CHAPTER – II

LITERATURE REVIEW ON NiO AND SnO$_2$:F AND PREPARATION TECHNIQUES

2.1 INTRODUCTION

Various methods of nickel oxide thin films deposition have been adopted by many researchers to deposit nickel oxide thin films on various substrates and different characterization techniques were carried out to study the prepared films. Electronic and sensor devices have been reported. NiO materials in thin films as well as powder forms, doped and un-doped forms have been developed. All are presented in the following sections.

2.1.1 Various Preparation Techniques and Salient Properties of NiO Films

Nickel oxide is a suitable material for electrochromic devices [1-6], an antiferromagnetic layer [7], p-type transparent conducting film [8], a functional sensor layer for gas sensor [9,10] and chemical sensor [11], solar thermal absorber [12], catalyst for oxygen evolution [13] and photoelectrolysis [14]. Nickel oxide thin films have been prepared by thermal evaporation [15], anodic oxidation [16], chemical deposition [17], atomic layer epitaxy [18], sol-gel [19], pulsed laser deposition [20, 21], electron beam evaporation [22-24], DC and RF magnetron sputtering [25, 26] processes. Nickel oxide thin films have both amorphous or polycrystalline structure [27]. The polycrystalline nature of the NiO thin film can have rhombohedral or cubic (FCC) system and the FCC structure is having lattice parameter of 0.4195nm [28]. Fujii et al [29] observed sputtered NiO films with good crystallinity and (100) preferred orientation at the substrate temperature of 150 °C and above.

Kumagai et al [30] observed that the sputtered NiO films, prepared by controlled growth with sequential surface chemical reactions, had an amorphous structure. Hotovy et al [31] prepared NiO thin films by reactive DC magnetron sputtering. The as-deposited film has amorphous structure and it changes to the FCC structure as the films are annealed. Atomic force microscope observations show clear grains after annealing at a
temperature of 700 °C. Hao Long Chen et al deposited NiO thin films by RF magnetron sputtering and they studied the dependence of film properties on substrate temperature, crystalline structure and natural aging effects [32]. The results show that the resistivity increases as the sputtering power increases and the preferred orientation changes from (111) to (200) when the substrate temperature varies from unheated condition to 350 °C.

Wang et al [33] observed that the resistivity of lanthanum nickel oxide thin films decreases rapidly, as the annealing temperature increases from 500 °C to 600 °C. The films annealed at 600 and 650 °C had resistivities lower than 10^{-4} cm. He also observed that the resistivity of the films decreases with increasing thickness. Chen et al [34] have studied the relation between the thickness of NiO film, prepared by RF magnetron sputtering, and their electrical and optical properties. He showed that the thicker NiO films develop well-defined microstructures. The crystallite sizes become larger and the transmittance decreases as the thickness of the film increases. Desai et al [35] prepared non-stoichiometric NiO thin films by pyrolytic decomposition. They discussed about the band gap calculation on the basis of optical absorption. The band gap value of 3.6 eV was found by this method. Smooth surface coverage of the NiO thin film was reported using SEM micrograph. Spray pyralysis method was employed to deposit NiO thin film by Patil and Kadam [36]. They also suggested the band gap calculation by optical absorption studies and showed that the value of band gap changes from 3.58 to 3.4eV with the increase in the film thickness. Varkey and Fort reported the band gap value of 3.25 eV for NiO films prepared by solution growth technique [37]. Mahmoud et al [38] prepared NiO films by spray pyrolysis technique and reported the effect of solution concentration on their structural, electrical and optical properties. They showed that the absorption versus photon energy curves revealed a direct transition with optical band gap (E_g), of 3.6 eV and indirect transition within the range 3.97 to 3.75 eV, as solution molarity increases from 0.05 to 0.3M.

Homogeneous nanoparticles of NiO have been synthesized, via reverse-miceller route, by Ahmad et al [39]. They showed that the FTIR spectrum has a broad absorption around 405 to 415 cm^{-1} and a weak absorption around 82 cm^{-1}. This can be assigned to nickel-oxygen interaction. Cyclic voltammetry studies show a well resolved anodic peak at 0.45 eV at the scan rate of 1 mV/s, which shifts to 0.47 V at the scan rate of 100 mV/s.
and the cathodic peak was also observed at 0.34 V, which remains at the same position irrespective of the sweep rate. The quasireversible nature of the voltammograms suggested the usefulness of these materials for ultracapacitor applications.

The electrochromic characteristics of vacuum evaporated NiO thin films were recorded by Velevska and Ristova [40]. They have calculated the coloration efficiency of the NiO thin films. Avendano et al [41] have also calculated the coloration efficiency of sputtered NiO thin films. Korosec et al [42] observed the thermal decomposition of sol-gel prepared NiO films from thermogravimetric measurements. The decomposition was completed up to the temperature of 350 °C and the degree of thermal decomposition is 50% after 15mins, 80% after 30mins and 100% after 60mins.

2.2 PREPARATION OF NiO THIN FILMS

Wang et al [43] have reported the preparation and characterization of highly oriented NiO (200) films by a pulse ultrasonic spray pyrolysis method. Cubic nickel oxide (bunsenite) films with a preferred (200) orientation and an average grain size of 15 nm were deposited on Si (111) substrate by a pulse ultrasonic spray pyrolysis method. The resulting films were characterized by XRD, SEM, AFM and XPS.

Lu et al [44] have reported the properties of nickel oxide thin films deposited by RF reactive magnetron sputtering. The NiO films were deposited by RF reactive magnetron sputtering from a Ni target in a mixture of oxygen and argon gases onto heated Si and corning 7059 glass substrates. The influences of process parameters including RF power, O2/Ar ratio and substrate temperature on the film properties such as O/Ni atomic ratio, crystallographic structure, preferred orientation, transmittance and resistivity were then investigated.

Patil et al [45] have reported the preparation and characterization of spray pyrolyzed nickel oxide (NiO) thin films from hydrated nickel chloride salt solution onto glass substrates. TGA and DTA techniques were used to study the thermal characteristics of the precursor salt. The effect of the volume of sprayed solution on structural, optical and electrical properties was studied using XRD, IR, optical absorption, electrical resistivity and thermoelectric power (TEP) techniques.
Hotovy et al [46] have reported the characterization of NiO thin films deposited by reactive sputtering. NiO thin films were deposited by DC reactive magnetron sputtering Ni in an Ar and O₂ mixed atmosphere at room temperature on unheated Si substrates. The oxygen content in the gas was varied from 10 to 50% and its effect on the deposition rate, structural, composition and electrical properties of the films were studied using thickness measurement, XRD, TEM, RBS and resistivity measurement.

Hotovy et al [47] have reported the deposition and properties of nickel oxide films produced by DC reactive magnetron sputtering. NiO thin films were prepared on Si substrates by DC reactive magnetron sputtering from a nickel metal target in Ar and O₂ with the relative O₂ content varied from 15 to 50%. The effects of the O₂ gas content on the deposition rate, structure, composition and electrical properties were investigated.

Hurtado et al [48] have reported the optical and structural characterization of nickel oxide based thin films obtained by chemical bath deposition on glass and silicon substrates. SEM images show aggregates of thin stacked sheets on their surface. In order to obtain thicker NiO films with good optical properties a procedure is developed performing several immersing annealing cycles.

Hotovy et al [49] have reported the influence of process parameters and annealing temperature on the physical properties of DC magnetron sputtered NiO thin films prepared on Si and alumina substrates. The effect of the sputtering mode and of annealing temperature on the physical properties of thin NiO films was studied using XRD, AFM and SEM.

Chen et al [50] have reported the characterization of RF magnetron sputtered NiO thin films. The structural, optical and electrical properties of NiO films were investigated using XRD, visible spectrum and Hall effect measurements. The dependences of film properties on substrate temperature, crystalline structure and natural aging effect were studied.

Zhou et al [51] have reported the influence of thermal annealing on optical properties and surface morphology of NiO₃ thin films. NiO₃ thin films were deposited by reactive DC-magnetron sputtering from a nickel metal target in Ar and O₂ with the relative O₂ content of 5%. XPS, TGA, SEM and optical studies were carried out. The
results showed that the changes in optical properties and surface morphology depended on the temperature.

Zheng et al [52] have reported the preparation and electrochemical properties of nickel oxide by molten-salt synthesis. Well-crystallized NiO nanoparticles with uniform morphology of hexagon plates were first fabricated by molten-salt synthesis method using NaCl as a flux at 1000 °C. NiO nanoparticles prepared by molten-salt synthesis method is homogenous and in high purity.

Caffio et al [53] have reported the early stages of NiO growth on Ag (001): A study by LEIs, XPS and LEED. Ultra thin NiO films were grown on the Ag (001) surface by evaporation of Ni in an O₂ atmosphere. The growth mechanism, composition and structure of the NiO layers formed in the early stages of deposition have been investigated.

Song et al [54] have reported the cross-sectional HR-TEM and energy dispersive X-ray analysis of the microstructure of electrochromic nickel oxide films on ITO. Microstructural features and the differences between high and poor-quality samples were studied and compared.

Eleruja et al [55] have reported the preparation and characterization of metalorganic chemical vapor deposited nickel oxide and lithium nickel oxide thin films deposited through the pyrolysis of nickel acetylacetonate and lithium nickel acetylacetonate, respectively in the temperature range 350-420 °C. The prepared solid source precursors were characterized using Energy Dispersive X-Ray Fluorescence (EDXRF), XRD and IR spectroscopy and analyzed using a variety of techniques.

Mallick et al [56] have reported the swift heavy ion irradiation induced texturing in NiO thin films grown on Si (100) substrate by electron beam evaporation and sintered at 500 and 700 °C and irradiated with 120 MeV Au⁹⁺ ions. The FCC structure of the sintered films was retained up to the highest fluence (3 × 10¹³ ions cm⁻²) of irradiation. In the low fluence (1 × 10¹³ ions cm⁻²) regime however, the evolution of the XRD pattern with fluence showed a wide variation, critically depending upon their initial microstructure.

Li et al [57] have reported the preparation and characterization of nanostructured Ni(OH)₂ and NiO thin films by a simple solution growth process. Nanostructured
Ni(OH)$_2$ thin films were prepared by a simple solution growth process with F$^-$ and NH$_3$ used as Ni$^{2+}$ coordination agents, and ammonia hydroxide solution used as OH$^-$ supplier to accelerate the hydrolyzation of nickel complex species.

Chung et al [58] have reported the fabrication of the cube textured NiO buffer layer by line-focused infrared heating for coated conductor application. Epitaxial growth of NiO on the bi-axially textured Ni–3 at.%W (Ni–3W) substrate as seed layer for coated conductor were studied.

Chou et al [59] have reported the novel alkaline earth silicate sealing glass for SOFC and the effect of nickel oxide on the thermal and mechanical properties. In this paper, the effect of NiO on glass forming, thermal, and mechanical properties was studied with two different approaches: glass making and composite glass and are compared.

Preda et al [60] have reported the study of the growth of NiO on highly oriented pyrolytic graphite by X-ray absorption spectroscopy. NiO has been grown by reactive evaporation of metallic Ni in an oxygen atmosphere ($2 \times 10^{-5}$ Torr) at room temperature. For large NiO coverages, the spectra resemble that of a NiO single crystal, thus indicating the formation of a stoichiometric NiO thin film on the HOPG substrate.

Reguig et al [61] have reported that NiO thin films have been grown on glass substrate by intermittent spray pyrolysis deposition. The properties of the film was studied and it was reported that NiO thin films crystallized in cubic structure and the grain size was around 25 – 30 nm. All the films were p-type. By comparing with the properties of films deposited by classical spray techniques it was concluded that the precursor concentration is critical which induces strong perturbations in thin films properties.

Sheng-Yue Wang et al [62] have reported that cubic nickel oxide films with a preferred (200) orientation and an average grain size of 15 nm were deposited by pulse ultrasonic spray pyrolysis method. The films were characterized by X-ray diffraction, scanning electron microscopy, atomic force microscopy and X-ray photoelectron spectroscopy. Highly crystalline NiO films with (200) orientation were obtained at 360 °C substrate temperature.

Berkat et al [63] have reported that NiO thin films were obtained by spray pyrolysis method. Prepared films were p-type semiconductors with a band gap of 3.5 eV.
The X-ray diffraction studies revealed that all the films are crystallized in the cubic NiO phase. The films are orientated along (111) plane. The X-ray photoelectron spectroscopy results identified the presence of hydroxyl groups at the surface of the films, where as the electron probe micro-analysis showed that the films were stoichiometric in the bulk.

Kamal et al [64] have deposited nickel oxide films onto glass substrate at different substrates temperatures. X-ray diffraction showed that for low $T_{sub}$, amorphous films have been obtained, while at higher $T_{sub} > 275^\circ C$ crystalline NiO films were grown with preferential growth along (111) plane. Analysis of the spectral absorption confirmed direct and indirect transitions. Infrared spectral reflectance showed presence of nickel chloride in films formed at $T_{sub} \leq 225^\circ C$.

Kaweno et al [65] have studied matrix-type NiO-SDC composite -particles synthesized by spray pyrolysis method. The calcined matrix-type NiO-SDC composite particles at 500 and 1000 °C showed the high performance of SOFC anode. From the electrochemical characterization, the matrix-type structure was effective to reduce the ohmic loss. It was found that the addition of citric acid into the starting solution for spray pyrolysis led to the high-dispersed matrix-type NiO-SDS composite particles with spherical shape, which showed the high performance of the anode, without any pre-heat treatment of the starting solution.

Yoshida et al [66] have prepared NiO-samaria doped ceria (SDC) composite powders by spray pyrolysis method at temperatures between 400 and 1000°C. The variation of the particle structure was investigated by X-ray diffraction (XRD), X-ray absorption fine structure (XAFS), Scanning Electron Microscope (SEM), and Transmission Electron Microscope (TEM), Energy-dispersive X-ray spectroscopy (EDS).

Wang et al [67] have reported the eutectic assisted synthesis of nano-crystalline NiO through chemical precipitation. Cubic NiO nanocrystallites with the particle size of 15-20 nm were successfully prepared through the decomposition of the precursor and eutectic as the assistant. The prepared NiO nanocrystallites have better morphology and uniform granularity.

Li et al [68] have reported the preparation and characterization of NiO nanoparticles through calcinations of malate gel. NiO nanoparticles have been successfully prepared by calcining malate gel, using basic nickel carbonate (BNC) and
malic acid as the raw materials and H₂O as the solvent. The reaction was studied by TG-DTA, XRD and FT-IR. The particle size of NiO increased with the increase in temperature.

Wu et al [69] have reported the effect of synthesis method on the physical and catalytic property of nanosized NiO. Nanosized NiO material was prepared by four different methods. Their physicochemical properties were investigated through SEM, BET, XRD and O₂-TPD characterization. The results indicated that NiO nanoparticles synthesized by different methods have variant diameters, shape and distribution.

Sasi et al [70] have reported the preparation and characterization of nanostructured NiO thin films by reactive-pulsed laser ablation technique. XRD studies indicate enhancement in growth along (111) and (200) crystal planes with increase of substrate temperature. AFM studies indicate a self-assembly of NiO nanocrystals. The optical band gap and electrical resistivity of the films synthesized under different conditions are also discussed.

### 2.3 PREPARATION OF NiO NANO PARTICLES

Xing et al [71] have reported the synthesis and electrochemical properties of mesoporous nickel oxide. Structure characterizations indicate a good mesoporous structure for the prepared nickel oxide samples. NiO with a controlled pore structure can be used in much larger amounts to fabricate electrodes.

Hajry et al [72] have reported the low-temperature growth and properties of flower-shaped β-Ni(OH)₂ and NiO structures composed of thin nanosheets networks through the simple aqueous solution route by using nickel chloride and ammonium hydroxide at 65°C in 4 h. The shape of nanosheet networks in β-Ni(OH)₂ was sustained after thermal decomposition to NiO however, some broken nanosheets were also observed from the flower-shaped structures of NiO.

Li et al [73] have reported the preparation and characteristics of NiO-coated nano-fibriform silica. NiO-coated nano-fibriform silica (NFS) was prepared by an excessive soakage method and was characterized. Comparison of NiO-coated NFS and NiO(Ni)-coated sol–gel silica as catalysts reveals that NiO-coated NFS may be an effective catalyst and that NFS may be a good catalyst carrier.
Xia et al [74] have reported the XRD analysis was done. The FTIR results showed presence of free hydroxyl ion and water in the NiO thin films. The electrochromic properties of NiO thin films were investigated.

Liu et al [75] have reported the growth of the oxidized nickel nanoparticles on a DNA template in aqueous solution. The synthesized products have been characterized by AFM and XPS. The results showed that uniformly oxidized nickel nanoparticles can be grown and assembled on a DNA template. These assembled small NiO nanostructures may have some potential application as catalysts, magnetic materials or electrochromic films.

Bahadur et al [76] have reported the effect of heat treatment on pore structure in nano-crystalline NiO synthesized by a precipitation route. Powder samples were heat treated at 300, 600 and 900 °C, and pore structure evolution was followed by small angle neutron scattering (SANS) technique. SANS measurements were carried out also on pelleted samples in order to study the modifications of pore morphology due to heat treatment.

Beach et al [77] have reported the solvothermal synthesis of nanostructured NiO, ZnO and Co$_3$O$_4$ microspheres. The microspheres were shown to exhibit a morphology resembling a collection of platelets with nanoscale thickness.

Palacin et al [78] have reported the core-level electronic properties of nanostructured NiO coatings. Nanostructured NiO films with different thicknesses were grown on nanoporous alumina membrane substrates by reactive evaporation of Ni in an oxygen atmosphere. The reactive deposition process was assisted by a low energy oxygen ion-beam in order to increase the NiO input into the pores. SEM observations reveal a well adhered film of NiO on the substrate.

Meneses et al [79] have reported the kinetics of formation of NiO nanoparticles by X-ray absorption spectroscopy. The effects caused in the initial stage of particles growth by different heating rates are investigated. XAS results show that the particles disorder appears for high heating rates and growth process is faster for low heating rates.

Wu et al [80] have reported the effect of synthesis method on the physical and catalytic property of nanosized NiO material prepared by four different methods. Their physicochemical properties were investigated. The results indicated that NiO
nanoparticles synthesized by different methods have variant diameters, shape and distribution.

Yi et al [81] deposited Nickel oxide thin films with a thickness of 200 nm on both Si (111) and NaCl (100) substrates by spray pyrolysis method, using ethanol solution and nickel acetylacetonate as the source material. The resulting films were identified as NiO films with poor preferred (110) orientation. Surface uniformity of the films was confirmed by SEM and uniform color of the films. SEM and TEM investigation showed that the NiO films on Si (111) substrates consisted of particles less than 20 nm, while the films on NaCl (100) consisted of spherical particles with sizes of 100 nm and these particles were in fact comprised of densely packed nanocrystallites of size less than 10 nm.

Stopic et al [82] have reported submicrometer NiO and Ni powders obtained by ultrasonic spray pyrolysis of aqueous solution of NiCl₂ followed by thermal decomposition. Particle size of the prepared powders can be controlled by the change of reaction temperature and the concentration of initial solutions. Pyrolysis temperature in the range from 973 to 1273K, non-agglomerated ideally spherical NiO with a mean diameter of 0.5 – 0.8 μm were obtained. Ideal spheres of NiO particles were prepared due to sufficient residence time of droplets in the drying and pyrolysis process. The process of Nickel formation proceeds through a previous transformations followed by the reduction of NiO into nickel.

2.4 PREPARATION OF NiO THIN FILMS FOR ELECTROCHROMIC DEVICES

Magana et al [83] have reported the electrochemically induced electrochromic properties in nickel oxide thin films deposited by DC magnetron sputtering. In this, NiO thin films were produced by DC magnetron sputtering on ITO substrates. The structural properties of the films were studied by XRD, SEM and TEM in conventional and high-resolution modes. The electrochemical properties were studied by the cyclic voltammetry technique.

Avendano et al [84] have reported the optimized nickel-oxide based electrochromic thin films. Reactive DC magnetron sputtering was used to make oxide films based on Ni, NiV₀.₀₈, NiAl₀.₅₆, NiMg₀.₈ and NiV₀.₀₈Mg₀.₅. All of these films were
capable of showing electrochromism in KOH. The addition of Al or Mg increased the luminous transmittance significantly, while the charge capacity was maintained.

Ferreira et al [85] have reported the electrochromic nickel oxide thin films deposited under different sputtering conditions. In this work, non-stoichiometric nickel oxide (NiOₓ) films were deposited by RF reactive sputtering of a metallic nickel target in an O₂-Ar atmosphere. The films were cubic NiO, with preferred orientation in the (111) direction. Lattice parameters increased with increasing oxygen flux during deposition, but decreased with increasing power.

Miquel et al [86] have reported the nickel-oxide sol-gel films from nickel diacetate for electrochromic applications. Nickel diacetate tetrahydrate, and nickel diacetate dimethyl amino ethanol, were successfully used to deposit NiOₓ thin films on conductive glass substrates by sol-gel techniques for large area electrochromic applications. The NiOₓ films were characterized by XRD, TEM and AFM.

Seo et al [87] have reported the conductivity switching characteristics and reset currents in NiO films for various NiO films deposited by DC reactive sputtering method. By reasoning out conductivity switching mechanisms from the switching characteristics and introducing multilayers consisting of NiO layers with different resistance values, the reset current have been reduced by two orders of magnitude.

Abe et al [88] have reported the electrochromic properties of sputtered NiO thin films in neutral KCl electrolytes. Thin films of NiO, were deposited by reactive RF sputtering at 40, 60 and 100 W and their electrochemical and electrochromic properties were examined using neutral KCl electrolytes. Higher charge capacity and higher optical modulation were obtained for a Ni oxide film deposited at low sputtering power and low deposition rate.

Abe et al [89] have reported the electrochromic properties of sputtered Ni oxide thin films in acidic KCl solutions. KCl concentration was kept constant at 1 M while H₂SO₄ concentrations were varied from 0 to 50 mM. EC coloration efficiency was found to be ~30 cm²/C in all the solutions, and maximum charge capacity and maximum change in optical density were obtained in a 1 M KCl solution with 0.5 mM H₂SO₄.

Bouessay et al [90] have reported electrochemically inactive nickel oxide as electrochromic material. Nickel oxide thin films were grown at room temperature under
an oxygen pressure of $10^{-1}$ mbar, using pulsed laser deposition. The influence of the film thickness, potential window, and extended cycling on the electrochromic properties was studied by means of complementary electrochemical, XRD and electron microscopy techniques.

Mahmoud et al [91] have reported the opto-structural, electrical and electrochromic properties of crystalline nickel oxide thin films prepared by spray pyrolysis. The effect of solution concentration on their structural, electrical and optical properties of prepared films was studied. Analysis of the absorption versus photon energy curves revealed a direct transition with optical band gap, $E_g$ of 3.6 eV and indirect transition within the range 3.97-3.75 eV as solution molarity increases from 0.05 to 0.3 M.

Yashimura et al [92] have reported the cross-sectional observations by HR-TEM of the structure of nickel oxide electrochromic thin films in the as-deposited state and the bleached state. Electrochromic thin films are prepared by reactive DC magnetron sputtering. The images show that the surface morphology of the as-deposited and bleached samples are quite different.

Velevska et al [93] have reported the electrochromic properties of NiO$_x$ prepared by Low Vacuum Evaporation onto FTO coated glass substrates. CV studies, optical studies and FT-IR studies were carried out.

Azens et al [94] have reported the sputter-deposited nickel oxide for electrochromic applications. Thin films were produced by sputtering of metallic Ni in Ar/O$_2$ and Ar/O$_2$/H$_2$ atmospheres. Systematic studies of these films were carried out in electrochromic devices.

Avendano et al [95] have reported the electrochromism in nickel oxide films containing Mg, Al, Si, V, Zr, Nb, Ag or Ta. This paper reports on electrochromism in films based on nickel oxide with a variety of additives. The films were prepared by reactive DC or RF magnetron co-sputtering. The bleached state absorption could be significantly lowered when the additives was Mg, Al, Si, Zr, Nb or Ta, i.e., a type known to form oxides with large optical band gaps.

Chigane et al [96] have reported the electrochromic properties of nickel oxide thin films prepared by electrolysis followed by chemical deposition. NiO$_x$ thin films were
prepared onto transparent conductive tin oxide substrates by chemical process. Compared with the NiOx films prepared simply by anodic deposition, the films obtained through the chemical process showed different mode of electrochromism.

Urbano et al [97] have reported electrochromism in lithiated nickel oxide films deposited by RF sputtering from an LiNiO2 target. Samples deposited under Ar and O2 atmosphere and high power, or pure Ar atmosphere and low power showed a 70% transmittance charge and a stable voltammetric profile after some cycles.

Martini et al [98] have reported the electrochromic properties of NiO-based thin films prepared by sol-gel and dip coating. Films deposited on ITO substrates were prepared by dip coating. The effects of Ni concentration, Ti content and temperature of firing on the electrochromic efficiency was reported.

Ying Wang et al [99] have reported the nanocrystalline NiO thin film anode with MgO coating for Li-ion batteries. The nanocrystalline NiO thin films with the mean size of ~30 nm are prepared by pulsed laser reactive ablation in an oxygen ambient and subsequent coated by MgO on the NiO film surface. As compared with bare NiO, coated NiO film electrode heat treated at 500 °C exhibits excellent structural stability and electrochemical performance.

Nuli et al [100] have reported nanocrystalline tin oxides and nickel oxide film anodes for Li-ion batteries, fabricated by vacuum thermal evaporation of metallic tin or nickel. XRD and SEM measurements showed that the prepared films are of nanocrystalline structure with the average particle size <100 nm. The electrochemical properties of these film electrodes were examined by galvanostatic cycling measurements and cyclic voltammetry.

Yoshio Abe et al [103] have reported the electrochromic properties of Ni oxide thin films in diluted acidic electrolytes and their stability. Electrochromic (EC) properties of sputtered Ni oxide films have been examined in 1 M KCl acidic aqueous solutions with H2SO4 concentrations of 0-50 mM.

Ozkan et al [102] have reported the sol-gel deposited nickel oxide films for electrochromic applications. The films were produced by spin and dip-coating techniques on ITO/glass and corning glass (2947) substrate. The surface morphology, crystal
structure, and EC characteristics of the coatings were investigated by SEM, EDS, AFM, XRD and CV.

Baschloo et al [103] have reported the spectroelectrochemistry of nanostructured NiO prepared by heating Ni(OH)\textsubscript{2} sol-gel films at a temperature of 300-320 °C. Nanostructured NiO (bunsenite) behaves as a p-type semiconductor and has an indirect band gap of 3.55 eV. It shows a strong anodic electrochromic effect, as it changes color from transparent to brown-black upon application of positive potentials.

Wu et al [104] have reported the ion transport in electrochromic nickel oxide thin films. Dynamic process of ion injection into nickel oxide film in both KOH and LiClO\textsubscript{4}-PC electrolyte were studied using electrochemical measurement. Results showed that the film displays complex transport behavior which depends on the deposition rate of the film, the environment and sequence of heat treatment, the adopted electrolyte.

Ristova et al [105] have reported the chemical bath deposition and electrochromic properties of NiO\textsubscript{x} films prepared on two kinds of substrates: Glass and glass/SnO\textsubscript{2}:F. Films were thermally treated at 200 °C for 10 min in atmosphere. The texture, microstructure and composition were examined by optical microscopy, XRD patterns and XPS analysis of the surface layer.

Kadam et al [106] have reported the studies on electrochromic properties of nickel oxide thin films prepared by spray pyrolysis technique onto FTO coated glass substrates from nickel chloride solution. Transparent NiO-thin films were obtained at a substrate temperature 350 °C. The films were cubic NiO with preferred orientation in the (111) direction. IR spectroscopic studies, CV, CA and spectrophotometry were done.

Xia et al [107] have reported the morphology effect on the electrochromic and electrochemical performances of NiO thin films on ITO substrate prepared by chemical bath deposition (CBD) and sol–gel method, respectively. Both the films have polycrystalline cubic NiO, but have distinct morphology. The electrochemical properties of both the NiO thin films were investigated in 1 M KOH electrolyte by means of cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements.

Arakaki et al [108] have produced electrochromic films of NiO\textsubscript{x} and WO\textsubscript{3} were produced by the spray pyrolysis method. The nickel-oxide-based coatings were obtained from an aqueous solution of nickel nitrate. Those obtained below 300 °C did not show
any diffraction peak when subjected to X-ray diffraction analysis, and those obtained above 400 °C shows a diffraction pattern corresponding to the cubic NiO. Films obtained below 300 °C showed an electrochromic effect with an electrochromic efficiency of 30 cm²/C.

2.5 PREPARATION OF NiO FILMS FOR SENSOR AND OTHER APPLICATIONS

Noh et al [109] have reported the electrical properties of nickel oxide thin films for flow sensor application. In this work, Ni oxide thin films, with thermal sensitivity superior to Pt and Ni thin films, were formed through annealing of Ni films deposited by a RF magnetron sputtering. Because of their high resistivity and very linear TCR, NiO films are superior to pure Ni and Pt thin films for flow and temperature sensor applications.

Hotovy et al [110] have reported the sensing characteristics of NiO thin films as NO₂ gas sensor. In this paper, the results concerning the characterization of nickel oxide thin films deposited by DC reactive magnetron sputtering was presented. The structure and surface morphology of the samples have been analyzed by XRD AFM and SEM, techniques.

Hotovy et al [111] have reported the preparation of nickel oxide films for gas sensors applications. NiO thin films were prepared by De reactive magnetron sputtering from a nickel metal target in an Ar and O₂ mixed atmosphere in two sputtering modes. The films prepared in the oxide-sputtering mode were amorphous while the films in metal-sputtering mode exhibited polycrystalline (fcc) NiO phase.

Krishnakumar et al [112] have reported the magnetic linear dichroism studies of in situ grown NiO thin films. The thickness dependence of magnetic linear dichroism (MLD) of in situ grown NiO (001) films on Ag (001) substrate at the NiL₂ absorption edge was reported. Antiferromagnetic domains at the surface of NiO (001) films are found to be preferentially aligned in plane.

Nam et al [113] have reported the X-ray absorption spectroscopy studies of nickel oxide thin film electrodes for super capacitors. NiO films were synthesized by
electrochemical precipitation of Ni(OH)$_2$ followed by heat-treatment in air at various temperatures (200-600 °C). Their structure and electrochemical properties were studied.

Xu et al [114] have reported the synthesis and characterization of mesoporous electrochemical active material NiO with fcc structure for electrochemical capacitor using supramolecular as template and urea as hydrolysis controlling agent. The synthesized product was characterized physically by TG analysis, XRD, TEM and Brunauer-Emmett-Teller specific surface area measurement.

Gondal et al [115] have reported the laser enhanced photo-catalytic removal of phenol from water using p-type NiO semiconductor catalyst. The characteristics of phenol removal using laser induced photo-catalytic process were investigated. The dependence of phenol removal on laser energy (100–250 mJ) and laser irradiation time (0–60 min) was studied.

Zhao et al [116] have reported the NiO/NiAl$_2$O$_4$ oxygen carriers prepared by sol-gel for chemical-looping combustion fueled by gas. Chemical-looping combustion with inherent CO$_2$ enrichment depends on the high-powered oxygen carriers. The experimental results show that the sol-gel-derived NiO/NiAl$_2$O$_4$ oxygen carriers demonstrate an extremely good recycling ability of reduction–oxidation reaction.

Veghel et al [117] have reported the anti-ferromagnetic contrast in NiO (0 0 1) studied with threshold photoemission electron microscopy. A detailed study is presented of the potential of threshold photoemission electron microscopy (PEEM) for the imaging of anti-ferromagnetic (AF) domains of NiO (0 0 1).

Lee et al [118] have reported a self-heating gas sensor with integrated NiO thin-film for formaldehyde detection. The novel micro formaldehyde gas sensor developed in this study is ideal for applications aimed at preventing and controlling sick building syndrome (SBS).

Nikolic et al [119] have reported the far-infrared properties of sintered NiO. Far infrared reflection spectra of NiO polycrystals sintered at 1100 °C for various times (30–240 min) were measured at room temperature. The measured spectra depended on the sintering time due to differences in the microstructural morphology of the material.

Razpotnik et al [120] have reported the synthesis of nickel oxide/zirconia powders via a modified Pechini method. The effect of different chelating agents, e.g., ascorbic and
citric acid, on the thermal decomposition of gels and on the morphology of final products, was studied. The results show that the powders prepared with ascorbic acid could be used for preparation of SOFC anodes.

2.6 LITERATURE ON PREPARATION AND PROPERTIES OF SnO$_2$:F FILMS

Shanthi et al [121] reported the deposition of transparent electrically conducting tin oxide and fluorine doped tin oxide films on alkali free corning borosilicate glass plates in the temperature range of 375-450 $^\circ$C by spray pyrolysis method. The visible transmittance and electrical resistivity of the films decreased with the increase in fluorine concentration. Increase in free carrier concentration results in decrease of transmission percentage slightly from undoped films.

Gordillo et al [122] investigated on highly transparent and conducting SnO$_2$ thin films deposited by the spray pyrolysis techniques using tin chloride and SnCl$_4$ as precursor solutions and NH$_4$F and HF as sources of doping impurities. A comparative study revealed that samples prepared using SnCl$_2$ and HF has lower values of resistivity than those obtained from SnCl$_4$ and NH$_4$F. SnO$_2$ films with resistivities of about $2.5 \times 10^{-4}$ $\Omega$cm and transmittance greater than 90% were obtained. XRD measurements indicated that SnO$_2$ films, prepared from SnCl$_4$, have a preferential growth along (200) direction whereas samples from SnCl$_2$ has a tendency to grow preferentially along (101), (211) and (301) directions. The introduction of fluorine impurities in the SnO$_2$ samples gave rise to decrease of its resistivity by a factor of 20 without causing significant changes.

De Wall et al [123] studied the electrical properties of fluorine doped SnO$_2$ films and showed that this type of coating behaves as a semi metal. The optical properties showed a high electron density of about $3 \times 10^{26}$ m$^{-3}$. Above 200$^\circ$C, thermal aging is observed particularly in vacuum which affects the D.C. resistivity slightly. Pommier et al. [124] studied the transmission and resistivity of large area fluorine doped tin oxide thin films prepared by spray pyrolysis method. The solution for coating is pulverized with a neutral gas (e.g: Nitrogen gas), so that it arrives at the substrate in the form of very fine drops.
Bruneaux et al [125] investigated on the structural and electrical properties of polycrystalline sprayed SnO$_2$ films formed at 500°C in a wide concentration range ($7 \times 10^{17}$ cm$^{-3} < N_a < 4 \times 10^{20}$ cm$^{-3}$). The characterization studies revealed that i) The grain size is in the 20-80 nm range ii) There are number of planar defects which are thought to reduce the bulk mobility of the crystallites iii) Fluorine doping increases the density of twins. The dependence of resistivity on the carrier concentration $N_a$ can be accounted for within the frame of the grain boundary scattering.

Agnihotri et al [126] deposited thin layers of conducting (SnO$_2$:F) films of 3 ohm per square sheet resistance on borosilicate glass for potential applications in SIS solar cells. The layers exhibit 90% optical transmission at the solar maximum (0.5 μm). A direct allowed transition at 4.1 eV and an indirect allowed transition was also observed at 2.65 eV. A technique of marking ohmic contacts with SnO$_2$:F is also given. Manifacier et al [127] reported highly conductive and transparent thin films of SnO$_2$:F prepared using simple pyrolytic method. The prepared films were highly chemical resistant, transparent and conductive. This method is effective for the preparation of films, on an industrial scale, in solar energy conversion systems. For these purposes, the scattering observed in the properties of these layers should be of no practical importance.

Manifacier et al [128] studied and prepared highly conductive and transparent thin films of SnO$_2$:F using the pyrolytic spray method. The electrical and optical properties of these layers are studied in relation to their dopant concentrations and their stoichiometric derivation. The films obtained by SnO$_2$:F layers have the best overall properties such as higher transparency and lower sheet resistance, resistivities ranging between 4 and $6 \times 10^{-4}$ Ωcm with transparency exceeding 85% over the visible and near infra-red range of the spectrum. Agashe et al [129] studied and deposited transparent and conducting thin films of SnO$_2$:F on alkali free corning 7059 glass substrates by spray pyrolysis. The films deposited with the optimized process have a sheet resistance of 4 Ω/□, an average visible transmission of 86% (0.4-0.9 μm) and a thickness of 0.165 μm. The electrical conductivity of the SnO$_2$:F films was approximately $10^5$ Ω$^{-1}$cm$^{-1}$. The films were polycrystalline and the oxide phase observed was SnO$_2$ in cassiterite structure. Since doping generally favours defect induced film growth, heavily doped films were randomly oriented. Rearrangement of grains in the films was apparent for thicker films.
Thick r.f. sputtered films of SnO$_2$ doped with Sb exhibit moderate optical transmission and high electrical conductivity Vossen et al [130]. The preferred system for high transmission applications is SnO$_2$:Sb which was found to be useful, stable and reproducible even in thickness as small as 50 Å. Film transmission averaging 98% in the visible has been achieved with a sheet resistivity of 30 KΩ/□. The bulk resistivity of the films thicker than 300 Å is 0.006 Ωcm. The resistivity increases to 0.05 Ωcm at a thickness of approximately 50 Å, because high resistivity surface layer becomes an appreciable fraction of the total film volume.

Asomoza et al [131] have reported the resonant nuclear reaction technique to determine fluorine content in SnO$_2$ films prepared by spray pyrolysis. Singhet et al [132] deposited SnO$_2$:F on a thin SiO$_x$ layer grown in concentrated HNO$_3$ and on n-Si substrates with (100) orientation. X-Ray photo electron spectroscopy studies of the SnO$_2$:F films revealed fluorine doping in SnO$_2$. Bhardwaj et al [133] have prepared SnO$_2$:F films by spray pyrolysis of an alcoholic solution of SnCl$_4$ with NH$_4$F as dopant on glass substrates. At a doping level of 1.2 wt% the lowest resistivity (about 5.4 x 10$^{-4}$ ohm cm) and the highest figure of merit (about 10$^{-2}$ ohm$^{-1}$) were obtained. A direct band gap of 4.27 eV and an indirect band gap of 2.73 eV were deduced from optical data.

Krishnakumar et al [134] have prepared highly conducting transparent fluorine doped tin oxide films on glass substrates by employing SnCl$_2$ by spray pyrolysis from alcoholic solutions. Ma et al [135] have presented the structural, electrical and optical properties of transparent conducting F-doped textured SnO$_2$ films prepared by atmospheric pressure chemical vapour deposition (APCVD). Polycrystalline SnO$_2$:F films having a variable preferred orientation have been obtained with resistivity as low as 5 x 10$^{-4}$ ohm cm with carrier concentration between 3.5 x 10$^{20}$ and 7 x 10$^{20}$ cm$^{-3}$ and Hall mobilities from 15.7 to 20.1 cm$^2$/Vs. The average transmittance of a 655 nm film is as high as 94% in the visible spectrum and the maximum infrared reflectance is about 92%. The figure of merit 7.12 x 10$^{-2}$ ohms$^{-1}$ is the highest amongst the results reported on doped SnO$_2$ films.
2.7 PREPARATION TECHNIQUES

Transparent semiconductor oxide films with high conductivity and optical properties can be prepared by various techniques, e.g., RF sputtering, chemical spray pyrolysis, DC sputtering, chemical vapour deposition, electrodeposition, and electron beam evaporation.

In this chapter, the details of the preparation of Nickel oxide (NiO) films by DC reactive sputtering and electron beam evaporation techniques are presented. The complete configuration of these techniques and the procedures that have been adopted to deposit NiO films are elaborated. The optimized conditions for depositing NiO films under each technique are also presented which are used for characterization in their respective Chapters IV and V respectively. SnO$_2$:F films were carried out by engaging the chemical spray pyrolysis technique and the deposition steps are explained in detail here and the results in Chapter VI. The literature related to NiO and SnO$_2$ are presented in this chapter.

2.8 ELECTRON BEAM EVAPORATION (EBE) TECHNIQUE

Amongst the various techniques available, one of the physical vapor deposition methods, electron beam evaporation technique [136-139] is the widely used method for the deposition of superior quality oxide thin films. It offers flexibility in the control over various deposition parameters and easy adaptability of this technique for commercial purposes. As far as the electron beam evaporation is concerned, very thin films with a good surface finish can be obtained and there is no restriction on the type of substrate. The some of the disadvantages of other evaporation methods are that the sources include possible contamination by crucibles, heaters and support materials and the limitation of relatively low input power levels, which make them difficult to deposit pure films or evaporate high melting point materials at appreciable rates. Electron beam heating eliminates these disadvantages and has, therefore, become the most widely used vacuum evaporation technique to prepare highly pure films. In principle, this type of source enables evaporation of virtually all materials at almost any rate. The another major advantage of this technique is, multiple source units are available for the sequential or parallel deposition of more than one material [140-142].
Pressure is the most widely quoted system variable in vacuum technology, and this fact has generated a large number of units that have been used to define it under various circumstances. Basically, two broad types of pressure units have arisen in practice. The pressure is defined as the rate of change of the normal component of momentum of impinging molecules per unit area of surface. Thus, the pressure is normally defined as a force per unit area, the unit are dynes/cm² (CGS) or N/m² (MKS). Vacuum levels are now commonly reported in SI units or pascals; 1 pascal (Pa) = 1 N/m². The definitions of some units together with important conversions are [143]:

1 atm = $1.013 \times 10^6$ dynes/cm² = $1.013 \times 10^5$ N/m² = $1.013 \times 10^5$ Pa

1 Torr = 1 mmHg = $1.333 \times 10^3$ dynes/cm² = 133.3 N/m² = 133.3 Pa

1 bar = 0.987 atm = 750 Torr

Mean-free path is an important property of the gas that depends on the pressure, which is defined as the mean distance traveled by molecules between successive collisions. At atmospheric pressure, the mean free path of the molecules in air = $6 \times 10^{-6}$ cm ($10^{-4}$ cm = 1 micron; 1 micron = $10^{-3}$ Torr). Since the number of collisions between vapor and gas molecule is limited, at low pressures, the vapor molecules propagate in straight line paths. This principle is used in vacuum deposition.

For the preparation of NiO films by electron beam evaporation technique, we have used 12” Hind High Vacuum coating unit (model 12A4D) with electron beam solid state power supply (EBG-PS-3K). The vacuum coating unit used in the experiments comprised of a collar with bell jar (coating chamber) pumped by a conventional oil diffusion pump backed by an oil rotary pump. The schematic diagram of the vacuum coating system is shown in Fig. 2.1. The photograph of coating unit and electron beam power supply that has been employed in the present work is shown in Fig. 2.2. Some key notes on the various pumps that have been used in the coating unit to create the desired vacuum is elaborated below.
Fig. 2.1 The schematic diagram of the vacuum coating system
Fig. 2.2 Photograph of coating unit and electron beam power supply
2.8.1 Rotary pump

Hind Hivac coating unit is having direct driven rotary vane type vacuum pump. The rotary vane pump contains an eccentrically mounted rotor with spring loaded vanes. During rotation the vanes slide in and out within the cylindrical interior of the pump, enabling a quantity of gas to be confined, compressed and discharged through an exhaust valve into the atmosphere. The whole stator/rotor assembly is submerged in suitable oil. Single stage vane pumps have an ultimate pressure of \(10^{-2}\) Torr, and two stage pumps can reach \(10^{-4}\) Torr. Rotary pumps are frequently used to produce the minimal vacuum required to operate both oil diffusion and turbomolecular pumps, which can then attain far lower pressures.

2.8.2 Vapor pump or oil diffusion pump

This is the main pump to obtain the desired high vacuum. Diffusion pumps are designed to operate in the molecular flow regime and can function over pressures ranging from well below \(10^{-10}\) Torr to about \(10^{-2}\) Torr.

Diffusion pumps have been constructed with pumping speeds ranging from a few liters per second to over 20,000 lit/sec. Pumping is achieved through the action of a fluid medium (typically silicon oil) that is boiled and vaporized in multistage jet assembly. As the oil vapor stream emerges from the top nozzles, it collides with and imparts momentum to residual gas molecules, which happen to bound into the pump throat. These molecules are thus driven towards the bottom of the pump and compressed at the exit side where they are exhausted. The pump fluid should have a high molecular weight so that each molecule carries considerable momentum and can therefore make effective collisions with several gas molecules before all its momentum is lost. It should have a very low pressure. Silicon oil DC 704 satisfies these requirements.

2.8.3 Other Accessories

Generally, bell jar i.e., coating chamber may be made on pyrex glass or metals. The diameter of the bell jar may be 6” or 12” or 19”. Substrates to be coated may be kept either on top or bottom, if the source is of filament type. In the case of electron beam
evaporation the source is of the form of crucible made up of graphite, necessarily the substrates must be kept on top.

To measure the level of pressure, the pirani and penning guages are used. Pirani guage measures pressures down to $10^{-3}$ Torr, while the penning guage measures up to $10^{-6}$ Torr.

2.8.4 Electron Beam Gun

Electron beam gun power supply is designed to drive necessary power to electron bent beam gun with all necessary interlocks and safety devices. In the work accelerated electron gun, the electric field is maintained between the cathode and the evaporant (the work), whereas, in the self-accelerated electron gun, the space between anode and the work is field free. In both the guns, the path of the electron beam is a straight line. Therefore, either the gun or the substrates must be mounted off to the side. This restriction in the arrangement of electron source and substrate can be removed by bending the electron beam through a transverse magnetic field. For laboratory and bell-jar- type operations, however, the bent-beam gun has become most popular because they are compact, of universal applicability, and not rate-limited. Forcing the electrons into curved paths also allows effective separation of gun structure and vapor source without resorting to long distances.

The transverse field is provided by an electromagnet, which permits focusing during operation. Other models have permanent magnets and variable operating voltage to adjust the beam. Relatively large area elongated cathodes are employed to increase the electron-emission current. This facilitates gun operational voltages below 10 KV without sacrificing power. The cathode, although close to the evaporant, is in an offset position and shielded, hence protected against deposits and erosion by ion bombardment. Commercial models offer powers between 2 and 10 KW with accelerating voltages from 3 to 10 KV. They all use a water-cooled copper hearth to support the evaporant, and most of the guns are bakeable to facilitate out gassing. Depending upon the degree of thermal contact between evaporant and support, temperatures up to 3500 °C may be achieved so that refractory metals as well as oxides can be evaporated.
2.8.5 Working Principle of Electron Beam Evaporation

The electron beam method of evaporation is of interest to both decorative and functional metallizers. A wide variety of materials including refractory metals, low vapor pressure metals (such as platinum), and alloys can be evaporated. Since the electron beam method concentrates large amounts of heat on a very small area, high rates of deposition are possible. The process (Fig. 2.3) begins under a vacuum of $10^{-5}$ torr or less. The gun assembly is located outside the evaporation zone to avoid becoming contaminated by evaporant. A high voltage DC is the power supply for this operation. The voltage is typically 10 to 30 KV with a wattage ranging from 10 to 30 KW. This power is used to heat the tungsten filament, inside the electron beam gun when the filament becomes hot enough, it begins to emit electrons. These electrons form a beam. The deflection/focusing apparatus is designed using either permanent magnet or electromagnets to create a field which can shape and direct the path of the electrons. This is necessary because the electron is emitted in a random manner and must all be directed to the very small area where the evaporation will occur.

A magnetic field is used since it can directly attract the negatively charged electron. Lenses or other mechanical focusing devices would be ineffective and, subject to the heating process themselves. Now, the electrons are focused on the material to be evaporated (NiO pellet). When the electron beam strikes the target surface, the kinetic energy of motion is transformed by the impact into thermal energy (heat). It is important to remember that the energy given off by a single electron is quite small and that the heating is accomplished simply by virtue of the vast number of electrons hitting the evaporant surface. This is the energy, which vaporizes the target material. The energy level achieved in this manner is quite often more than several million watts per square inch. Compare this to the heat given off by a 100 W light bulb and you can begin to appreciate the magnitude of heat generated. Due to the intensity of the heat generated by the electron beam, the evaporant holder must be water cooled to prevent it from melting.
Fig. 2.3 Electron beam evaporation system
2.8.6 Merits of Electron Beam Evaporation Process

- The deposition rate in this process can be as low as 1 nm per minute to as high as few micrometers per minute.
- The material utilization efficiency is high relative to other methods and the process offers structural and morphological control of films.
- Due to the very high deposition rate, this process has potential industrial application for wear resistant and thermal barrier coatings in aerospace industries, hard coatings for cutting and tool industries, and electronic and optical films for semiconductor industries.

2.9 DC REACTIVE SPUTTERING (DCRS) TECHNIQUE

Sputter deposition technique has been also used to deposit NiO films on glass/SnO₂:F/ITO coated glass substrates. The vacuum coating accessories are the same as described earlier for EBE system. So the working principle of DCRS alone is described in this section.

2.9.1 Magnetron Source

Magnetron source of 2” dia is supplied in the system. It is in the sputter up configuration from the base plate. The body is on stainless steel and the magnets are made of ferrite/semarium. The magnets are arranged in concentric ring to give a dense field for the cathode. The circulation of water indirectly cools the target.

The substrate ion current and the quality of the coatings are increased with the development of multi-magnetron geometry with magnetic field linkage. This arrangement is called as closed-field magnetron sputtering shown. The magnets within the magnetrons are arranged, such that, alternating poles are next to each other resulting in the linkage of field lines. This prevents electrons escaping to the chamber walls, resulting in much higher ion current densities.

2.9.2 Working Principle of Magnetron Sputtering

Magnetron sputtering is a process, which the coating material is dislodged and ejected from the solid surface due to the momentum exchange, associated with surface
bombardment by energetic particles. To enable the ignition of plasma usually argon is introduced into the vacuum chamber between the target and the substrate. In the DC-sputtering a negative potential, up to some hundred volts, is applied to the target (NiO) and the substrate (glass) is grounded. This large difference in potential forms the plasma, which is caused by ionization of the Ar atoms in the intense electric field. This ionization results in a negatively charged electron and positively charged argon ion. These argon ions are accelerated towards the target material. Bombardment of the target with these high-energy ions leads to sputtering of the target atoms forming a coating on the substrate and chamber walls.

After the material is sputtered from the target, a small amount of oxygen is mixed with the plasma-forming gas and it reacts with the sputtered material to form oxide of the target material (Fig. 2.4 a). Hence it is called as reactive DC magnetron sputtering. On the other hand, electrons in the plasma are captured by the magnet, which is placed below the target. These electrons are forced into a spiral path, due to the Lorentz force, with a radius that is usually much less than the dimensions of the plasma and deposition system. These electrons cause a further ionization of the gas, resulting in the increase in ion current and hence faster deposition rates at lower pressure. The lower pressure in the chamber helps to create a cleaner film and the lower target temperature in this unbalanced magnetron sputtering enhances the deposition of high quality films. The DC reactive sputtering system is shown in Fig. 2.4 b.

2.10 CHEMICAL SPRAY PYROLYSIS TECHNIQUE

Spray pyrolysis has been developed extensively by Chamberlin and co-workers [144, 145]. After that, many research articles and review articles [146-149] related to spray pyrolysis processing and the range of thin films deposited by this method for various applications have appeared in the literature. Recently a comprehensive review of all possible thin film materials that could be deposited by spray pyrolysis technique for various applications has been published [150].
Fig. 2.4 (a) Photograph of DC reactive sputtering system and (b) Principle of DC reactive sputtering
2.10.1 Physical aspects of chemical spray pyrolysis

Spray pyrolysis involves spraying a solution, usually aqueous containing soluble salts of the constituent atoms of the desired compound on to a heated substrate. Every sprayed droplet reaching the hot substrate surface undergoes pyrolytic (endothermic) decomposition and forms thin films with cluster of crystallites.

A block diagram of a general spray pyrolysis set-up is shown in Fig. 2.5. Filtered carrier gas and solution are fed into a spray nozzle at a predetermined constant pressure and flow rate respectively. Substrate is placed inside a tubular furnace, which is powered by an external heater supply. The thermocouple in the feedback network delivered proportional output to the temperature monitor unit. Uniform coating over larger area on a substrate can be achieved by mechanical/electromechanical movement of either the nozzle or substrate holder or both. The spray set-up should be inside an enclosed chamber with an exhaust duct to remove vaporized constituents and to provide a stable flow pattern. The droplet size and distribution of droplets in the spray cone mainly depend on the geometry of the spray nozzle. The typical mode of droplet formation in a spray head is shown in Fig. 2.6.

In the spray cone, there exist three regions. Region A is in front of the nozzle, where the liquid is being lifted off the tip and accelerated into the main air cone turbulent-vortex region and the length of this region mainly depend on the flow rate of the precursor. The expanding helical shape of the aerosol envelope is seen at the confluence of regions A and B, where the droplets are formed by the turbulence of the air stream. Region C is the outside region of the main aerosol cone, where low velocity droplets are seen when the nozzle is not suitably designed.
Fig. 2.5 Chemical spray pyrolysis set-up
Fig. 2.6 Droplet formation at the spray nozzle
2.10.2 Chemical aspects of chemical spray pyrolysis

The chemicals used as solvent for spray pyrolysis must satisfy a variety of conditions for obtaining good quality films. The required conditions are: (i) they should have lower surface tension (ii) they should undergo a thermally activated chemical reaction leading to proper thermal decomposition and good quality thin films and (iii) the remainder of the constituents of the chemical should be volatile at the pyrolytic temperature.

These conditions are met by a number of combinations of chemicals and each combination has its own thermodynamic and kinetic considerations [151].

During pyrolytic decomposition, the constituents of the droplets vaporize during their transit towards the substrate or reacts on the surface after splashing. The pyrolytic process, in which the reaction occurs just above the surface of the heated substrate, is called heterogeneous reaction. If both the reactant and the product molecules are present in the gas phase or on the heated substrate then it is termed as homogeneous reaction. The homogeneous reaction is not desirable, which impede the film growth rate leading to irregular surfaces with powder formation [152-154].

In heterogeneous reaction, the droplets undergo pyrolytic (endothermic) decomposition leading to formation of films with single crystallites or cluster of crystallites. The other volatile by-products and the excess solvent escape in the vapor phase. The substrate provides the required thermal energy for this type of decomposition and subsequent recombination of the constituent species by thermal diffusion. This reaction process results in the sintering and recrystallization of the clusters of crystallites giving rise to coherent films.

2.10.3 Growth kinetics of thin films

The ideal condition of the film formation involves the deposition of the material atom by atom and layer by layer from the vapor phase of a material. Atomistic condensation takes place at the earliest stage of observation, in the form of a three dimensional nuclei which then grow to form a continuous film by diffusion-controlled processes. This condensation is the net result of equilibrium between the absorption and desorption processes taking place in the vicinity of the substrate surface. Many
theoretical models of condensation are proposed by various researchers that are consistent with the experimental observations [155, 156].

2.10.4 Characteristic Features of Spray Pyrolytic Process

(a) Growth Rate

In spray pyrolytic decomposition process, the growth and nature of the film surface depend on chemical nature and concentration of precursors, temperature of the substrate, droplet size during atomization and the various spray parameters. As mentioned in the previous section, chemicals used for spray pyrolysis must satisfy a variety of conditions. Usually, a number of combinations of chemicals meet these conditions. Each combination has its own thermodynamic and kinetic considerations. An oxide film can be prepared from variety of starting materials including nitrates, carbonates, halides etc. The choice of anion in the metal salt depends on the thermodynamic driving force and these salts are in decreasing order of thermodynamic force [157]. The heat of reaction is also a required thermodynamic factor and a non-equilibrium reaction proceeds towards accumulation of anion/cation species. Organometallic compounds have also been used because of its low temperature decomposition. In addition to this, their high vapor pressure allows the use of vapor transport rather than a liquid transport technique [158-160]. The variation of growth rate as a function of molarities of precursor also been discussed and the growth mechanism is discussed viz. Rideal-Eley and Langmuir-Hinshelwood mechanism [161]. The continuous increase in growth rate with molarity indicates that the growth rate is governed only by the cation containing species.

Moreover, in the case of transparent oxide films, the thickness increases linearly with time of spray (that is, with the amount of sprayed solution). Also, the growth of thin films is temperature dependent [162-164]. At low temperatures, the growth rate is controlled by activated processes, such as adsorption, surface diffusion, and chemical reaction and desorption. The growth rate is thus controlled by the reaction kinetics and the molecules are accumulated in front of the substrate. However, at high temperatures, the activated processes occur so fast and the molecules do not damp up on the substrate (that is, growth rate is diffusion limited) [165]. Growth rate also depends on the size of
the droplets, because the decomposition of droplet is temperature dependent. If the droplet size is large, the heat absorbed from the surroundings will not be sufficient to vaporize entirely the solvent on the way to the substrate and adversely affect the kinetics of the reaction [154].

(b) Substrate Temperature Effect

Since the dynamics of the evaporation and pyrolytic reactions are strongly temperature-dependent process, the substrate temperature has the most significant effect on the quality of the films. The role of the substrate temperature on film formation and microstructure are investigated by Viguie et al [147]. Films grown at lower temperature are amorphous [166, 167], whereas deposited at higher temperature are polycrystalline [168].

Usually, slow reactions at lower temperatures would yield foggy and diffusively scattering films. High substrate temperature yield thinner, continuous and hard films. At still higher temperatures, re-evaporation of anionic species may take place, resulting in metal rich deposits. Clearly, if the deposition conditions are not optimum, obtained films are powdery, non-adherent and low dense.

(c) Film Composition

Film composition is expected to depend on the kinetics of the spray process and the thermodynamics of the pyrolytic processes. Incomplete pyrolytic reactions yield intermediate compounds, which is trapped as impurity in the film. These impurity concentration decreases with increasing substrate temperature during pyrolysis. For chloride salts, addition of HCl to the solution has been found to reduce the chlorine content in the film. The conductivity of TO film is attributed to the multivalency tin ions and/or chlorine ions. The deviation from stoichiometry is controlled by the water and alcohol content in the spray solution. Water molecules provide oxygen and alcohol acts as a reducing agent. Use of a carrier gas does not seem to affect the concentration of incorporated oxygen vacancies.
(d) Parameters and the film quality

The preparation parameters involved in this spray method are many, whose interaction or even existence is sometimes difficult to access. The spraying method involves the decomposition (at high temperature, around 300-500 °C) of a mineral compound such as tin chloride penta hydrate or indium chloride dissolved in a solution of water and alcohol. Water is used as an oxidizing agent. The most important parameters of preparation are the nature and the temperature of the substrate, the time of deposition, the composition of the solution to be sprayed and the gas flow rate.

(e) Carrier gas pressure

The carrier gas is used to atomize the solution into fine particles. Higher pressure yields fine particles increasing which can produce mist of the particles. By controlling the pressure, the required size could be obtained but to have uniformity in the size, corona spray should be adopted. This pressure also affects the substrate temperature and hence to be optimized.

(f) Nozzle – substrate distance

Heterogeneous reaction is critically decided by this parameter. Closer to the substrate will lower the substrate temperature resulting to powdery deposits. The area of spray increases as this distance increases but not constantly. The flow rate and compressed air pressure will also affect the area along with this parameter.

(g) The solution and its concentration

Higher concentrations of the solution will yield mostly powdery deposits. There is a chance of the nozzle to be blocked when the hotness of the substrate reaches it at lower flow rates. Lower concentrations will alter the substrate temperatures and hence to be optimized. The stoichiometry of the film formed depends completely on the concentration and its ratio of the various species in it.

Other parameters like nozzle diameter, the type of carrier gas, rate of flow of the solutions, time of spray and the volume of the solutions also affect the film and its
quality. The texture of the films, its transparency and the thickness could be controlled by controlling these parameters.

2.11 SUBSTRATE CLEANING

The substrate cleaning procedures are the special art in thin film deposition. The cleanliness of the substrate is a pre-requisite for obtaining good quality films with reproducible properties. It exerts a decisive influence on the film growth and adhesion.

2.11.1 Substrate cleaning by washing and drying

The selection of the substrate decides the type of cleaning to be adopted in the process. The cleanliness of the substrate surface exerts a decisive influence on film growth and adhesion.

This process occurs many times in the cleaning process. Generally, distilled water is recommended but in semiconductor industry deionized water is recommended. After a careful cleaning and washing process, linen cloth or hot oven or acetone is recommended for drying the cleaned surfaces.

In the present work, the 7059 corning microscopic glass substrates and fluorine doped tin oxide coated (FTO or SnO$_2$:F) glass substrates were chosen for the deposition of NiO films.

The glass substrates were degreased by the following cleaning procedure to remove the unwanted impurities normally present on the surface of the glass plates when exposed to the atmosphere.

(i) The glass substrates are washed in soap solution (extran) by scrubbing the surfaces with the cotton swab dipped in liquid soap till they pass the breathe figure test to remove oil, grease etc.

(ii) The glass slides are then rinsed thoroughly in deionized water to remove any traces of the soap solution left on the surface.

(iii) Then the substrates are soaked in chromic acid and heated to about one hour to dissolve the fine silica layer formed on the surface and to make a new surface for deposition of the film.
(iv) Finally the substrates are rinsed thoroughly in deionized water and dried with acetone.

The surface of fluorine doped tin oxide coated substrates was cleaned gently rinsed with deionized water and dried with acetone. These well-degreased substrates were also cleaned by the HT cleaning process in the coating unit (as discussed earlier) before the deposition of NiO films.

2.12 FILM PREPARATION

The well cleaned microscopic glass and FTO coated glass substrates by the above mentioned cleaning procedures have been used for the preparation of NiO thin films by electron beam evaporation technique. This section contains the detailed procedures for the preparation of NiO films.

2.12.1 NiO film preparation by EBE technique

NiO films were prepared by electron beam evaporation technique using a HIND HIVAC vacuum coating unit with electron beam power supply.

The degreased substrates were mounted on the substrate holder and placed into the coating chamber. NiO powder (purity ~ 99.99%) was made into pellets by using a suitable die of about 20 mm diameter with 4 mm thickness. These palletized NiO targets were taken in graphite crucibles and kept on water cooled copper hearth of the electron gun, inside the vacuum chamber. Now the chamber was closed and evacuated using the rotary and diffusion pumps. After achieving the required vacuum i.e., high vacuum of the order of $1 \times 10^5$ mbar, the evaporation process was started.

In the electron gun, the electrons extracted from a d.c heated cathode of tungsten filament, by the application of electric field, pass through an anode and deflected through an angle of 270° by the magnetic field and reach the target material. The surface of NiO pellets on the graphite crucible was scanned by the resultant and deflected electron beam with an accelerating voltage of 5 kV and a power density of about 1.5 kW/cm². The ablated material (NiO pellet) was evaporated and the evaporated vapor phase condensed and deposited as thin film on the substrate. The homogeneous distribution of evaporated NiO particles on the substrate was attained by continuously rotating the substrate during
deposition. The distance of the substrate from the target material is about 25 cm. The observed films are uniform, pinhole free, well adherent to the substrates and transparent in nature. The deposition was carried out at room temperatures. The room temperature prepared films were further annealed (post heat-treated) at 400 °C and 500 °C in the presence of vacuum environment.

2.12.2 NiO film preparation by DC reactive sputtering technique

Thin NiO films were deposited on glass substrates using a Hind Hivac Magnetron Sputtering system. The films were deposited by DC reactive magnetron sputtering from a Ni target (50 mm in diameter, thickness of 3 mm, 99.9 % pure) in a mixture of oxygen and argon onto glass substrates. The relative partial pressure of oxygen to argon, defined as the ratio of $p(O_2)/p(O_2 + Ar)$, was fixed at 33.3 %. Sputtering deposition was performed at a gas pressure of 5x10^{-3} mbar. The substrates were kept at room temperature (RT) and then NiO thin films annealed at 400 °C and 500 °C.

2.12.3 SnO$_2$:F film preparation by chemical spray pyrolysis technique

In the present work, SnO$_2$:F thin films were prepared on 2.5 x 2.5 cm glass substrates using tin oxalate in ethyl alcohol. The spray solution was prepared by dissolving different amounts of tin oxalate and NH$_4$F for predefined molarities of F% as 5, 10, 15, 20, 25 and 30 in ethyl alcohol. The solution was sprayed by compressed air on the pre-cleaned glass substrate held at various temperatures between 325 °C and 525 °C. Ethanol has a very low boiling point (80 °C) and hence it becomes volatile at the high substrate temperature leaving only the desired product. The spraying solution is always buffered with small amount of hydrochloric acid to increase the solubility and to prevent precipitation in the solution.

Well cleaned substrate was placed inside the tubular furnace to attain the desired temperature. The temperature controller employed was SANSEL (Model STC 002). The compressed air from an ELGI compressor, along with the precursor was then allowed to enter into the spray nozzle. A fine aerosol was produced at the neck of the nozzle. This aerosol was then directed to the substrate by the incoming air current. On reaching the substrate surface, oxide of titanium was formed by the pyrolytic action on the substrate.
surface as deposits and by-products in the form of gases were removed by the exhaust fan. Deposited films were removed from the spray chamber after allowing the furnace on its own to reach room temperature and were stored in a moist free environment.

2.13 CONCLUSIONS

This chapter summarized the detailed mechanism of operation of the EBE, DCRS and CSP techniques. A detailed methodology for the preparation of NiO and SnO$_2$:F films is also described in this chapter.

Before the deposition of films on SnO$_2$:F substrates, the above said deposition conditions have been optimized on glass substrates. The sequential characterization studies on the films carried out to explore their various properties are summarized in the following chapters. A detailed literature on the various techniques engaged for the deposition of NiO and SnO$_2$:F films with different properties has also been presented in this chapter. Also, it summarizes the properties related to various devices such as about electrochromic and sensor devices.
REFERENCES


