CHAPTER-IV
4.0 Introduction:

One of the foremost application areas of today’s gas sensors is their use in the automotive and industrial sector for environmental protection. The fast growth in motor traffic and high level of emissions from industry in particular have driven increasing research and development activity including work on gas-sensors. Therefore, there is an urgent need for a new generation of miniature, intelligent, low-cost, low power consumption and easy-to-use sensors for detecting a range of important pollutant species (e.g. NO₂, NH₃, SO₂, CO, CO₂ and hydrocarbon).

SnO₂, In₂O₃ or ZnO are commonly used in the most recent generation of sensors as the gas-sensitive material, but they show some disadvantages mainly due to the lack of long term stability. Hence, a new sensing material is required to exhibit higher performance than the traditional materials. Among useful semiconducting metal oxides as sensing materials, nickel oxide (NiO) has been extensively investigated for detection of toxic gases such as NO₂, NH₃, H₂ and CO due to their prominent characteristics.

Nickel oxide, which is usually taken as model for p-type semiconductor, is an attractive material for sensor applications.

Most attractive features of NiO are:

- Excellent durability and electrochemical stability,
- Low materials cost,
- Large spin optical density and
- Possibility of manufacturing by variety of techniques.

In the present investigation, nickel oxide (NiO) thin films were prepared using electron beam evaporation technique which useful for preparing device quality films useful for sensor applications.
NiO films were grown on glass substrates by using electron beam evaporation of high-purity (99.9%) NiO pellets. A 10 mm diameter NiO pellet was used as a source target for evaporation. The NiO target was placed in copper crucibles and kept in the water-cooled copper hearth of the electron gun for evaporation. The substrates were placed normal to the evaporation source at a distance of about 50 mm. Before deposition, the material was slowly out gassed with a shutter blocking the vapour from the sample surface. The films were deposited at different substrate temperatures and different evaporation times and annealed at different temperatures and studied the effect of substrate temperature, thickness and annealing temperature on the properties of NiO thin films.

The quality of the experimental films was studied by studying the films structure, microstructure, composition, surface morphology, optical and electrical properties. The thickness of the films was estimated using depth profilometer. In order to study the structural quality of the experimental films, X-ray diffraction analysis was used as tool to identify the crystallographic structure, grain size and lattice parameter. Raman studies were also performed to see the phases of NiO. The composition of the films was analyzed using energy dispersive spectroscopy (EDS). The microstructure and surface morphology were determined using scanning electron microscope (SEM) and atomic force microscope (AFM). The optical properties of the experimental films were studied using UV-Vis spectrophotometer. The resistivity, mobility and carrier concentration of the films were determined using Hall Effect studies. Finally the usefulness of the films towards NO₂ gas sensing applications was performed by measuring the change in film resistance in the presence of the NO₂ gas.

In order to see the usefulness of the NiO thin films for possible applications in gas sensors, the films were prepared at different substrate temperatures, different thicknesses and the deposited films were annealed at different temperatures and the deposition parameters were optimized by studying the structure, composition, morphology, electrical and optical properties.
4.1. Effect of substrate temperature on the properties of NiO thin films:

In order to study the effect of substrate temperature on the properties of NiO films, the films were deposited at various substrate temperatures ranging from 303 K to 573 K. Pure NiO (99.9%) pellet with 10 mm diameter was used as the source material for electron beam evaporation. The source to substrate distance was maintained constantly at 50 mm for all the depositions. The films were deposited on Corning 7059 glass substrates. The base pressure of the deposition chamber was maintained at $6.6 \times 10^{-5}$ Pa and working pressure was maintained at $2.0 \times 10^{-4}$ Pa. The accelerating voltage of the electron gun was maintained at 5 kV with filament current of 120 min. By maintaining the evaporation time around 10 min., the NiO thin films were obtained with a thickness of 150 nm. The films were deposited at various substrate temperatures by keeping the other deposition conditions as constant. The effect of substrate temperature on the structural, morphological, compositional, optical and electrical properties were analyzed systematically and results obtained were given below.

- The crystal structure of the films was identified to be polycrystalline with cubic structure. The films prepared at room temperature exhibited (200) orientation. As the substrate temperature increased to 373 K, an additional peak of (220) appeared along with (200). On further increasing the substrate temperature to 473 K, the intensity of the (220) peak was increased and becomes sharper and the (200) peak was disappeared. When the films formed at higher substrate temperature of 573 K, another peak with increased intensity was observed along (111) orientation and the intensity of the (220) peak was decreased.

- The grain size of the films increased from 6 nm to 17 nm as the substrate temperature increased from 303 K to 473 K there after it decreased to 15 nm at 573 K.
It is evident from the EDAX spectra that no other elemental peaks other than Ni, O were observed for all the films deposited at all the substrate temperatures.

From AFM studies, the topography revealed that the surface roughness was increased from 6 to 12 nm as the substrate temperature increased from 303 K to 573 K.

From SEM micrographs, it was observed that the films deposited at room temperature have smooth surface and the films formed at a higher substrate temperature had fine and uniform grains.

The Raman spectra of the film deposited at (RT) 303 K can be found very weak peak at 300 cm\(^{-1}\), 580 cm\(^{-1}\) and another peak at 800 cm\(^{-1}\), whereas the films deposited at a substrate temperature of 373 K, 473 K and 573 K showed Raman peaks located around 580 and 800 cm\(^{-1}\).

All the films showed direct transitions and the optical band gap of the films increased with increasing the substrate temperature and was in the range 3.56 to 3.88 eV.

The electrical resistivity of the films gradually decreased to 7.4 \(\times\) 10\(^{-2}\) Ohm-cm with increasing the substrate temperature to 573 K.

From these observations, it was concluded that films deposited at a substrate temperature of 473 K exhibited better crystallinity with large grain size.

4.2. Effect of film thickness on the properties of the NiO thin films

In order to study the effect of film thickness on the properties of NiO films, the films were deposited at various deposition times (6, 8, 10 and 12 minutes) for preparing films with thicknesses \((T = 90, 120, 150\) and \(180\) nm) at a substrate temperature of 473 K and keeping the other deposition conditions as constant. The effect of film thickness on the properties of the films was studied by studying the structure,
composition, microstructure and surface morphology, optical and electrical properties. The findings of the observations were given below:

- All the prepared films exhibited (220) orientation. The grain size of the films increased from 6.8 nm to 17 nm as the thickness of the film increases from 90 to 150 nm and decreased to 15 nm at a film thickness of 180 nm.

- From the EDAX Spectra, no other elemental peaks other than Ni, and O were observed for all the films.

- The Raman spectrum revealed no other phases except NiO.

- The topography obtained from AFM studies revealed that the surface roughness was increased from 6 to 19 nm with increasing the thickness of the films.

- From SEM micrographs, it was observed that the as-deposited NiO thin films exhibited dense surface and fine grains were observed when the films deposited at higher thicknesses and the grain size was increased with increasing the film thickness.

- All the films showed direct transitions and the optical band gap slightly increased with increasing the film thickness.

- The electrical measurements revealed that, the resistance slightly decreased with increasing the film thickness and saturates at higher thicknesses.

From these observations, it was noticed that the films deposited at a thickness of 150 nm showed better structural and electrical properties.

4.3. Influence of thermal annealing on the properties of NiO thin films:

Thermal annealing is one of the most important factor, since annealing temperature can improve the crystal quality and reveal structural defects in thin films. During the annealing process, the structure and the stoichiometric ratio of the films change due to the movement of dislocations and defects. In this study,
the NiO thin films were deposited at room temperature with a thickness of 150 nm by keeping the other deposition parameters as constant. The as deposited films were air annealed at different temperatures in the range room temperature to 500°C and studied the effect of annealing temperature on the properties of the films. The following were the observations made in this study.

- The structural analysis of the films revealed that all the films exhibited polycrystalline nature with cubic structure. The intensity of the preferred orientation increased with increasing the annealing temperature. The films annealed at a temperature of 400°C showed improved crystallinity along (220) orientation. The films annealed at higher temperature of 500°C the intensity of the (220) peak decreased another orientation along (1 1 1) direction was observed.

- From SEM analysis, it was observed that the as-deposited NiO thin films exhibited dense surface and fine grains were observed at 300°C annealed films and the grain size was increased with increasing annealing temperature.

- The as-deposited films exhibited a very smooth surface, with a mean roughness of 8.81 nm. On increasing the annealing temperature to 300°C columnar structures grew independently. The surface roughness increased with increasing the annealing temperature.

- No significant change in the composition was observed in the films annealed at different temperatures.

- The reduction in the number of unsaturated bonds decreased the density of localized states in the band structure, consequently increased the optical band gap with increasing the annealing temperature.

- Thin films annealed at 400°C exhibited lowest resistivity compared to other films annealed at other temperatures.
In summary, it was observed that, the films annealed at 400°C with a thickness of 150 nm showed better electrical properties with high surface area. These films are suitable for gas sensing applications.

In order to see the applicability of the NiO thin films, the films deposited at room temperature with a thickness of 150 nm and annealed at 400°C were used for sensing the NO₂ gas. The sensitivity of the films depends on the NO₂ concentration and higher sensitivity was observed at gas concentration of 150 ppm.

Scope for the future work:

In order to improve the electrical performance of the NiO thin films with high surface area, future work will be undertaken to dope the NiO films with suitable dopants and to study the effect of doping on the electrical and morphological properties. And also systematic studies will be carried out to use these films for sensing the other pollutant gases.
List of Publications:

1. Effect of substrate temperature on the structural, optical and electrical properties of electron beam evaporated NiO thin films
   A. Madhavi, Ch. Seshendra Reddy, N. V. Ravindra, P. Lokesh and, P. Sreedhara Reddy

2. Characterization electron beam evaporated NiO thin films
   A. Madhavi, G.S. Harish and P. Sreedhara Reddy

3. Effect of annealing temperature on optical and electrical properties of electron beam evaporated NiO thin films
   A. Madhavi, G.S. Harish and P. Sreedhara Reddy

4. Influence of film thickness on the properties of NiO thin films deposited by electron beam evaporation
   A. Madhavi, G.S. Harish and P. Sreedhara Reddy
   Journal of Material Science & Technology (Communicated)
List of Conferences attended:

1. Structural and Electrical properties of NiO films deposited at various substrate Temperatures

2. Preparation and characterization of, NiO thin films for gas sensor applications

3. Influence of film thickness on the properties of electron beam evaporated NiO thin films
   National conference on recent trends in material science, SVDC, Kadapa during March 1-2, 2015.