at 300 °C as suggested by Williamson and Hall [12]:

$$\beta \cos \theta / \lambda = 1 / \varepsilon + \eta \sin \theta / \lambda$$

\[ \text{Eqn. (4.2)} \]

where, $\varepsilon$ = effective particle size

$\eta$ = effective strain and all other parameters are as defined in Chapter 2.

The strain calculations were carried out for Ru doped and pure ZnO calcined at 300 °C using (101) plane. The plot $\beta \cos \theta / \lambda$ Vs $\sin \theta / \lambda$ shows approximately a linear variation as seen in the Figure 4.6. (a-e).

![Figure 4.6. Lattice strain calculations for a) ZnO b) 0.3 wt%, c) 0.5 wt%, d) 1 wt% and e) 3 wt% Ru:ZnO](image)

The effective particle size and strain are calculated using a linear equation;

$$y = \eta x + 1 / \varepsilon$$

the slope of these lines give strain while their extrapolation on y-axis show the effective particle size. Taking strain into consideration the effective particle size with Ru concentrations was plotted (Figure 4.7.). Variations in the particle size using Scherrer’s formula and Hall equation are observed in close approximation with each other.
Figure 4.7. Effective particle sizes Vs Ru concentration using Hall equation

The negative slope for pure ZnO (Figure 4.6.(a)) indicates the presence of effective compressive strain in the crystal lattice and positive slopes with Ru doping Figure 4.6. (b-e) attributes to the presence of tensile strain. Higher magnitude of slope for lower Ru doping (< 1 wt %) leads to increase in strain with increase in particle size as compared with the pure ZnO. However, higher than 1 wt % doping of Ru results in decrease of slope, indicating lowering of the tensile strain which can be attributed to the particle size effect. These observations lead to propose that the size dependent strains in the particles are governed by Ru concentration in the ZnO.

The ionic radius of Ru$^{4+}$ (132 pm) being significantly higher than Zn$^{2+}$ (72 pm), the incorporation of Ru in the ZnO alters the lattice parameters in consonance with the lattice strain. The change in lattice parameters as seen in ZnO calculated by least squares method are $a = 3.245\, \text{Å}$ and $c = 5.227\, \text{Å}$ while for 3wt% Ru: ZnO are $a = 3.250\, \text{Å}$ and $c = 5.269\, \text{Å}$ indicating marginal increase in the ‘a’ parameter and significant increase in ‘c’ parameter after doping. The measure of lattice distortion i.e. the change in $a/c$ ratio from 0.621 for pure ZnO to 0.616 for 3 wt% Ru:ZnO also suggests the tensile state of the lattice on Ru doping.
4.3.2. Texture coefficient analysis

As seen from the major peak intensities of the planes in the XRD for undoped and Ru doped samples, Harris analysis [14] may indicate change in texture coefficient with change in composition. The texture coefficient \( P(h, k, l) \) and the preferred orientation indicator of the \((h, k, l)\) planes are conferred by the following relationship:

\[
P(h, k, l) = \frac{I(h, k, l)}{I_0(h, k, l)} * \left\{ \frac{1}{n} \sum \frac{I(h, k, l)}{I_0(h, k, l)} \right\}^{-1}
\]

for \( i = 1, 2, 3 \ldots n \)

where, \( I(h, k, l) \) = diffraction intensity of the \((h, k, l)\) plane of the sample under investigation

\( I_0(h, k, l) \) = intensity of the \((h, k, l)\) plane of the standard sample

\( n \) = number of reflections present

The values of texture coefficient determined for three major peaks are mentioned below.

<table>
<thead>
<tr>
<th>Plane ((h, k, l))</th>
<th>Pure ZnO</th>
<th>0.5 %Ru:ZnO</th>
<th>3%Ru:ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>((100))</td>
<td>1.604</td>
<td>1.037</td>
<td>0.993</td>
</tr>
<tr>
<td>((002))</td>
<td>1.697</td>
<td>0.898</td>
<td>0.937</td>
</tr>
<tr>
<td>((101))</td>
<td>1.101</td>
<td>0.816</td>
<td>0.978</td>
</tr>
</tbody>
</table>

As seen from the values calculated for texture coefficient using Eqn.(3), there is non-uniform variation in their values indicating distortion of the lattice with Ru doping.

4.3.3. TEM Studies

The TEM image for Ru: ZnO calcined at 300 °C shows irregular shaped (oval and spherical) particles of average diameter in the range of ~ 20 to 50 nm as observed in Figure 4.8. (a & b).
Figure 4.8. (a) TEM image of 1wt%Ru in ZnO

Figure 4.8. (b) TEM image of 1wt%Ru in ZnO
The HRTEM image of the same shown in Figure 4.8 (c), reveals fringes of (101) planes with the lattice spacing of 0.247 nm between two adjacent planes indicating (101) as a growth direction.

Figure 4.8. (d) EDS of 1 wt%Ru in ZnO.
The elemental analysis done using EDS confirms the presence of Ru. The Cu peaks seen in the Figure 4.8. (d) comes from the copper grid on which the sample is loaded.

### 4.3.4. Gas Sensing Behavior

Even though the ZnO phase was formed at 200 °C, the fluctuating values observed in resistance after electroding indicated poor mechanical stability of the pellets. Hence these samples were not used for further gas response study. The pellets calcined at 400°C become more compact (dense) because of decreased porosity and hence showed very little or rather no response towards any of the gases.

The gas sensing characteristics were performed using experimental set up described earlier in Chapter 2. Pellets calcined at 300 °C were used for gas sensing study at the two operating temperatures. According to Figure 4.9., ZnO synthesized by citrate gel method is found to have better sensing response towards LPG, as reported in literature [18, 19].

![Figure 4.9. Gas response (%S) with 500 ppm as a function of wt%Ru in ZnO for different operating temperatures (°C).](image)

The LPG response earlier reported by us using hydrazine route [20] is ~ 2500 for 200 ppm, which is much higher than the present findings of 525 for 500ppm of LPG. Such
noteworthy difference in LPG response can be attributed to the method of synthesis which cause change in surface defect states and the morphology. On Ru doping the response towards LPG decreases while it systematically increases for ethanol up to 0.5 % Ru and then onwards gradually decreases upto 1 wt % followed by saturation. While pure ZnO shows high response for LPG which gradually decreases with Ru content until 1 wt% and then reaches a constant value of sensitivity. This can be attributed to the difference in reducing capacity of the two gases on doped and undoped composition. For both ethanol and LPG the highest response is obtained at the operating temperature of 275 °C above which it decreases, suggesting this temperature to be an optimum for sensing both the gases.

LPG is a mixture of hydrocarbon containing CH₄, C₃H₈, and C₄H₁₀ wherein the reducing hydrogen species are bound to carbon atoms. Therefore, during the process of response at higher operating temperatures, LPG dissociates into reactive reducing components on the zinc oxide surface. The overall reaction of LPG molecules with adsorbed oxygen from the surface of ZnO can be explained as follows:

\[ C_nH_{2n+2} \rightarrow H_2O + C_nH_{2n} + 1/2 O_2 (g) + e^- \] 

.....Eqn.(4.4)

The other probable reaction on ZnO surface depending on the availability of thermal energy and the reducing atmosphere

\[ C_nH_{2n+2} + O_2 \rightarrow CO + CO_2 + H_2O \] 

.....Eqn.(4.5)

where, \( C_nH_{2n+2} \) represents CH₄, C₃H₈ and C₄H₁₀.

In ethanol (C₂H₅OH) following reaction may occur on the ZnO surface:

\[ C_nH_{2n+1}OH \rightarrow C_nH_{2n} + H_2O \] 

.....Eqn.(4.6)

\[ C_nH_{2n} \rightarrow CO_2 + CO + H_2O \] 

.....Eqn.(4.7)

Figure 4.10. shows LPG response as a function of Ru concentration at an operating temperature of 275°C for different gas concentrations. It is seen that response increases with LPG concentration upto 500 ppm, above which it saturates, similar trend is also observed for ethanol gas (Figure 4.11.).
According to Xiangfeng et al. sensitivity towards ethanol [19] for ZnO increases linearly from 50 ppm to 1000 ppm upto 380 °C while Tang et al. [17] have found 358 °C to be an optimum operating temperature. The response and recovery time shown in the Table 4.2. indicates that for both ethanol and LPG the response and recovery times are almost similar.
4.4. Conclusions

A wet chemical citrate gel method produces Ru doped and undoped ZnO nanoparticles in the range of 3-4 nm at 200 °C. The carbon content coming from citric acid was reduced with increase in calcination temperature. The strain calculations using Hall equation show a positive slope in Ru doped ZnO indicating the presence of tensile strain as compared to the compressive strain observed in ZnO. The average particle size variations using Scherrer’s formula is in agreement with that obtained by Hall equation.
The texture coefficient variation indicates the lattice distortion with Ru doping. Samples calcined at 200 and 400 °C were not suitable for gas sensing as they are unstable due to incomplete combustion of carbonaceous matter at 200 °C and high densification at 400 °C. However the samples calcined at 300 °C were found to be optimum for gas sensing study mainly due their nanoform and porous nature. The gas sensing response is found to depend upon the method of synthesis and Ru content in ZnO. Pure ZnO exhibits selective response towards LPG while on doping with 0.5 % Ru it shows high sensitivity towards ethanol which on further doping decreases.
References