Comparative Study of Zinc Oxide Nanostructures Synthesized by Oxidization of Zinc Foil and Zinc Powder

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology

In

Metallurgical & Materials Engineering

By

ANIMESH KUMAR SINGH (107MM023)

RADHAKANTA KISHAN (107MM029)

Department of Metallurgical & Materials Engineering

National Institute of Technology

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Under the Guidance of

Prof. S. N. Alam

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2011

National Institute of Technology

Rourkela

Certificate

This is to certify that the thesis entitled, **"Comparative Study of Zinc Oxide Nanostructures Synthesized by Oxidization of Zinc Foil and Zinc Powder"** submitted by **Animesh Kumar Singh (107MM023) and Radhakanta Kishan (107MM029)** in partial fulfillment of the requirements for the award of Bachelor of Technology Degree in Metallurgical & Materials Engineering to the National Institute Of Technology, Rourkela (Deemed University) is an authentic work carried out by them under my supervision and guidance. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any Degree or Diploma.

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ABSTRACT:-

ZnO is one of the most promising semiconductor material in the UV range due to its wide band gap (3.37 eV) and large exciton binding energy (60 meV). So a study of the nature of oxidation of Zn in order to synthesize ZnO is very essential. Here we have tried to study the oxidation behavior of Zinc foil and Zinc powder by oxidizing them in muffle furnace and then carrying out analysis to know if nanostructure is formed or not using SEM, EDX studies along with XRD and DSC/TG. Nanostructures of ZnO were found to grow only at temperatures above 600^{o}C. The surface of the Zn foil is filled with nanostructures of ZnO like nanowires and nanoribbons whereas these structures are not seen in the case of ZnO powder when both the Zn foil and powder were oxidized in the furnace in air in the temperature range 500-600^{o}C. Some indication of probable formation of nanostructure can be seen in sample oxidized at 800^{o} C.

Keywords: - Zinc oxide, Nanostructures, Oxidation.

CHAPTER 1

INTRODUCTION

INTRODUCTION:

Zinc oxide (ZnO), a representative of II–VI semiconductor compounds, is a technologically important material. ZnO has a unique position among the semiconducting oxides due to its piezoelectric and transparent conducting properties, high electrical conductivity and optical transmittance in the visible region. These properties make it ideal for applications like transparent conducting electrodes in flat panel displays and window layers in thin film hetero junction solar cells. Due to these properties combined with its low cost and nontoxicity ZnO has been recognized as a promising alternative material to transparent conducting indium tin oxide (ITO). ZnO has a wide band gap (3.37 eV) and a large exciton binding energy (60 meV), exhibiting many potential applications in areas such as laser diodes, gas sensors, optoelectronic devices and devices for solar energy conversion. The ZnO nanostructures are found to have potential application in nano devices such as nano gas sensor. ZnO in the form of nanostructures would enhance the gas-sensing properties of gas sensors due to its high surface area. Apart from this, bio-safe characteristics of ZnO make it very attractive for biomedical applications. A method for economical mass production and determination of conditions favorable for the synthesis of ZnO nanostructures would therefore be very useful. This is why the study of synthesis of ZnO nanostructures and understanding the ZnO nanostructures is of great interest and technological importance [1-7].

Recently, various synthesis techniques have been developed to fabricate ZnO nanocrystals with different shapes, which include metal-catalyzed vapour-liquid-solid (VLS) growth, physical vapor deposition (PVD), chemical vapor deposition (CVD), metal-organic vapor-phase epitaxy, metal-organic CVD, template-assisted growth and oxidation method [4-11]. Many of these techniques however are complicated needing high temperature for synthesis and also require a long reaction time. Apart from this, these techniques also utilize toxic components and require expensive experimental setup. The oxidation method on the other hand is a simple low-cost technique and very commonly used for the synthesis of ZnO nanostructures. Here we have shown that ZnO nanostructures could be very successfully synthesized by the simple method of oxidation. Knowing the exact temperature and holding time required for the synthesis of the ZnO nanostructures by this technique would be of great use. We have tried to ascertain

how the morphology of ZnO changes with oxidation temperature. The effect of longer holding time at a particular oxidizing temperature was also studied. Zhang et al. [8] have successfully synthesized ZnO nanostructures by oxidizing Zn foils at 700°C in air without the presence of any catalyst and carrier gas. Sekar et al. [9] reported that ZnO nanowires were grown on Si (100) substrates by oxidation of metallic Zn powder at 600°C without the use of catalyst. Here the ZnO synthesized by the simple process of oxidation of pure Zn have been found to have rod like, belt like, wire like and needle like morphologies. A wide range of morphologies of ZnO nanostructures have been reported previously in literature [2, 3, 12, 15]. This simple method of oxidation of Zn for the synthesis of ZnO nanostructures is economical as it requires a very simple experimental setup and uses the oxygen from the air. Knowledge of the exact parameters required for the synthesis of ZnO nanostructures by this route would be of great technological importance.

An economical and environment friendly route has been used here for the synthesis of ZnO on Zn. Different morphologies of ZnO both nanostructured and microstructured have been achieved by us by controlling the oxidation temperature and the holding time. The change in the morphology of ZnO with oxidation temperature as well as holding time has been tracked. Nanostructures such as nanowires, nanorods, nanobelts and nanoneedles were seen on the metallic Zn substrate. The ZnO formed on Zn has also been found to be highly stoichiometric.

CHAPTER 2

LITERATURE REVIEW

2.1 Properties of ZnO:

2.1.1Crystal structure of ZnO

2.1.2 Mechanical properties

2.1.3 Electronic properties

2.1.4 Optical Properties

2.1.5 In below table we mention some physical properties of ZnO

2.2 Applications

2.3 Synthesis techniques

2.3.1 Physical vapor deposition (PVD)

2.3.2 Chemical vapor deposition (CVD)

2.1 Properties of ZnO:

2.1.1Crystal structure of ZnO:

Zinc oxide crystallizes in three forms: hexagonal wurtzite, cubic zincblende, and the rarely observed cubic rocksalt. The wurtzite structure is most stable at ambient conditions and thus most common. The zincblende form can be stabilized by growing ZnO on substrates with cubic lattice structure. In both cases, the zinc and oxide centers are tetrahedral. The rocksalt (NaCl-type) structure is only observed at relatively high pressures about 10 GPa.

Hexagonal and zincblende polymorphs have no inversion symmetry (reflection of a crystal relatively any given point does not transform it into itself). This and other lattice symmetry properties result in piezoelectricity of the hexagonal and zincblende ZnO, and in pyroelectricity of hexagonal ZnO.

More stable state of ZnO is wurtzite structure, which has a hexagonal unit cell with lattice parameters a = 0.3296, and c = 0.52065 nm. The oxygen anions and Zn cations form a tetrahedral unit. The entire structure lacks of central symmetry. The structure of ZnO can be simply described as a number of alternating planes composed of tetrahedrally coordinated O^{2-} and Zn^{2+} ions, stacked alternatively along the c-axis [23-27]. This is shown in the figure 2.1

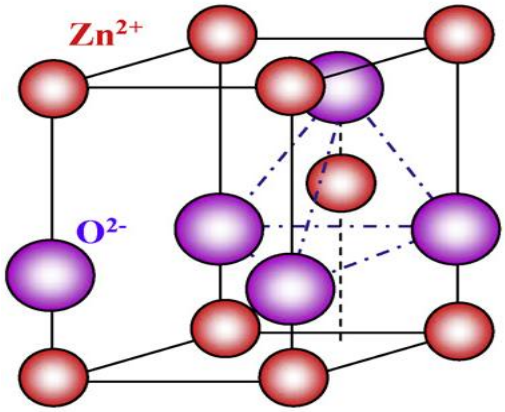


Figure 2.1 Crystal structure of the ZnO (the of tetrahedrally coordinated O^{2-} and Zn^{2+} ions)

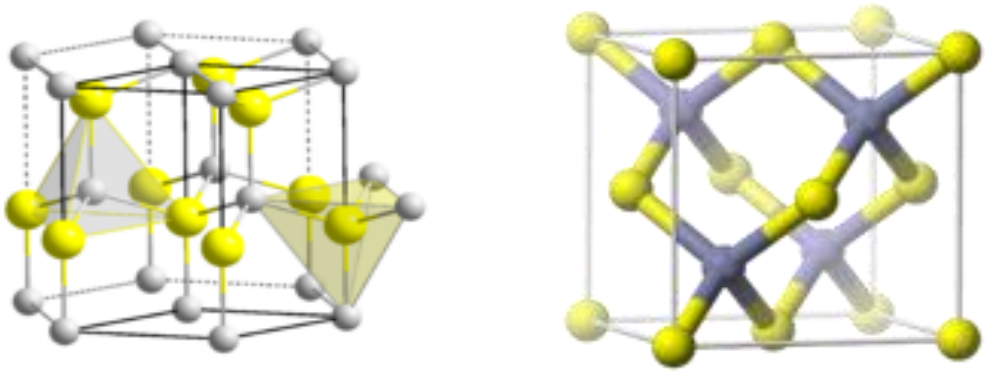


Figure 2.2 Wurtzite structure model of ZnO, which has non-central symmetry [23].

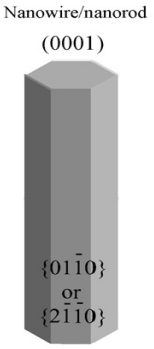


Figure 2.3 The ZnO Nano rod structure is shown below figure. It was grow vertically to the ZnO foil [23].

2.1.2 Mechanical properties:

ZnO is a relatively soft material with approximate hardness of 4.5 on the Mohs scale. Its elastic constants are smaller than those of relevant III-V semiconductors, such as GaN. The high heat capacity and heat conductivity, low thermal expansion and high melting temperature of ZnO are beneficial for ceramics Among the tetrahedrally bonded semiconductors, it has been stated that ZnO has the highest piezoelectric tensor or at least one comparable to that of GaN and AlN. This property makes it a technologically important material for many piezoelectrical applications, which require a large electromechanical coupling.

2.1.3 Electronic properties:

ZnO has a relatively large direct band gap of ~3.3 eV and a relatively large excitation binding energy (60 meV) compared to thermal energy (26meV) at room temperature. Advantages associated with a large band gap include higher breakdown voltages, ability to sustain large electric fields, lower electronic noise, and high-temperature and high-power operation. The bandgap of ZnO can further be tuned to ~ 3-4 eV by its alloying with magnesium oxide or cadmium oxide.

Most ZnO has n-type character, even in the absence of intentional doping. Reliable p-type doping of ZnO remains difficult. This problem originates from low solubility of p-type dopants and their compensation by abundant n-type impurities. Current limitations to p-doping do not limit electronic and optoelectronic applications of ZnO, which usually require junctions of n-type and p-type material. Known p-type dopants include group-I elements Li, Na, K; group-V elements N, P and As; as well as copper and silver. However, many of these form deep acceptors and do not produce significant p-type conduction at room temperature.

2.1.4 Optical Properties:

ZnO nanostructure material has good optical properties. ZnO nanostructures have very wide range of applications in optical filed. ZnO nanorods are very useful in laser to very fast optical pumping, to make population inversion in energy levels. And produce high power laser beams. ZnO is a wide band gap semiconductor that displays luminescent properties in the near ultra violet and the visible regions. The emission properties of ZnO nanoparticles in the visible region widely depend on their synthetic method as they are attributable to surface defects.

The Photoluminescence (PL) spectra of ZnO nanostructures have been widely reported. Excitonic emissions have been observed from the PL spectra of ZnO nanorods. It is shown that if we confine the quantum size then it can greatly enhance the exciton binding energy but an interesting observation is that the green emission intensity increases with a decrease in the diameter of the nanowires. This is because of the larger surface-to-volume ratio of thinner

nanowires which favours a higher level of defects and surface recombination. Red luminescence band has also been reported for which doubly ionized oxygen vacancies are considered responsible. Quantum confinement was also observed to be responsible in causing a blue shift in the near UV emission peak in the ZnO nanobelts. Some other fields of application include optical fibers, surface acoustic wave devices, solar cells etc [30,31].

2.1.5 Physical properties of ZnO [2,7]:

Property	Value
Molecular formula	ZnO
Molar mass	81.4084 g/mol
Appearance	Amorphous white or yellowish white powder.
Odour	Odourless
Density	5.606 g/cm^3
Melting point	1975 °C
Boiling point	2360 °C
Solubility in water	0.16 mg/100 mL
Refractive index	2.0041
Lattice Constants	a_o = 0.32469 Å c_o = 0.52069Å
Relative Dielectric Constant	8.66
Energy Gap	3.4 eV Direct
Intrinsic Carrier Concentration	< 10^6 /cc
Exciton Binding Energy	60 meV
Electron effective mass	0.24
Electron mobility (at 300 K)	200 cm^2/V.sec.
Hole Effective mass	0.59
Hole mobility (at 300 K)	5-50 cm^2/V.sec

2.2 Applications

The applications of zinc oxide powder are numerous, and the principal ones are summarized below. Most applications exploit the reactivity of the oxide as a precursor to other zinc compounds. For material science applications, zinc oxide has high refractive index, good thermal, binding, antibacterial and UV-protection properties. Consequently, it is added into various materials and products, including plastics, ceramics, glass, cement, rubber, lubricants, paints, ointments, adhesive, sealants, pigments, foods, batteries, ferrites, fire retardants, etc.

2.2.1 Rubber manufacture

About 50% of ZnO use is in rubber industry. Zinc oxide along with stearic acid activates vulcanization, which otherwise may not occur at all. Zinc oxide and stearic acid are ingredients in the commercial manufacture of rubber goods. A mixture of these two compounds allows a quicker and more controllable rubber cure. ZnO is also an important additive to the rubber of car tyres. Vulcanization catalysts are derived from zinc oxide, and it considerably improves the thermal conductivity, which is crucial to dissipate the heat produced by the deformation when the tyre rolls [30].

2.2.2 Medical uses

Zinc oxide as a mixture with about 0.5% iron (III) oxide (Fe_2O_3) is called calamine and is used in calamine lotion. Reflecting the basic properties of ZnO, fine particles of the oxide have deodorizing and antibacterial action and for that reason are added into various materials including cotton fabric, rubber, food packaging, etc [30]. Zinc oxide is well known for its ability to neutralize acid and for its mild bactericidal properties, making it an ideal component in body cream/antiseptic healing cream to help reduce soreness and redness. It is also used in medical tapes and plasters, some toothpaste formulations and in dental cements. [30]. Due to its ability to absorb ultraviolet light, ZnO is also used in sunscreens and sun blocks to prevent sunburns [30].

Zinc oxide is a constituent of cigarette filters for removal of selected components from tobacco smoke. A filter consisting of charcoal impregnated with zinc oxide and iron oxide removes significant amounts of HCN and H_2S from tobacco smoke without affecting its flavor [31].

2.2.3 Food additives

Zinc oxide is added to many food products, e.g., breakfast cereals, as a source of zinc, a necessary nutrient. (Other cereals may contain zinc sulfate for the same purpose.) Some prepackaged foods also include trace amounts of ZnO even if it is not intended as a nutrient [30]. Zinc oxide is used in compound animal feeds and mineral premixes as a source for the essential element zinc [30]. Zinc oxide is used to manufacture zinc gluconate, now found in cold prevention lozenges [31].

2.2.4 Anti corrosive coatings

Zinc oxide is an excellent inhibitor of fungi, mildew and mould [31]. Paints containing zinc oxide powder have long been utilized as anticorrosive coatings for various metals. They are especially effective for galvanized Iron. The latter is difficult to protect because its reactivity with organic coatings leads to brittleness and lack of adhesion [30]. Zinc oxide paints however, retain their flexibility and adherence on such surfaces for many years. One of its exceptional features is its opacity to ultraviolet light in the finished coatings, which improves weatherability. The oxide is not discolored by sulphur compounds in the atmosphere, as occurs in some lead pigments.

2.2.5 Electronic applications

ZnO has wide direct band gap (3.37 eV or 375 nm at room temperature). Therefore it's most common potential applications are in laser diodes and light emitting diodes (LEDs). Transparent thin-film transistors (TTFT) can be produced with ZnO.

Zinc oxide nanorod sensors are devices detecting changes in electrical current passing through zinc oxide nanowires due to adsorption of gas molecules. Selectivity to hydrogen gas was achieved by sputtering Pd clusters on the nanorod surface. The addition of Pd appears to be effective in the catalytic dissociation of hydrogen molecules into atomic hydrogen, increasing the

sensitivity of the sensor device. The sensor detects hydrogen concentrations down to 10 parts per million at room temperature, whereas there is no response to oxygen. [30]

ZnO has high biocompatibility and fast electron transfer kinetics. Such features advocate the use of this material as a biomimic membrane to immobilize and modify biomolecules [30]. Transparent thin-film transistors (TTFT) can be produced with ZnO. As field-effect transistors, they even may not need a p-n junction, thus avoiding the p-type doping problem of ZnO. Some of the field-effect transistors even use ZnO nanorods as conducting channels [31].

The piezoelectricity in textile fibers coated in ZnO has been shown capable of "self-powering nanosystems" with everyday mechanical stress generated by wind or body movements [30]. Zinc oxide is used in zinc-carbon dry cells, zinc-silver oxide batteries, nickel oxide-cadmium batteries and even in secondary batteries. In fuel cells, zinc oxide is used as electrode material, cathodic material and as a fuel element. In solar energy cells it can act as a photo catalyst [30].

2.3 Synthesis

Keeping in view the extensive uses of ZnO, various types of synthesis techniques have been formulated over the years. ZnO nanostructures can be synthesized by several methods such as sputtering technique, vapour deposition, pulsed laser deposition (PLD), metal organic chemical vapour deposition (MOCVD) and oxidation. Some other methods are vapour liquid-solid process and anodization. Unfortunately, many of the stated techniques are problematic, needing high temperature for synthesis, and having long reaction time, utilize toxic components and involve costly equipments. The oxidation method is a simple, low-cost and most commonly used technique for the synthesis of ZnO nanostructures. However, the deposition of zinc oxide by vapour deposition has seen increased research activity over the past several years as the need for high quality zinc oxide thin films has increased. A key advantage of chemical vapour deposition is its ability to easily incorporate dopants into films [17-26].

We have lot of techniques to synthesize ZnO nanostructures. These techniques are mainly divided into 3 categories that are shown below table.

SYNTHESIS TECHNIQUES	SUB CATEGORIES
Physical vapor deposition (PVD)	Cathodic Arc Deposition Electron beam physical vapor deposition Evaporative deposition Pulsed laser deposition Sputter deposition
Chemical vapor deposition (CVD)	Vapor phase epitaxy (VPE) Rapid thermal CVD (RTCVD) Hybrid Physical-Chemical Vapor Deposition (HPCVD) Metalorganic chemical vapor deposition (MOCVD) Hot wire CVD (HWCVD) Atomic layer CVD (ALCVD) Plasma-Enhanced CVD (PECVD)

2.3.1 Physical vapor deposition (PVD):

Physical vapor deposition (PVD) is a variety of vacuum deposition and is a general term used to describe any of a variety of methods to deposit thin films by the condensation of a vaporized form of the material onto various surfaces (e.g., onto semiconductor wafers). The coating method involves purely physical processes such as high temperature vacuum evaporation. PVD have different subcategories that are shown below.

Cathodic Arc Deposition: In which a high power arc discharged at the target material blasts away some into highly ionized vapor.

Electron beam physical vapor deposition: In which the material to be deposited is heated to a high vapor pressure by electron bombardment in "high" vacuum.

Evaporative deposition: In which the material to be deposited is heated to a high vapor pressure by electrically resistive heating in "low" vacuum.

Pulsed laser deposition: In which a high power laser ablates material from the target into a vapor.

Sputter deposition: In which a glow plasma discharge (usually localized around the "target" by a magnet) bombards the material sputtering some away as a vapor.

2.3.2 Chemical vapor deposition (CVD) [35]:

Chemical vapor deposition (CVD) is a chemical process used to produce high-purity, high-performance solid materials. The process is often used in the semiconductor industry to produce thin films. In a typical CVD process, the wafer (substrate) is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit. Chemical vapor deposition is divided into subcategories that are shown below.

Rapid thermal CVD (RTCVD): Rapid thermal CVD (RTCVD) - CVD processes that use heating lamps or other methods to rapidly heat the wafer substrate. Heating only the substrate rather than the gas or chamber walls helps reduce unwanted gas phase reactions that can lead to particle formation.

Hot wire CVD (HWCVD): Hot wire CVD also known as catalytic CVD (Cat-CVD) or hot filament CVD (HFCVD). Uses a hot filament to chemically decompose the source gases.

CHAPTER 3

EXPERIMENTAL

3.1 EXPRIMENTAL

3.1.1 Synthesis of ZnO Nanostructure by oxidation techniques

3.2 Experimental Instruments

3.2.1 Scanning electron microscopy

3.2.2 Energy Dispersive X-Ray Spectroscopy

3.2.3 Differential scanning calorimetry

3.2.4 X-ray diffraction techniques

3. EXPRIMENTAL:

In our experiment Zinc powder and zinc foil are oxidized in order to study the formation of nanostructures.

3.1 Synthesis of ZnO Nanostructure by oxidation techniques:

In this experiment pure Zn (foil or powder) was taken in silicon crucible, the crucible size is average 1.5cm in diameter (cone shape) 2.5cm in depth. The crucible which contain a Zn (foil or powder) was put in the furnace, the furnace heating was switched on and time was recorded after the furnace reached the holding temperature i.e. say 200^{o}C, 300^{o}C, 400^{o}C, 500^{o}C, 600^{o}C, 700^{o}Ca and 800^{o}C. Then the sample was held at that temperature for 2 hrs and finally the samples were furnace cooled. Zn (foil or powder) after cooling shows a change in color is from its initial white to gray indicating the formation of ZnO nanorods.. This nanorods was characterizes by JEOL JSM-6480LV scanning electron microscope, EDX, DSC and XRD.

In this experiment we oxidized both Zinc foils and Zinc powder at various temperatures (200^{o}C, 300^{o}C, 400^{o}C, 500^{o}C, 600^{o}C, 700^{o}C and 800^{o}C) and the holding time was 2 hr and oxidizing atmosphere was maintained thus muffle furnace was used.

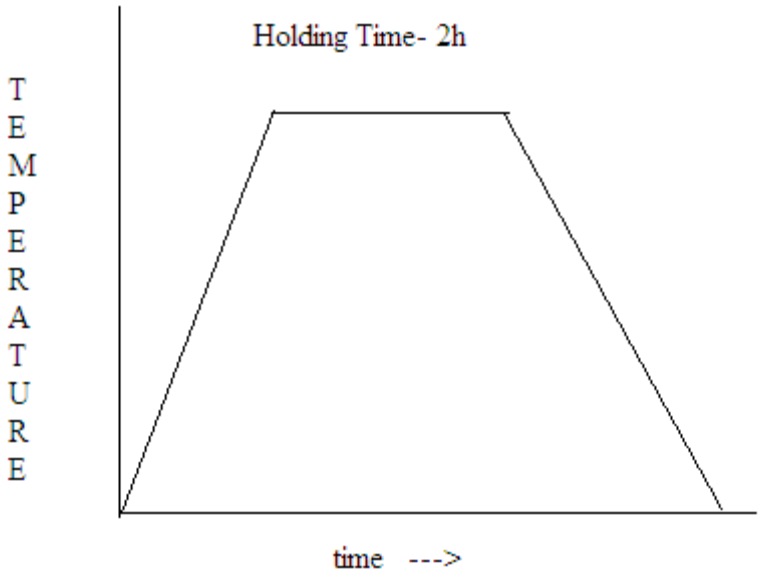
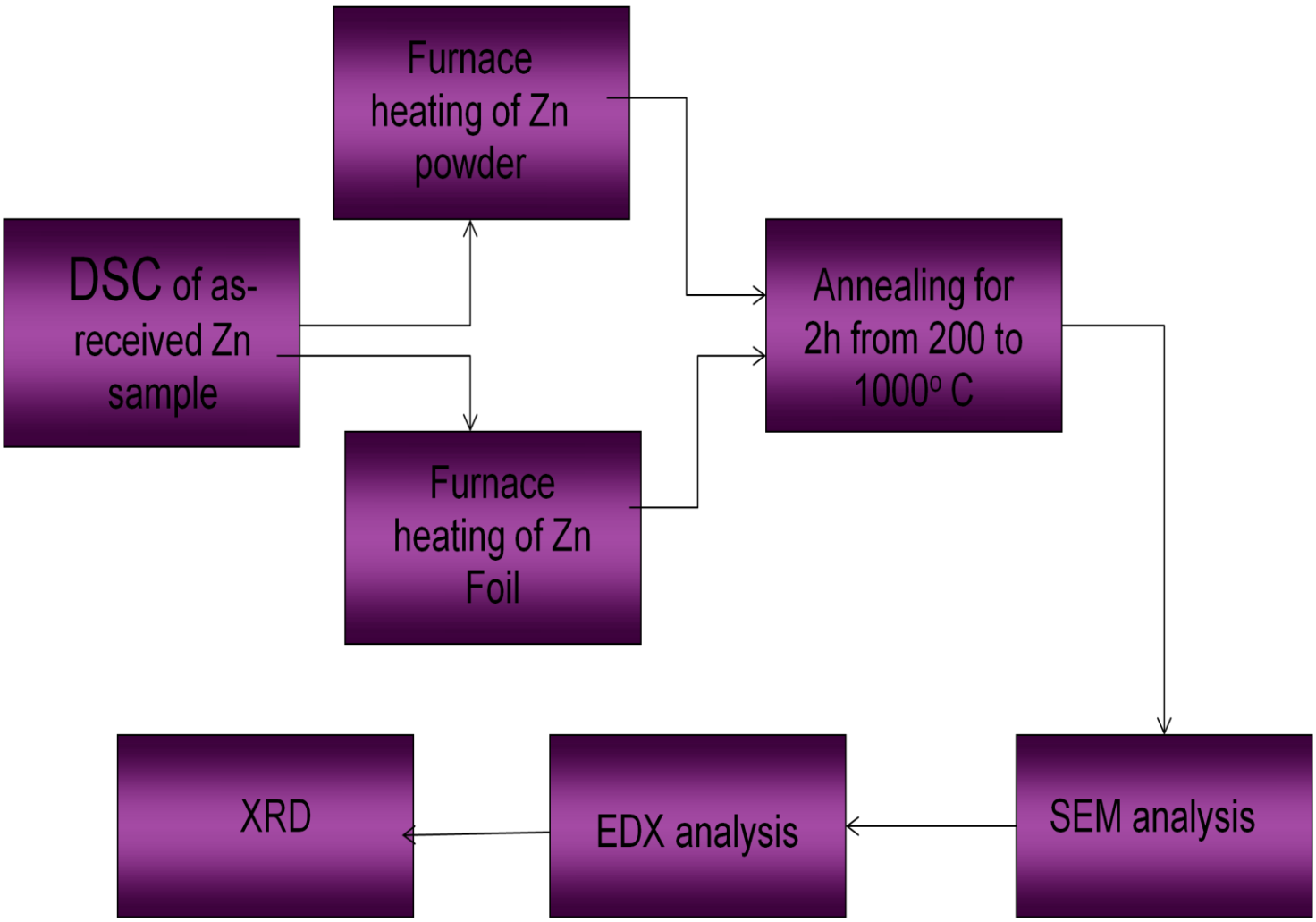


Fig 3.1: Schematic view of heating process

3.2 Experimental Route



3.2 Experimental Instruments

3.2.1 Scanning Electron Microscopy:

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity. SEM can produce very high-resolution images of a sample surface, revealing details about less than 1 to 5 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample.

Fig.3.4: JEOL JSM-6480LV SEM.

In most of the applications, the data collected is over a pre selected area of the sample surface and following this, a 2D image is generated that shows the various spatial variations. Conventional SEMs with a magnification range of 20X-30000X with a spatial resolution of 50-100 nm can scan areas which vary from 1 cm to 5μm in width. SEMs also have the ability to analyze particular points as can be seen during EDX operations which help in determining the chemical composition of the sample concerned [33].

The internal arrangement of SEM is shown below and SEM has following components

- Electron Source ("Gun")
- Electron Lenses
- Sample Stage
- Detectors for all signals of interest
- Display / Data output devices
- Infrastructure Requirements:

    a) Power Supply

    b) Vacuum System

    c) Cooling system

    d) Vibration-free floor

    e) Room free of ambient magnetic and electric fields.

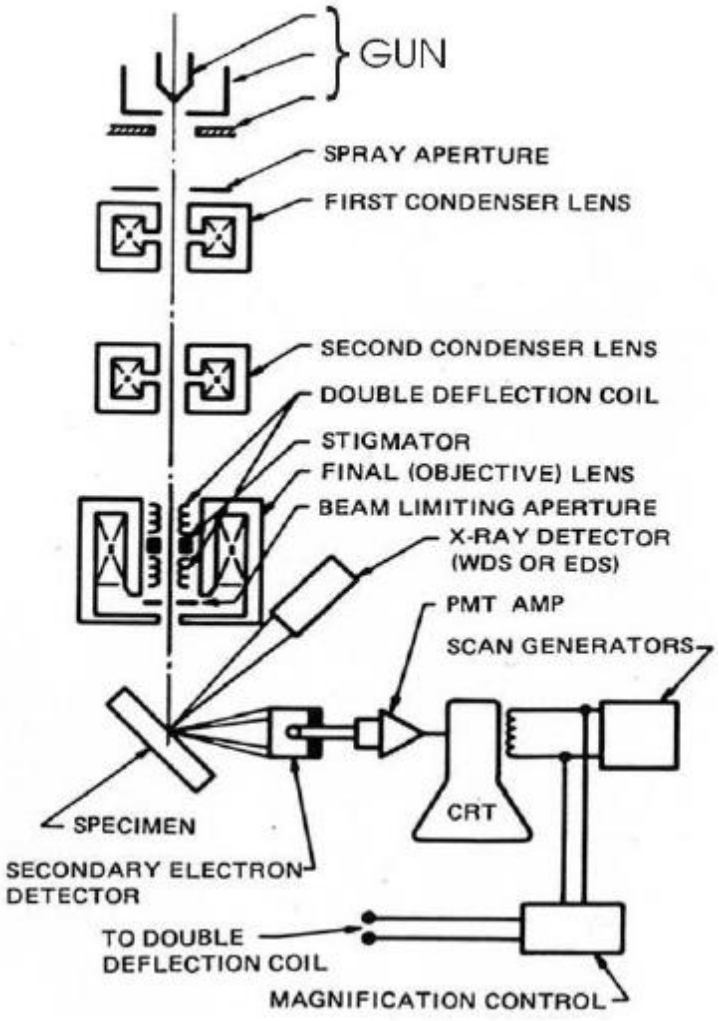


Fig.3.5: Schematic Diagram of Electron and x-ray optics of combined SEM- EPMA

3.2.2 Energy Dispersive X-Ray Spectroscopy:

Energy-dispersive X-ray spectroscopy (EDS or EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is one of the variants of X-ray fluorescence spectroscopy which relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of an element's atomic structure to be identified uniquely from one another [34].

3.2.3 Differential scanning calorimetry:

Differential scanning calorimetry or DSC is a thermo analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned [36].

Figure 3.6 Differential Scanning Calorimetry.

3.2.4 X-ray diffraction techniques:

X-ray diffraction (XRD) is a non-destructive type of analytical technique which provides valuable insight about the lattice structure of a crystalline substance like unit cell dimensions, bond angles, chemical composition and crystallographic structure of natural and manufactured materials. XRD is based on the principle of constructive interference of x-rays and the sample concerned which should be crystalline. The x-rays which are generated by a CRT are filtered, collimated and then directed towards the sample. The interaction that follows produces

constructive interference based on Bragg's law which relates wavelength of the incident radiations to the diffraction angle and lattice spacing [38].

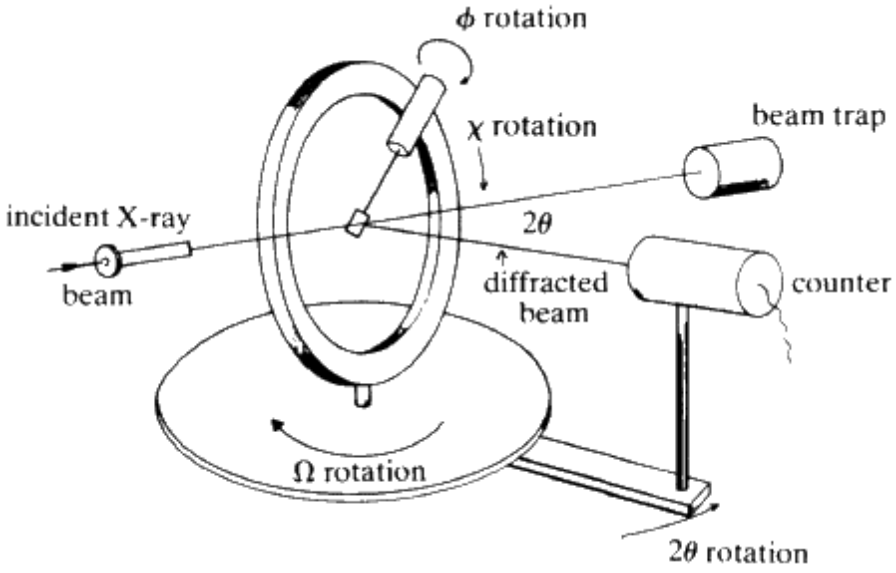


Fig.3.3: Schematic Diagram of a 4-Circle Diffractometer.

Image courtesy of the International Union of Crystallography [38].

CHAPTER-4

RESULTS AND DISCUSSION

4. Results and Discussion:-

ZnO is one of the most promising semiconductor material in the UV range due to its wide band gap (3.37 eV) and large exciton binding energy (60 meV). So a study of the nature of oxidation of Zn in order to synthesize ZnO is very essential.

ZnO growth on small area substrates is not very feasible. The melting point of Zn is and beyond 300^{o}C there is clear indication of the fact that the particle size of Zn starts increasing with the rise in oxidation temperature. Liquid phase sintering of Zn takes place only at temperatures above its melting point (419.53 ℃).

4.1 (a) As received Zn sample

Fig 4.1 (b) shows as received Zn sample used for the experiment under SEM. The surface of the as received Zinc contains 100% Zinc without any traces of Zinc oxide on its surface, this was confirmed by EDX analysis.

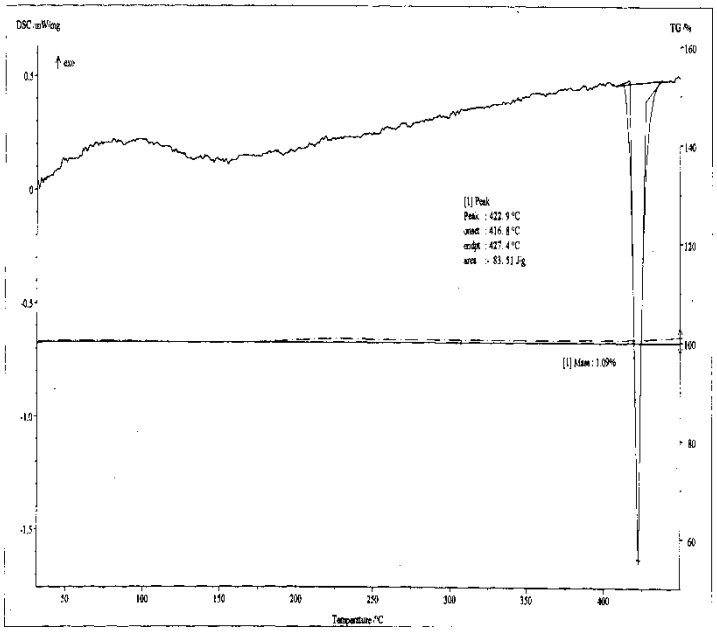


Fig4.1 (a) DSC/TG of Zinc Foil

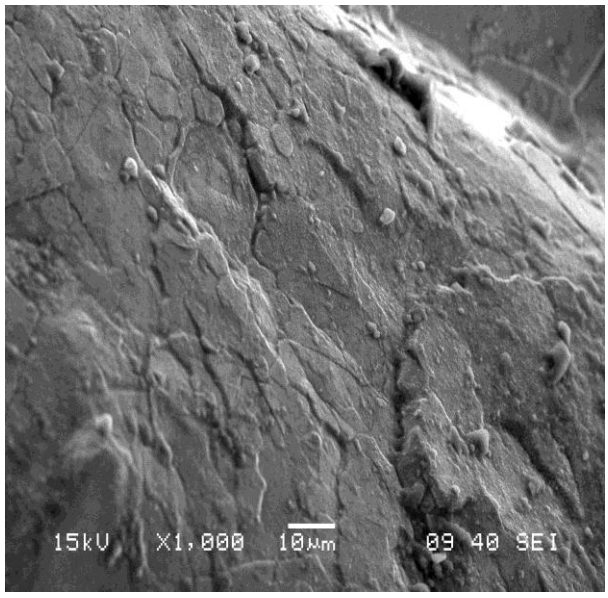


Fig. 4.1(b) : SEM showing the surface of the as-received pure metallic Zn

4.1 (b) Annealed for 2hr at 200^{o} C

When zinc powder is kept in oxidizing atmosphere at 200^{o} C for two long hours still we are unable to find any oxidation product on the zinc surface and powder has somehow clustered but not due to sintering and have given the appearance of islands. Due to this clustering the surface morphology is quite different from as received Zinc.

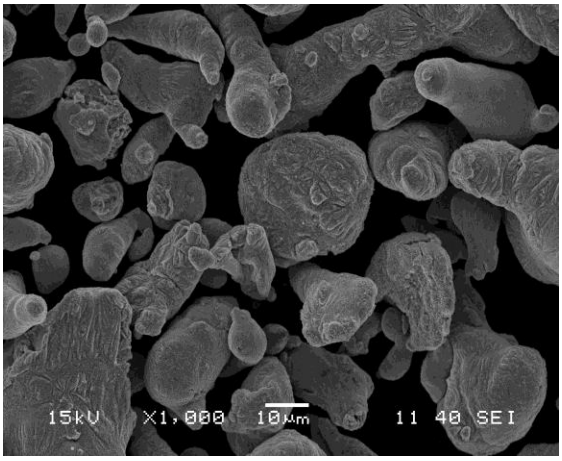
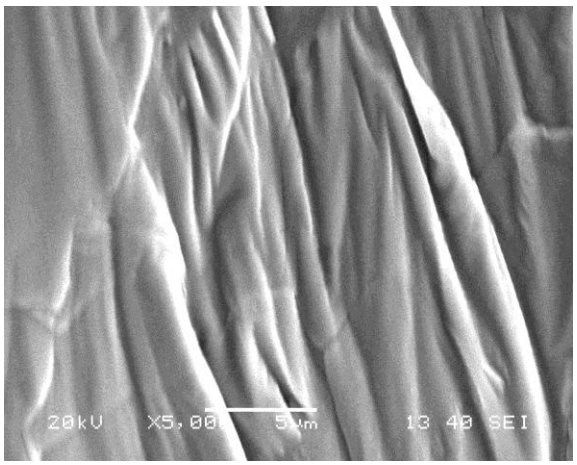


Fig. 4.2 : SEM showing the surface of Zn powder after oxidation at 200^{o} C for 2h

4.2 Annealed for 2hr at 300^{o} C

After 2 hours of annealing at 300^{o} C and going for EDX studies in case of Zn foil we are unable to find any traces of ZnO .In case of Zinc powder also no ZnO was found. The surface morphology in either of the case is totally different but foil one resembles something similar to as received Zinc. So in Zn foil there is no effect on heating at 300^{o}C for two hours whereas in powdered zinc there are morphological changes.



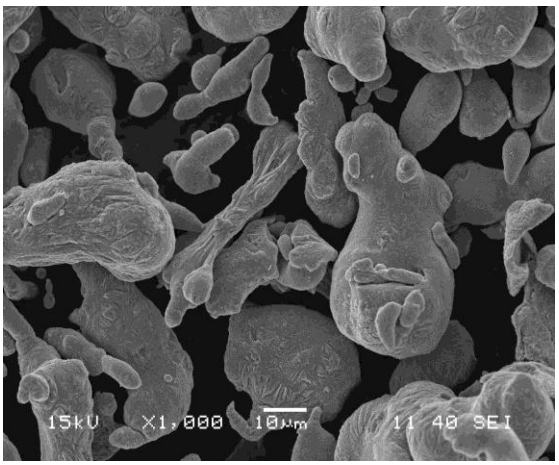


Fig. 4.3 (a): SEM showing the surface after oxidation at 300^{o} C for 2h of (a) Zinc foil (b) Zinc Powder

Annealed for 2hr at 400^{o} C

The structure in case of Zinc foil has become finer and presence of ZnO can be found by EDX Studies. The size is in the range of one tenth of micrometer. Whereas in case of oxidized Zinc powder which was kept in similar condition we confirmed the presence of ZnO in certain regions by EDX analysis. Necking also has started and some initial stage of sintering can be seen, but the size is in hundreds of micrometer

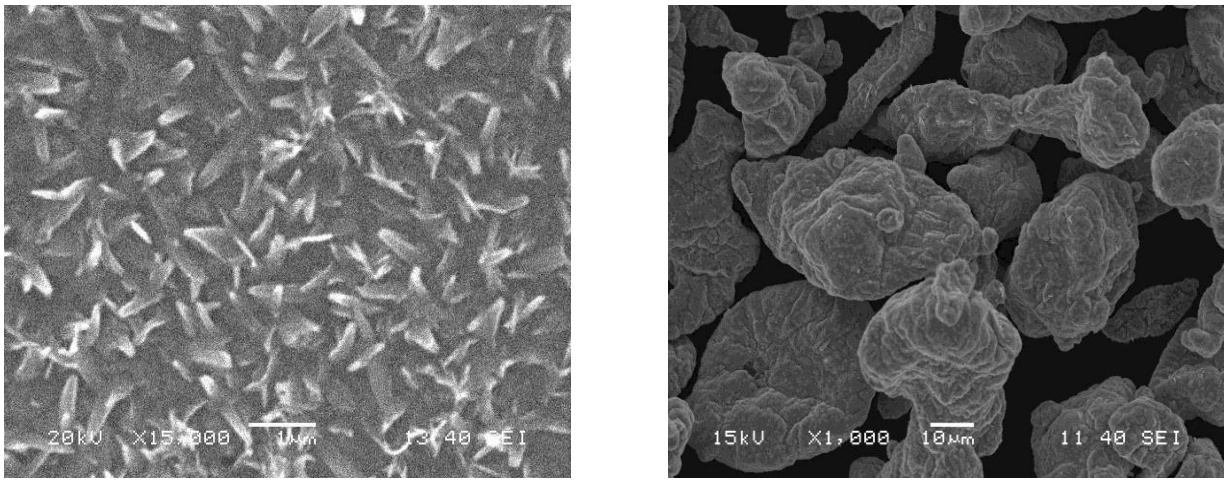


Fig. 4.4 (a): SEM showing the surface after oxidation at 400^{o} C for 2 h of (a) Zinc foil

(b) Zinc Powder

Annealed for 2hr at 500^{o} C

When the samples were annealed for two hours the Zn foil showed some reduction in size and was in EDX studies confirm the presence of zinc oxide as the ratio of Zn and O (21.59 at. % O and 24.51 at. % Zn) resembles it closely. The particles were in the order of nano ranges, i.e. ZnO nanostructures can be seen on the surface. Whereas in case of Zn powder the particle size after oxidation is far away from nanosize range. Here pits have been formed due to oxidation of the zinc powder. Now many more spots can be found were zinc oxide is present as compared to previous sample at 400^{o} C. The sintering has advanced and the particle size has increased.

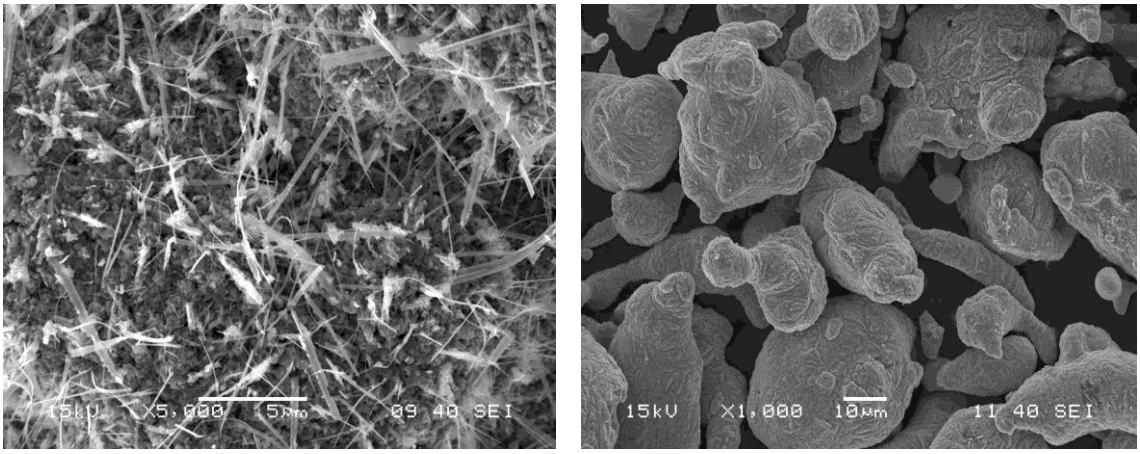


Fig. 4.5 (a): SEM showing the surface after oxidation at 500^{o} C for 2 h of (a) Zinc foil

(b) Zinc Powder

Annealed for 2hr at 600^{o} C

Fig. 4.6(a-b) shows that at 600^{o}C the surface of Zn is completely filled with nanostructures of ZnO. There is a wide range of nanostructures of ZnO on the Zn surface. Here the results are as expected the morphology of Zinc contains even finer particles .nanostructure particles can be very easily visualized in this case. The SEM picture gives a very good insight into it. In case of Zinc powder necking phenomenon is clearly evident and pore like appearance can be seen. The whole of the zinc surface has oxidized and the oxide is very uniform and adherent to the surface.

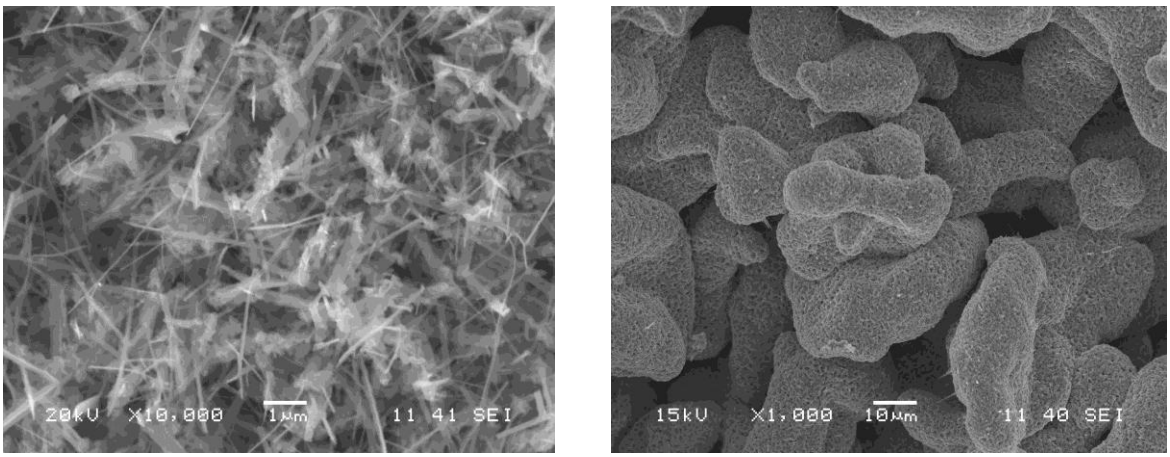


Fig. 4.6 (a): SEM showing the surface after oxidation at 600^{o} C for 2 h of (a) Zinc foil (b) Zinc powder

<u>Annealed for 2hr at 700^{o} C</u>

Fig. 4.7(a-b) shows that the oxidation of Zinc at 700^{o}C does not show any nanostructure of ZnO anymore. There is a gradual increase in the size of the ZnO structures with further increase in temperature. EDX analysis of the ZnO microstructure formed on the Zn surface by heat treating at 700^{o}C for 2h shows that the at. % of Zn (43.57 %) and O (56.43 %) are almost identical suggesting that highly stoichiometric ZnO is formed at this temperature. The particle size is not much affected in case of oxidized Zinc powder as compared to the 600^{o} C oxidation.

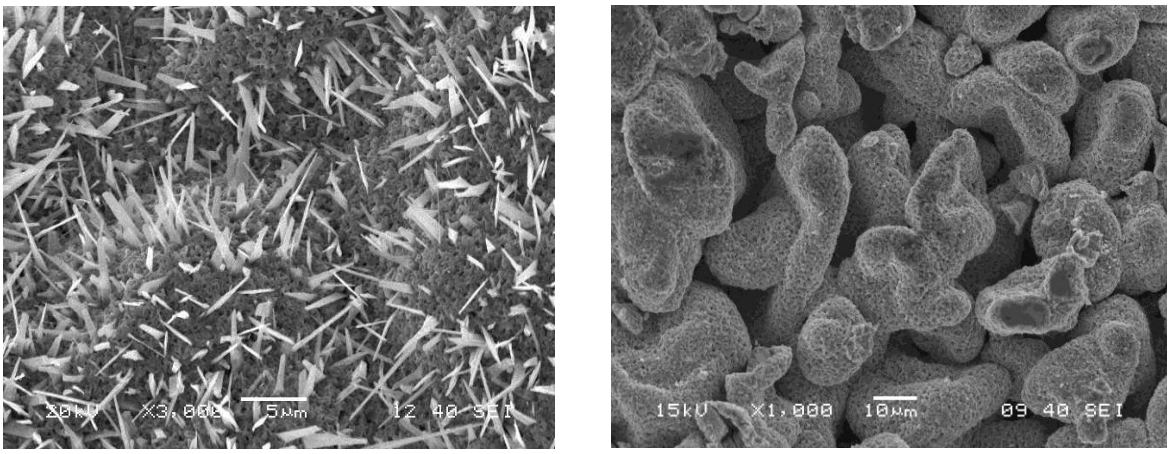


Fig. 4.7 (a): SEM showing the surface after oxidation at 700^{o} C for 2 h of (a) Zinc foil

(b) Zinc Powder

Annealed for 2hr at 800^{o} C

Here the zinc oxide that has grown on the surface is somehow smoother and seems to be highly adherent to the surface of the metallic Zn substrate. Although the oxide is now not in nano range The ZnO rods formed at this temperature has been found to be mostly triangular in shape and have different heights. Its thickness has reduced gradually from the base to the tip. Whereas in oxidized Zinc powder the morphology is totally changed and needle like fine oxide are grown on the metallic Zinc surface.

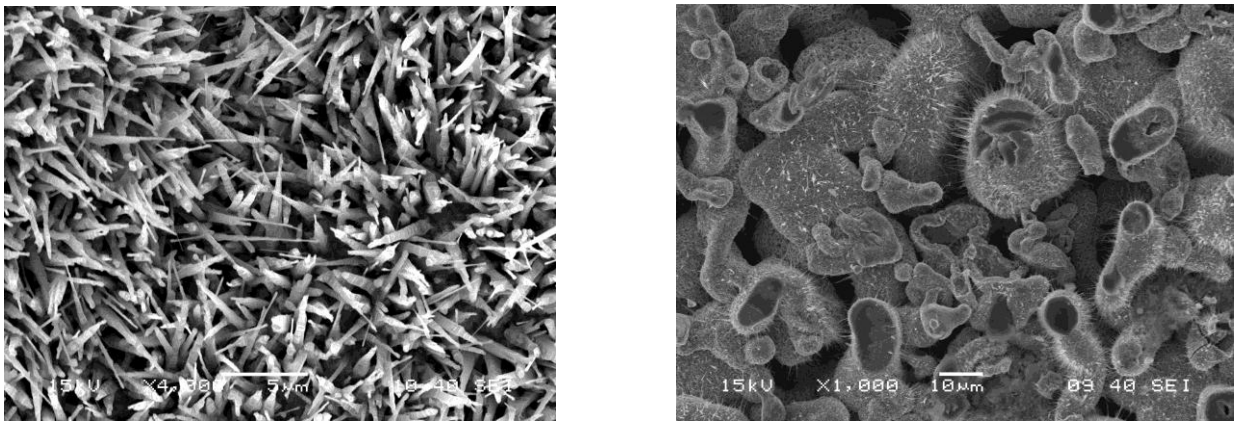


Fig. 4.8 (a): SEM showing the surface after oxidation at 800^{o} C for 2 h of (a) Zinc foil (b) Zinc Powder

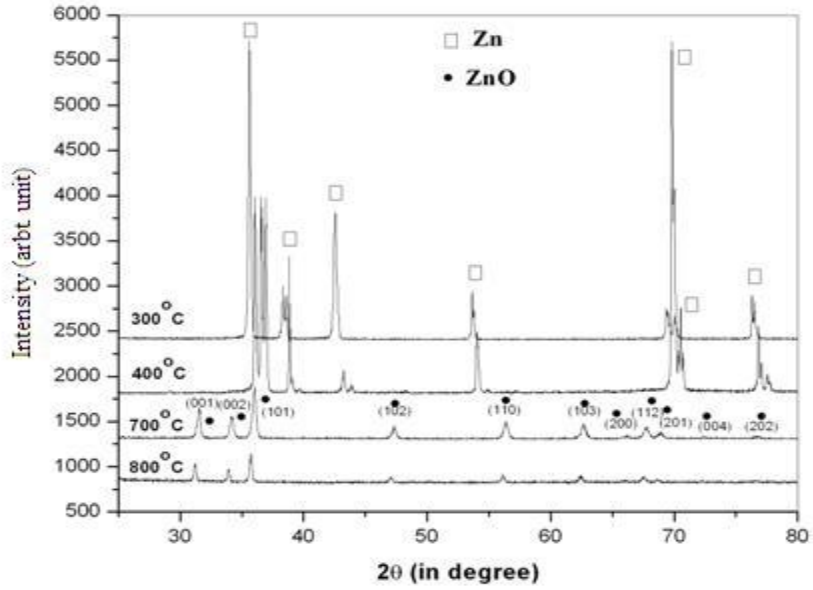


Fig 4.9 XRD peaks of Zn and ZnO at various temperatures

CHAPTER-5

CONCLUSION

CONCLUSION:-

1. The simple technique of oxidation of metallic Zn foils in air has been demonstrated as a very economical and effective technique for the synthesis of ZnO.

2. ZnO nanostructures were successfully synthesized by oxidizing pure Zn foils in the temperature range 400-600^{o}C. A large variety of nanostructures were seen at these oxidizing temperatures.

3. The structure and size of ZnO strongly depends on the oxidizing temperature. In contrast to Zn foils, Zn powder showed formation of ZnO nanostructures only at a relatively higher temperature of 600^{o}C or higher.

4. It is found that the growth of ZnO structures increases with increasing temperature of oxidation of the Zn foils. The SEM observation shows that needle like or rod like structures of ZnO could be formed at temperatures above 700^{o}C in case of Zn foils.

5. The needle like or rod like structure of ZnO were found to grow very uniformly in size and shape and were very densely located on the Zn foil surface at oxidation temperatures ranging from 700-800^{o}C in comparison to the various nano-structured ZnO which grew less densely and looked more scattered and non-uniform in size and structure.

6. Formation of ZnO was confirmed only at temperatures above 300^{o}C in the case of Zn foils. Comparison of the results of thermogravimetric and SEM analysis suggests that oxidation takes place only above 200^{o}C and structures of ZnO could be seen at oxidizing temperatures above 300^{o}C in case of Zn foils.

7. In the case of Zn powder oxidation starts at a much higher temperature and the ZnO structures could be observed at oxidation temperatures above 600^{o}C

CHAPTER-6

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