

Zinc Oxide Nanostructures Synthesized by Oxidization of Zinc

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

Bachelor of Technology

In

Metallurgical & Materials Engineering

By

MANISH KUMAR (10604026)

SHAKTISWARUP SAHU (10604041)



Department of Metallurgical & Materials Engineering

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Under the Guidance of

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Certificate

This is to certify that the thesis entitled, “Zinc Oxide Nanostructures Synthesized by Oxidation of Zinc” submitted by Manish Kumar (10604026) and Shakti Swarup Sahu (10604041) 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

Zinc oxide (ZnO) is a unique material that exhibits semiconducting as well as piezoelectric properties. Oxidation of pure metallic Zinc at low temperatures of 500-600°C for 2 h has resulted in a range of nanostructures of ZnO on the surface of metallic Zinc. These unique nanostructures clearly demonstrate that ZnO has a very rich family of nanostructures. These nanostructures could have applications in a wide range of areas like optoelectronics, sensors, transducers and biomedical sciences. In this article the various nanostructures of ZnO grown by the low temperature oxidation of metallic Zn has been reported. The structure and morphology of ZnO formed by oxidation of high purity metallic Zn at high temperatures (700-1000°C) was also analyzed. Oxidation of metallic Zn at higher temperatures of 700-1000°C for 2 h has resulted in a ZnO having a completely different needle like morphology. The change in the structure of ZnO formed on the surface of the metallic Zn as it was oxidized at different temperatures from 300 to 1000°C for 2 h is reported here. Energy dispersive x-ray spectroscopy and x-ray diffraction were performed in order to determine the composition of the nanostructures and the needle like structures.

1.0 Introduction

Zinc oxide (ZnO), a representative of II–VI semiconductor compounds, is a very versatile and important material. ZnO has a unique position among semiconducting oxides due to its piezoelectric and transparent conducting properties. It has a high electrical conductivity and optical transmittance in the visible region. These properties make it an ideal candidate for applications like transparent conducting electrodes in flat panel displays and window layers in solar cells [1-4]. ZnO has a wide band gap (3.37 eV) and a large exciton binding energy (60 meV) and exhibits many potential applications in areas such as laser diodes, solar cells, gas sensors, optoelectronic devices. A wide band gap has many benefits like enabling high temperature and power operations, reducing electronic noise, making sustenance in large electric fields possible and raising breakdown voltages. By proper alloying with MgO or CdO, the band gap can be tuned in the range of 3-4 eV. ZnO nanostructures have an active role to play in nano devices like nano gas sensors because the huge surface area enhances the gas sensing properties of the sensors. Apart from this, bio-safe characteristics of ZnO make it very attractive for biomedical applications. A method for economical mass production of ZnO nanostructures would therefore be very useful. This is why to study the synthesis of ZnO nanostructures and understanding the ZnO nanostructures is of great interest [5-7].

Physically, ZnO has the appearance of a white powder and is referred to as Zinc white or zincite. As far as solubility is concerned, it's almost insoluble in water and alcohol but it's readily soluble in acids like HCl even though it's tarnished in their presence. The mineral form of ZnO takes up a red or yellow colour instead of the usual white due to the presence of impurities like Manganese and other elements. Crystalline form of ZnO is thermochromic in nature and due to this it changes from white to yellow on heating and vice versa on cooling. ZnO displays amphoteric properties and it's also referred to as a II-VI semiconductor because Zinc belongs to the second group and Oxygen belongs to the sixth group of the periodic table [1-13].

ZnO has three crystal forms: the hexagonal wurtzite, the cubic zinc blende and the cubic rock salt which is rarely observed. The wurtzite structure is most commonly used as it has the highest stability under normal working conditions. Hexagonal and zinc blende structures don't display inversion symmetry

and it is properties like these that are responsible for the piezoelectricity and pyroelectricity of ZnO. ZnO is considered to be a soft material with a reading of 4.5 on the Mohs hardness scale. Its elastic constants are not that impressive but ZnO has got very good thermal properties like high melting point, high thermal capacity and conductivity and a low coefficient of thermal expansion which makes it suitable for use as a ceramic [1-17].

Recently, various synthesis techniques have been developed to fabricate ZnO nanocrystals with different shapes, which include metal-catalyzed vapour-liquid-solid (VLS) growth, physical vapour deposition (PVD), chemical vapour deposition (CVD), metal-organic vapour-phase epitaxy, metal-organic CVD, template-assisted growth and oxidation method [8-10]. Many of these techniques however are complicated needing a high temperature for synthesis and also have 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. ZnO nanostructures have been successfully synthesized by oxidizing Zn foils at 700°C in air without the presence of a catalyst and carrier gas [36]. Sekar and co-workers [9] reported that ZnO nanowires were grown on Si (100) substrates by oxidation of metallic Zn powder at 600°C. The synthesized ZnO materials have been found to have rod like, belt like, wire like and needle like morphologies. This route for synthesis of ZnO is economical as it uses the oxygen from the air [14-17, 21, 25].

Here an economical and environment friendly route has been used for the synthesis of ZnO on Zn substrate by oxidation of pure metallic Zn in a muffle furnace. Different morphologies of ZnO both nanostructured and microstructured have been achieved by us by controlling the oxidation temperature and the holding time. Nanostructures such as nanowires, nanorods, nanobelts and nanoneedles were seen on the metallic Zn substrate.

Table 1. Physical Properties of ZnO [1-14].

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	$a_0 = 0.32469 \text{ \AA}$ $c_0 = 0.52069 \text{ \AA}$
Relative Dielectric Constant	8.66
Energy Gap	3.4 eV Direct
Intrinsic Carrier Concentration	$< 10^6 / \text{cc}$
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

2.0 Literature Survey

2.1 Properties of Zinc oxide

ZnO is a versatile material that exhibits semiconducting, piezoelectric as well as pyroelectric properties. ZnO is a material that has a diverse range of nanostructures, whose configurations are far richer than any other known nanomaterials including carbon nanotubes [2, 4, 6, 11].

2.1.1 Physical properties

ZnO has a stable wurtzite structure with $a = 0.325$ nm and $c = 0.521$ nm [3]. The wurtzite structure has an ABAB hexagonal close packing (HCP) structure. The structure of ZnO consists of alternating planes composed of O^{2-} and Zn^{2+} ions which are tetrahedrally co-ordinated and stacked along the c-axis on an alternate basis (Fig. 2.1). The Zn^{2+} and O^{2-} ions create a normal dipole moment and instant polarization which results in a diversification of surface energy. The tetrahedral coordination in ZnO results in noncentral symmetric structure and consequently results in piezoelectricity and pyroelectricity in ZnO. Another important characteristic of ZnO is its polar surfaces. The most common polar surface is the basal plane. Extensive surface reconstructions are a means of obtaining a stable structure but ZnO - \pm (0001) are exceptions. They are atomically flat, stable and without reconstruction. Efforts to understand the superior stability of the ZnO \pm (0001) polar surfaces are at the forefront of research in today's surface physics. The other two most commonly observed facets for ZnO are $\{2\bar{1}\bar{1}0\}$ and $\{01\bar{1}0\}$, which are non-polar surfaces and have lower energy than the $\{0001\}$ facets [2, 12, 29, 30, 32, 49, 14, 20].

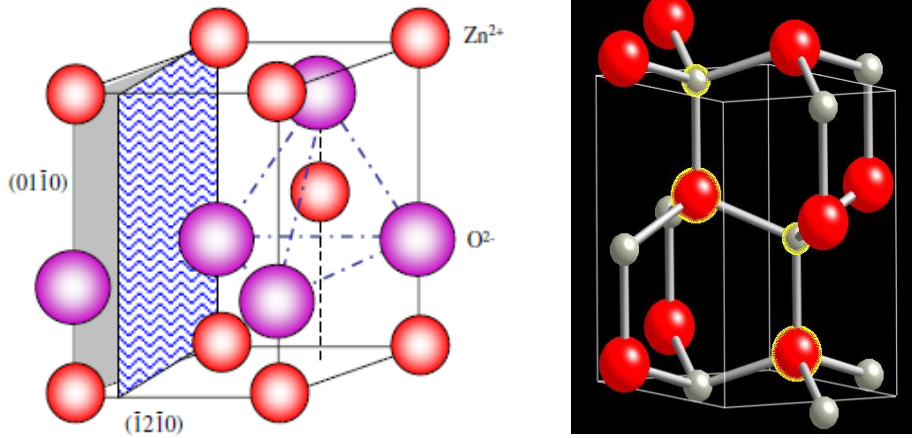


Fig.2.1: Wurtzite structure of ZnO [2].

Together with the polar surfaces due to atomic terminations, ZnO exhibits a large scale of novel structures that can be grown by varying the growth rates along these directions. One of the most important factors determining the morphology involves the relative surface activities of various growth facets under given conditions. Macroscopically, a crystal has different kinetic parameters for different crystal planes, which are emphasized under controlled growth conditions. Thus, after an initial period of nucleation and incubation, a crystallite will commonly develop into a 3D object with well-defined, low index crystallographic faces. Fig. 2.2(a-c) as reported by Zhong Lin Wang [2] shows a few typical growth morphologies of 1-dimensional nanostructures for ZnO. The morphology as shown in Fig. 2.2(d) [2] is dominated by the polar surfaces, which can be grown by introducing planar defects parallel to the polar surfaces. Planar defects and twins are observed occasionally parallel to the (0001) plane, but dislocations are rarely seen [1, 2, 11, 14].

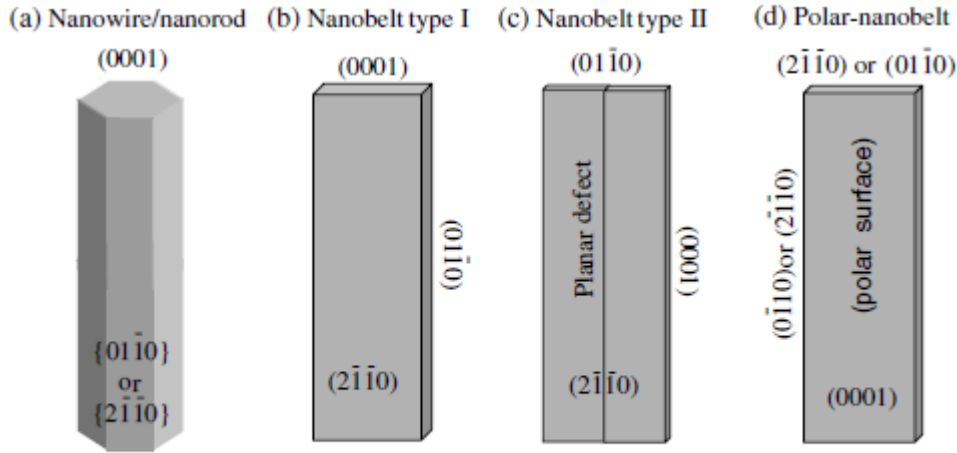


Fig. 2.2: Growth morphology of one dimensional ZnO nanostructures [2].

It is observed that when the dimensions of a semiconducting material keep decreasing i.e. from macro to micro to nano scale, some of the physical properties of that material undergo changes. This phenomenon is known as “quantum size effect” [4].

2.1.2 Electrical properties

Zinc oxide (ZnO) has a wide direct band gap (3.37 eV) and a relative large excitation binding energy (60 meV). Owing to its unique properties wide band gap and large excitation binding energy, ZnO has the potential to be applied chemical sensors, solar cells, luminescence devices etc. ZnO nanowires are also reported to have behaved like a n-type semiconductor due to the presence of interstitial defects and vacancies [4, 6, 11, 14, 20]. The major roadblock of ZnO for widespread applications in electronics and photonics is its problems with p-type doping. Quite a few p-type doping efforts have been reported like Ga and N co-doping method which resulted in the formation of low resistivity (0.5 $\Omega \cdot \text{cm}$) p-type ZnO thin films. Successful p-type doping for ZnO nanostructures will give a boost to their future prospects in nanoscale electronics and in the field of optoelectronics. P-type and n-type ZnO nanowires can serve as p-n junction diodes and LEDs. Field effect transistors (FETs) fabricated from them can be used to make complementary logic circuits [4, 20, 30, 32, 49, 50].

2.1.3 Optical Properties

Intrinsic optical properties of ZnO nanostructures are the focus of studies right now as they can be used for implementing photonic devices. As a part of these studies, 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 [4,8].

2.2 Applications

ZnO has got a wide array of applications. The reactivity of ZnO makes it ideal to be used as a precursor for obtaining other compounds of Zn. ZnO has proved to be a boon for materials science as it has got a combination of unique properties like UV absorption, anti microbial properties, steady thermal and optical properties. Be it ceramics, lubricants, ointments, adhesives or the rubber industry ZnO has got a very significant contribution [39, 43-49].

2.2.1 Rubber manufacture

The rubber industry is responsible for consuming about 50% of the ZnO that's produced globally. ZnO along with stearic acid are a must for activating the process of vulcanization in rubber manufacture. Rubber curing becomes faster and more controlled when a combination of these two substances is used. It's also a very important additive in car tyres. It helps in improving their thermal conductivity which helps the tyres to dissipate heat quickly when they are in motion thereby increasing their life span [49].

2.2.2 Medical uses

A mixture of ZnO with 0.5% Fe₂O₃ is known as Calamine and is used in manufacturing Calamine lotions. Fine particles of ZnO have anti microbial and deodorizing qualities and hence they are used for packaging purposes. These properties along with its ability of neutralizing acids makes it ideal for use in antiseptic creams, healing creams etc. they are also an important component of toothpastes and dental prosthetics. Due to its ability to absorb ultraviolet light, ZnO is also used in sunscreens and sunblocks to prevent sunburns. ZnO is also used in the making of cigarette filters as it helps in removing harmful substances like H₂S and HCN without affecting the flavour [49,50].

2.2.3 Food additives

ZnO is usually added to food products as a source of Zn which is considered to be a necessary nutrient as it helps in the performance of various physiological activities like growth and proper functioning of the sexual organs. ZnO is also added to fodder as a Zn supplement for livestock. Zinc oxide is used to manufacture zinc gluconate which is nowadays found in cold prevention lozenges [49,50].

2.2.4 Anti corrosive coatings

Zinc oxide is an excellent inhibitor of fungi, mildew and mould [50]. Paints which have ZnO are usually used as anti corrosive coatings for various metals like galvanized Zn which is especially hard to protect as it makes organic coatings brittle and unsuitable for adhesion [49]. ZnO paints on the other hand maintain their flexibility and adhesive properties for years on end. The UV blocking abilities of ZnO also play an important role in improving the resilience of the paint. Unlike some lead pigments that are available commercially, ZnO is impervious to the effect of sulphur compounds that are present in the atmosphere [43, 47].

2.2.5 Electronic applications

The wide band gap of ZnO enables it to be used for the purpose of making LEDs and laser diodes. Transparent thin-film transistors (TTFT) can also be produced with ZnO. Nanorod sensors made of ZnO are devices that detect fluctuations in electric current passing through the wires as a result of the

adsorption of gas molecules. The nanorods can be made partial towards H₂ gas by sputtering Pd clusters on the surface which help in dissociating the H₂ molecules thereby increasing the sensitivity of the nanorods. H₂ concentrations up to 10 ppm can be detected at room temperature without any response to O₂ [27,49].

Properties like biocompatibility have enabled ZnO to be used as a biomimic material to modify and immobilize biomolecules. As Field-effect transistors (FETs), they can function without even a p-n junction thus bypassing doping problems. This is why some FETs use nanorods made of ZnO as conducting channels. ZnO is also used in making Zn-C dry cells, Ni-Cd oxide batteries, Zn-Ag oxide batteries and also some secondary batteries. Another major area of ZnO application is fuel cell where it's used to make various parts like the electrodes and sometimes also as the fuel. It can also act as a photo catalyst in places like the solar cell [49, 50].

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, 33-38].

2.3.1 Proposed Method for ZnO Synthesis

Keeping in view the various aspects of ZnO synthesis, we have reached the conclusion that the simplest, cheapest and most effective way to synthesize ZnO is by oxidation method. Pure metallic Zn was oxidized in air in a muffle furnace at various temperatures ranging from 300°C to 1000°C for 2 h and the ZnO nanostructures and the microstructures formed on the Zn substrate were studied. The temperature at which the ZnO structures changed from nano to micro was also tracked.

3.0 Experimental

Zn having purity 99.9 % was obtained from RFCL Limited (RANKEM), India. The oxidation of metallic Zn was performed by heating the Zn at temperatures 300, 400, 500, 600, 700, 800, 900 and 1000°C for 2 h in a muffle furnace to obtain ZnO nanostructures on the surface of Zn. Zn was oxidized in a silica crucible. The atmosphere in the muffle furnace used for oxidation was air. Oxygen present in air was used for oxidizing Zn. The morphology of ZnO that was formed on metallic Zn was analyzed using a JEOL JSM-6480LV scanning electron microscope (SEM). In order to identify the composition of the nanostructures formed at lower oxidizing temperatures and the needle like structures formed at higher oxidizing temperatures, energy dispersive x-ray spectroscopy (EDX) and x-ray diffraction (XRD) were performed. The crystallographic structure of ZnO was analyzed with a Philips Pananalytical X' Pert x-ray diffractometer using Cu K α radiation ($\lambda = 0.15406$ nm). The JEOL JSM-6480LV scanning electron microscope was attached with a high angle and ultra-thin window type energy dispersive x-ray spectroscopy detector. An Oxford Instruments energy dispersive x-ray spectroscopy analyzer was attached. An INCAPenta FET- X3 with a powerful Si (Li) detector having a 30 mm² detecting crystal was used.

3.1 Scanning Electron Microscope

The scanning electron microscope (SEM) is a type of electron microscope that helps in forming an image of the sample surface by scanning. The electrons in the beam interact with the atoms in the surface to generate signals that shed valuable light properties like composition, topography and electrical conductivity. The so called 'signals' produced by an SEM include secondary and back-scattered electrons, characteristic x-rays, specimen current and light (due to cathodoluminescence). All SEMs usually have the ability to detect secondary electrons but it's highly unlikely that a single SEM will have the ability to detect all the signals mentioned above. SEM helps in obtaining high resolution images of specimens ranging in size from those visible to the naked eye to those which are just a few nanometers in size [28,41,43].



Fig.3.1: 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 5 μm in width. SEMs also have the ability to analyse particular points as can be seen during EDX operations which help in determining the chemical composition of the sample concerned [41].

Secondary electrons and backscattered electrons are most commonly used for the purpose of imaging samples: secondary electrons depict morphology and topography of the samples while backscattered electrons depict contrasts in composition in multiphase samples. X-rays are produced when incident electrons collide inelastically with the electrons of the atoms in the sample. As the excited electrons get back to their previous positions, they emit x-rays which is the characteristic property of a material. SEM analysis is said to be a non destructive analysis as the bombardment of electrons do not cause any damage to the samples in any way whatsoever [41].

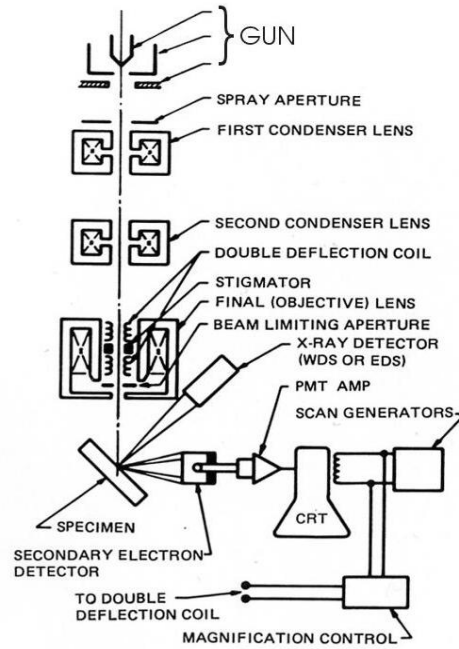


Fig.3.2: Schematic Diagram of Electron and x-ray optics of combined SEM-EPMA [41].

Essential components of all SEMs include the following:

- Electron Source ("Gun")
- Electron Lenses
- Sample Stage
- Detectors for all signals of interest
- Display / Data output devices
- Infrastructure Requirements:
 - Power Supply
 - Vacuum System
 - Cooling system
 - Vibration-free floor
 - Room free of ambient magnetic and electric fields[41]

Sample preparation is not really a problem in case of SEM analysis as the only requirement for a sample to undergo SEM analysis is that it should be conductive. It also allows a large amount of the sample to be focused at once as it has a large depth of field. The high resolution images obtained also help

in analyzing the spatial features closely. A combination of all these features has made the SEM one of the most popular instruments in the world on materials science [44].

3.2 Energy Dispersive X-Ray Spectroscopy

Energy dispersive x-ray analysis, also known as EDS, EDX or EDAX, is a technique used to identify the elemental composition of a sample. During EDS, a sample is exposed to an electron beam inside a scanning electron microscope (SEM). These electrons collide with the electrons within the sample, causing some of them to be knocked out of their orbits. The vacated positions are filled by higher energy electrons which emit x-rays in the process. By analyzing the emitted x-rays, the elemental composition of the sample can be determined. EDS is a very handy tool for performing the constitutional analysis of any kind of material [40].

3.3 X-Ray Diffraction

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 etc. 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. The x-rays that are obtained on diffraction are counted after proper processing. By altering the various parameters like the geometry of incident rays and the orientation of the detector and crystal, we obtain all possible diffraction directions of the lattice [31, 42].

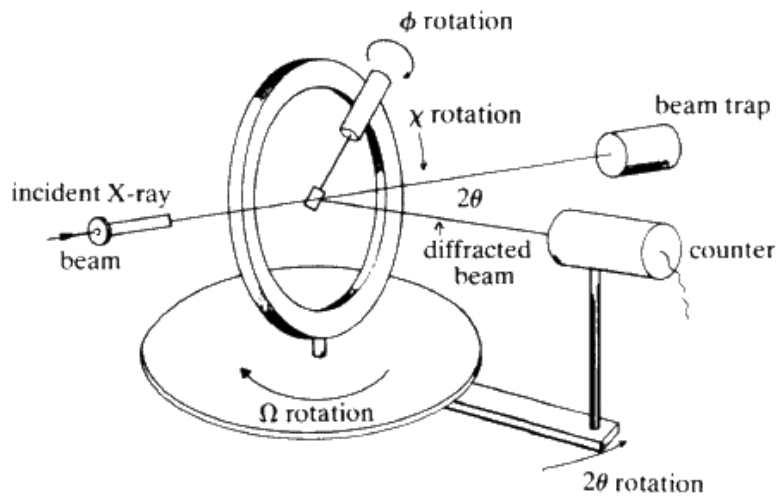


Fig.3.3: Schematic Diagram of a 4-circle diffractometer.

Image courtesy of the International Union of Crystallography [42].



Fig.3.4: PANalytical system diffractometer (Model: DY-1656).

Single-crystal diffractometers use either 3 circle or 4 circle goniometers. A goniometer usually refers to an instrument that helps in measuring angles or in rotating objects by precise angles. Fig. 3.3 shows a 4 circle goniometer. Each circle refers to one of the four angles (2θ , χ , ϕ , and Ω) that relate the

incident ray, crystal lattice and the detector to each other. Samples are first attached to brass pins. Then they are set up on the goniometer heads. By adjusting the X, Y and Z orthogonal directions we can adjust the centering of the crystal within the x-ray beam [42].

4.0 Results and Discussion

Nanostructures have attracted attention of researchers for their many important technological applications. The synthesis of nanostructures is a growing area of research. The synthesis of nanostructures by a low cost process would be of great technological importance. The ZnO nanostructures were synthesized by oxidizing pure metallic Zn. Pure metallic Zinc was heated at various temperatures ranging from 300 to 1000°C for 2 h. It should be noted that Zinc has a melting point of 419.5°C whereas its boiling point is 907°C. The choice of the range of oxidizing temperature was made in order to find out the change in the morphology of ZnO that was formed on Zn substrate. The aim was to track the change in morphology from nanostructured ZnO to microstructured ZnO as the oxidation temperature was increased. The holding time at all heat treating temperatures was either thirty 0.5 h or 2 h. Fig. 4.1(a) is the SEM image of the surface of pure metallic Zn. The result of EDX analysis in Fig. 4.1(b) shows that the composition of the sample is 100 at. % Zn.

Fig. 4.2 shows that at 300°C we find that there is no trace of formation of ZnO on the Zinc surface. The EDX result also confirms that the surface is 100 % pure Zn. From this result we can conclude that oxidation of Zn and formation of ZnO does not start at 300°C even when the pure Zn was held at this temperature for 2 h. The surface shows some changes as compared to the surface of the as-received Zinc. Fig. 4.3(a-b) shows that at 400°C the surface of Zn contains some ZnO structures. Fig. 4.4(a-b) shows that when Zn was held for 500°C for 2 h, the SEM images of the surface showed the formation of ZnO nanostructures. The composition of these nanostructures is also almost that of ZnO (21.59 at. % O and 24.51 at. % Zn). Fig. 4.5(a-b) shows that at 600°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. Fig. 4.6(a-b) shows that the oxidation of Zinc at 700°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. Fig 4.6(c) shows the EDX analysis of the ZnO microstructure formed on the Zn surface by heat treating at 700°C for 2 h 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.

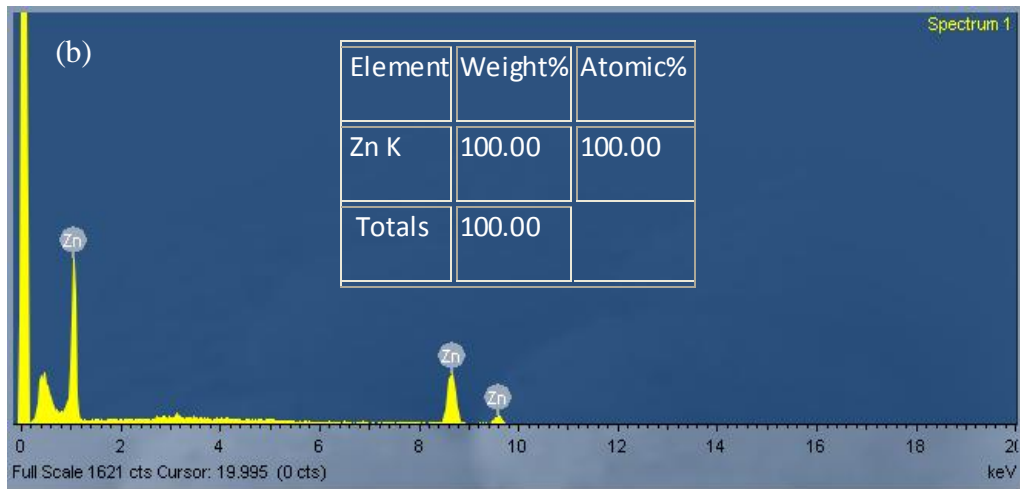
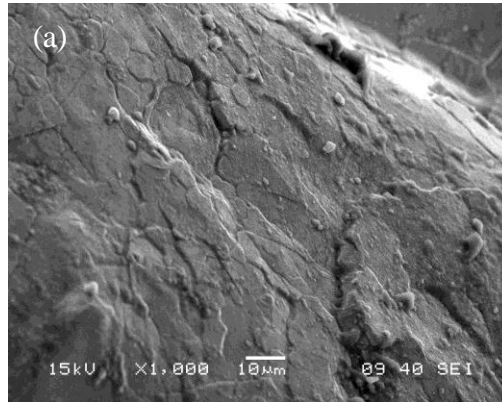


Fig. 4.1 (a): SEM showing the surface of the as-received pure metallic Zn. (b) EDX analysis of as-received pure metallic Zn.

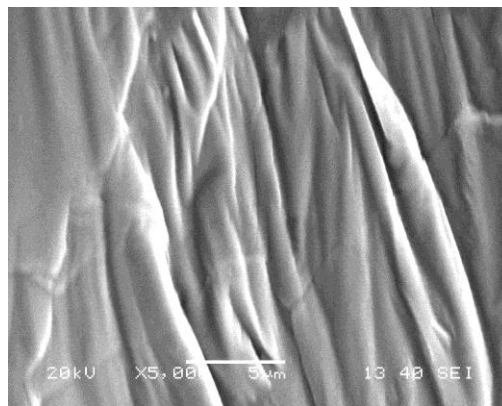


Fig. 4.2: SEM showing the surface of the Zn after oxidation at 300°C for 2 h.

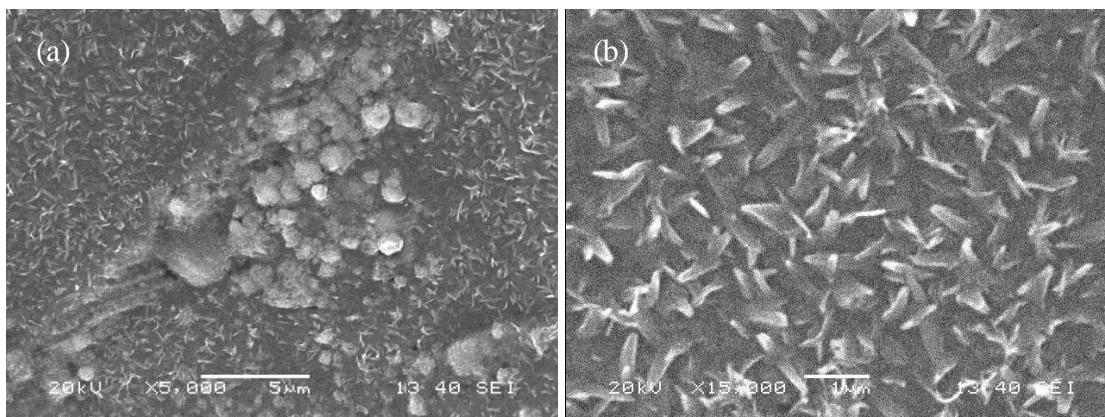


Fig. 4.3(a-b): SEM images showing ZnO nanostructures formed at 400°C on Zn substrate after holding for a period of 2 h.

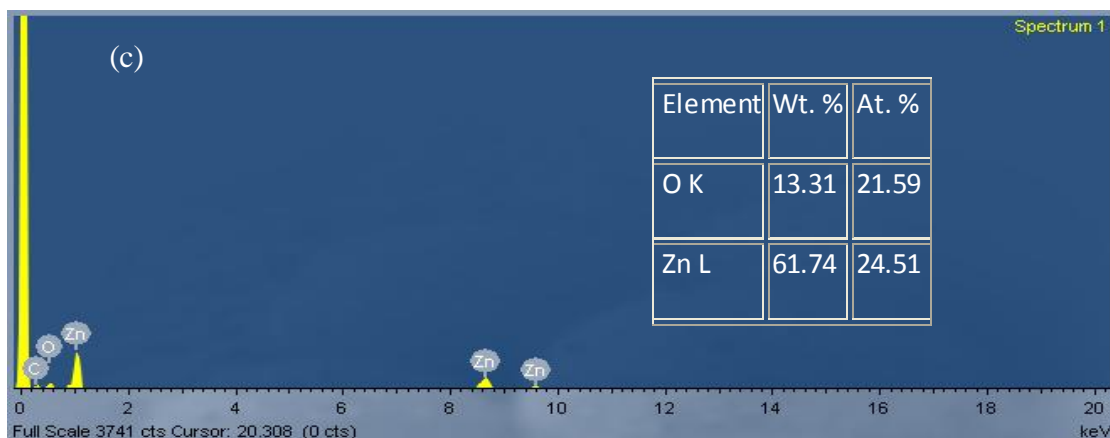
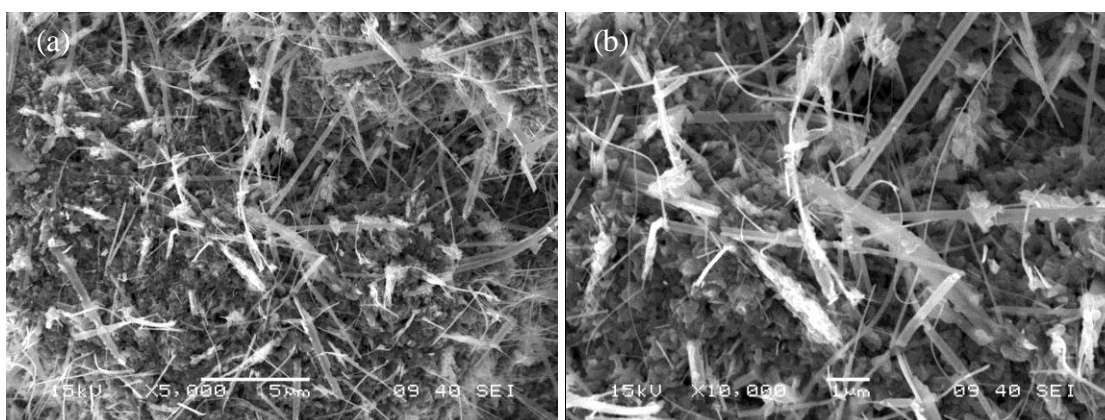


Fig. 4.4(a-b): SEM images showing ZnO nanostructures obtained on Zn substrate after holding at 500°C for 2 h. (c) EDX of the obtained sample

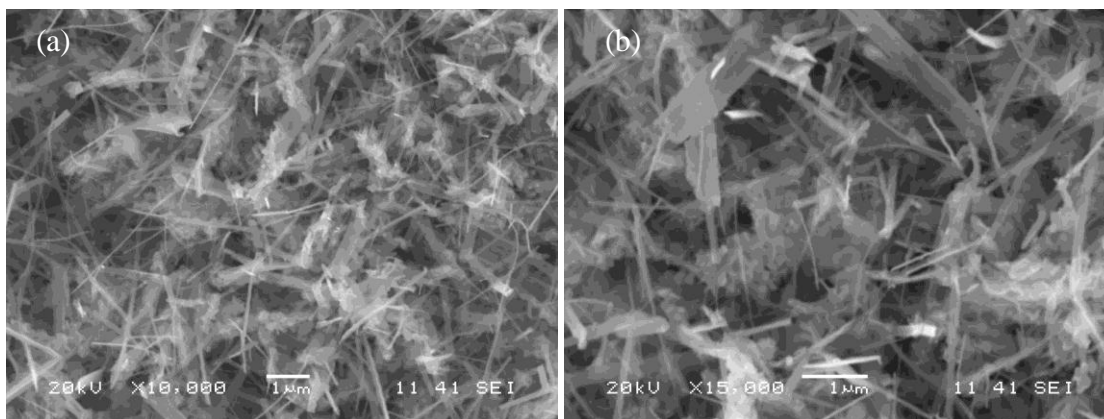


Fig. 4.5(a-b): SEM images showing ZnO nanostructures obtained on Zn substrate after holding at 600°C for 2 h.

Zn has a metallic lustre but after heating, the lustre of metallic Zn is lost and it starts to have a white coloured layer on it which is the typical colour of ZnO. The morphology of ZnO that was synthesized on Zn was investigated by using a SEM. The SEM observation shows that rod like or needle like structures of ZnO whose thickness reduced with height are formed at temperatures between 700-1000°C. The ZnO that has been grown on the surface of the metallic Zn at temperatures between 700-1000°C seems to have a very smooth surface and also seems to be highly adherent to the surface of the metallic Zn substrate. The ZnO rods formed at these temperatures have been found to be mostly triangular in shape and have different heights. Its thickness reduced gradually from the base to the tip. The thickness of the base of the ZnO structures formed on Zn surface after oxidation at 900°C for 0.5 h was less than 1 μm and there were a large majority of the ZnO structures having thickness much less than 1 μm. Fig. 4.8(a-b) shows that their heights were relatively large and some of the structures were almost 10 μm long. On the other hand, Fig 4.9(a-b) shows that the thickness of the base of the ZnO structures formed on the Zn surface after oxidation at 900°C for 2 h was less than 1 μm but a majority of them were thicker than the ZnO structures formed at 900°C for 0.5 h. This was possibly due to the longer period of holding time during oxidation which allowed the ZnO structures to grow in thickness. Their heights were comparatively much lower in the range of 3-4 μm. The ZnO structures formed by oxidation at 900°C for 0.5 h reduced in thickness along its height much faster as compared to the ZnO structures formed by oxidation at 900°C for 2 h. The ZnO structures that have been formed at 900°C for 2 h comparatively reduced in thickness along its height much more gradually. It can be concluded that holding Zn sample for a longer period of time at a particular temperature led to ZnO structures having larger cross sectional area

and relatively shorter heights. The ZnO structures that have been formed at 900°C for 2 h were faceted and triangular in shape and seemed to be more needle like or rod like whereas the ZnO structures that have been formed at 900°C for 0.5 h were not faceted and were also not triangular and seemed to have a more leaf like thinner structure.

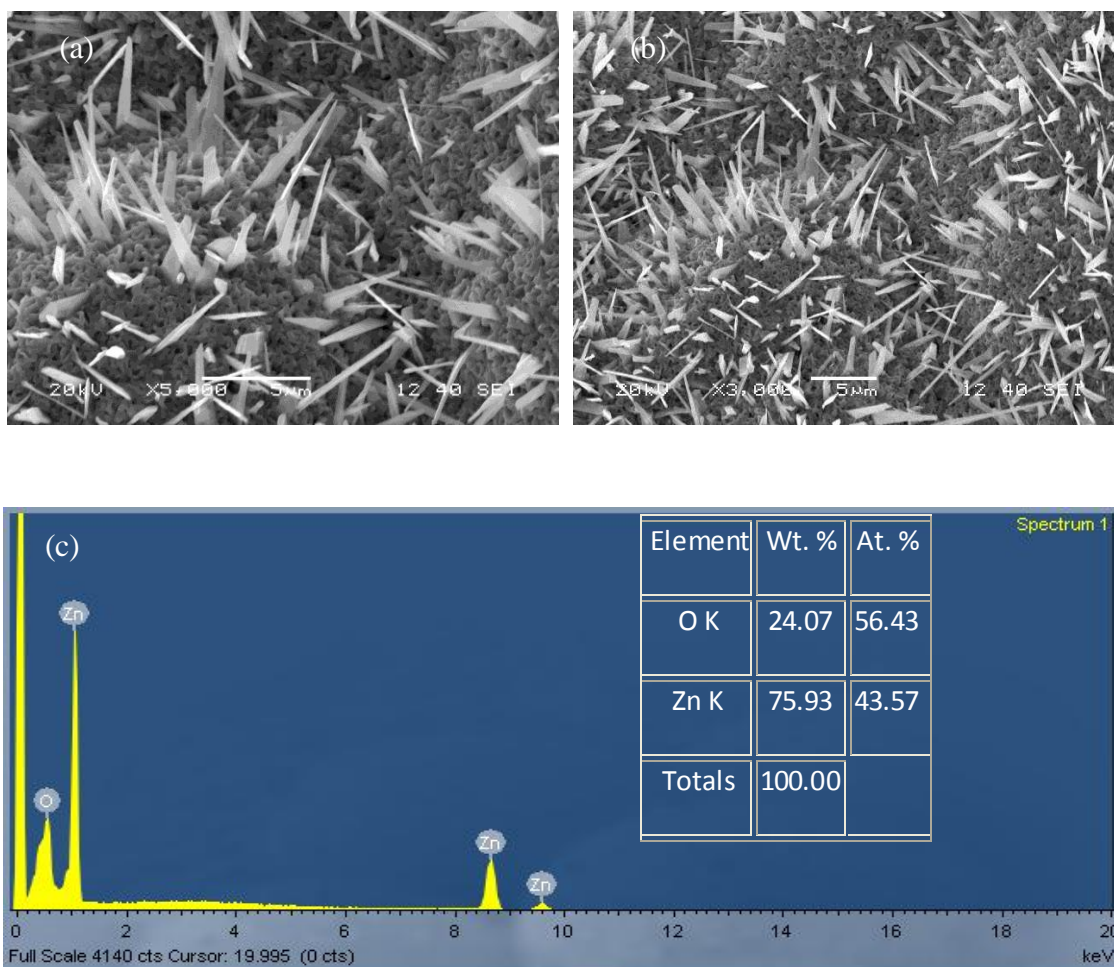


Fig. 4.6(a-b) SEM images of ZnO microstructures obtained on Zn substrate holding Zn at 700 °C for 2 h. (c) EDX of the protruded structure.

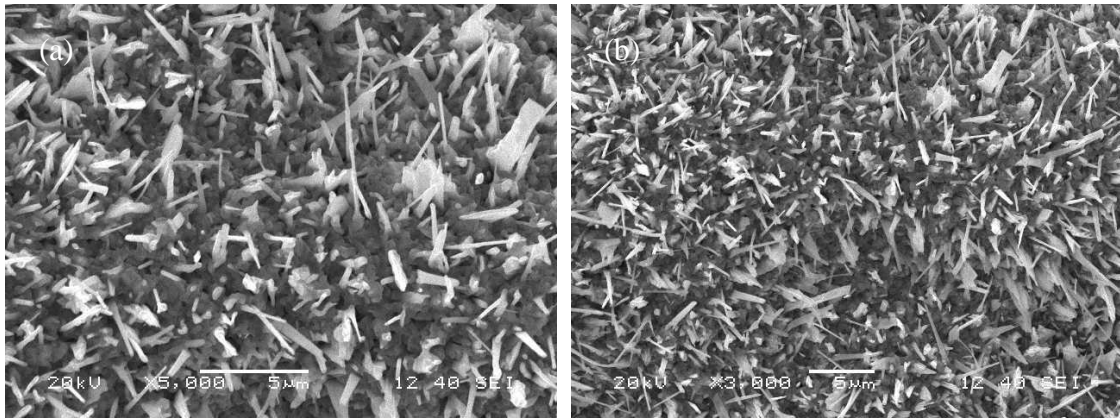


Fig. 4.7(a-b): SEM images showing ZnO structures obtained on holding Zn for 2 h at 800°C.

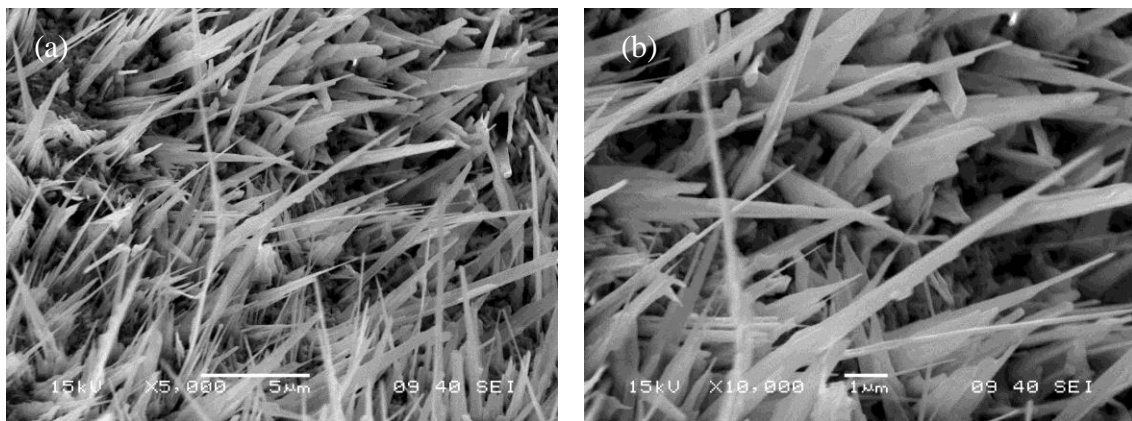


Fig 4.8(a-b): SEM images showing ZnO structures obtained on holding Zn at 900°C for 0.5 h.

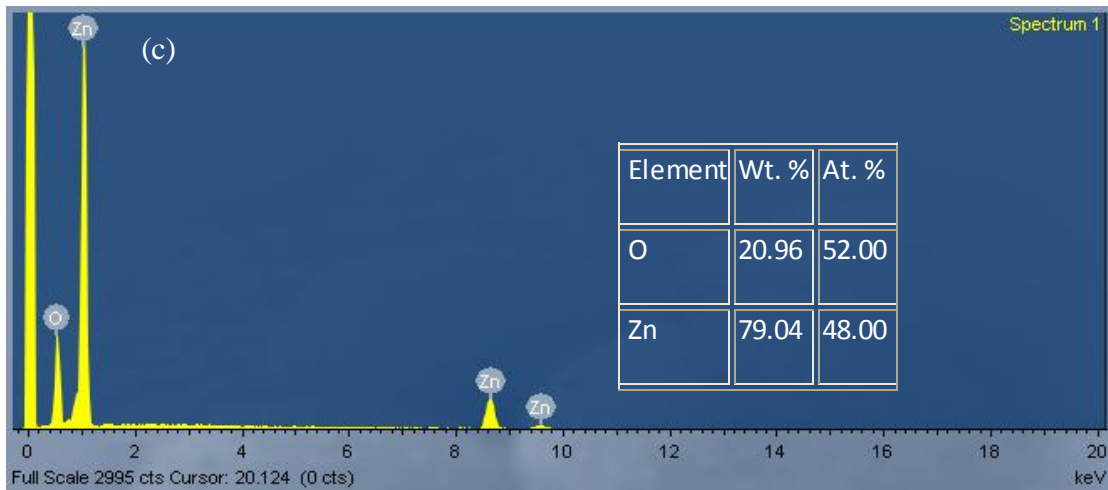
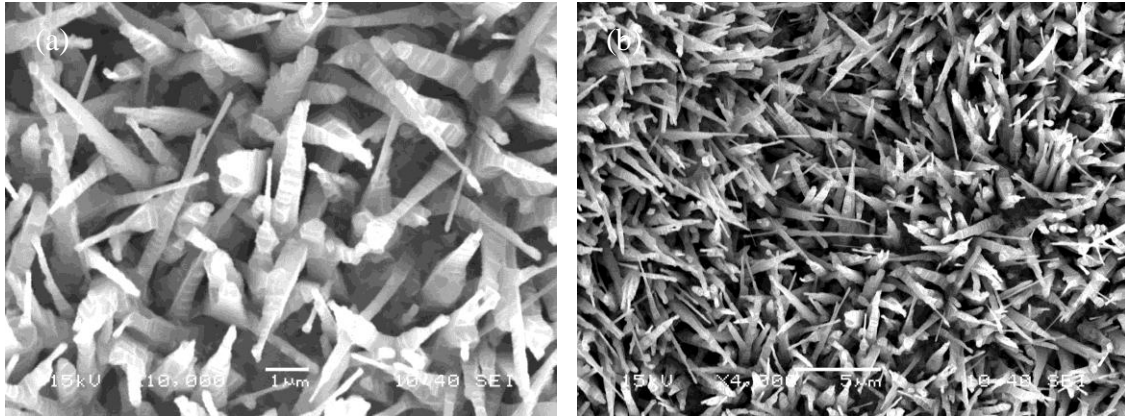


Fig 4.9(a-b): SEM images distinctly showing the triangular morphology of ZnO microstructures obtained on holding Zn at 900°C for 2 h. (c) EDX of the oxide microstructures.

Fig 4.9(c) shows the EDX analysis which confirmed that the at. % of oxygen in the ZnO nanostructure is 52 % and the at. % of Zn is 48 %. Nearly stoichiometric ZnO cloud can be synthesized by oxidation of Zn in air. The formation of nearly stoichiometric ZnO on glass substrates at high sputtering pressures has been reported [42]. ZnO nanostructures could be synthesized by oxidizing pure metallic Zn for 2 h at temperatures between 400-600°C. At oxidizing temperatures above 700°C needle like or rod like microstructures could be seen. Clearly, the size of ZnO depends on the oxidation temperature, i.e., higher the oxidation temperature, the larger the size of the ZnO structures. Higher temperatures lead to

more vigorous oxidation and results in mostly columnar needle or rod like structures which are faceted whereas oxidation at lower temperatures results in nanostructured ZnO. At oxidation temperatures ranging from 400-600°C nanostructured ZnO having different morphology was formed on the Zn substrate.

Fig. 4.10 consists of the XRD plot which shows that all the peaks of ZnO could be traced in the XRD profile of the sample formed by heat treating Zn at 700°C for 2 h. Formation of ZnO could not be traced from the XRD analysis at 300°C and 400°C although SEM image showed the formation of ZnO at 400°C. Possibly due to the low intensity of the peaks of the ZnO formed at 400°C as they had a relatively small size and also due to the lesser amount of ZnO formed at this temperature they could not be traced. So we can conclude that ZnO structures could be formed on the Zn substrates only at temperatures above 300°C.

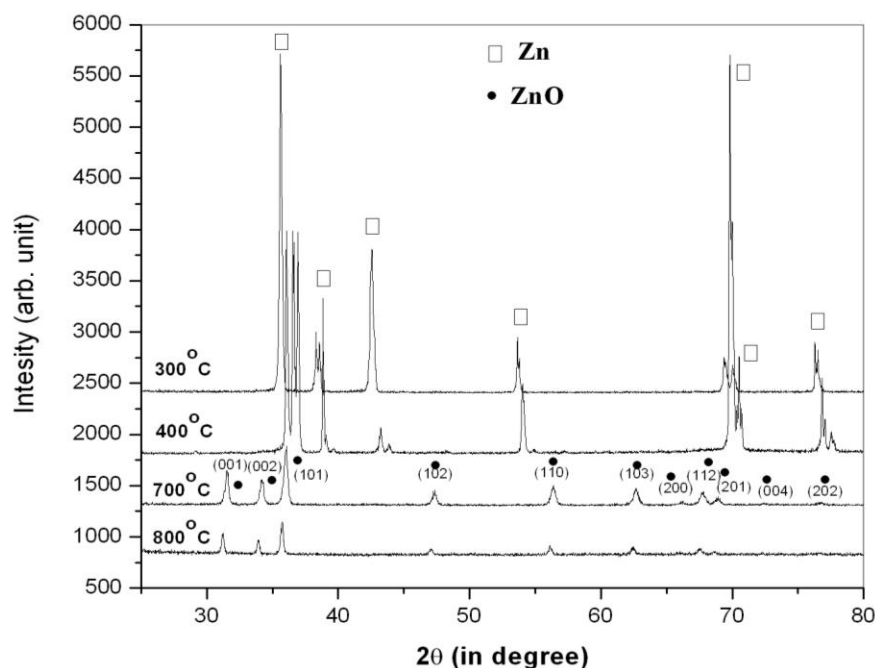


Fig. 4.10: XRD plots of Zn oxidized at 300°C, 400°C 700°C and 800°C for 2 h.

When metallic Zn was heat treated to 1000°C for 2 h Zn started to boil and vapourized as its boiling point is 907°C. As the silica crucible in which Zn was oxidized was not covered all the Zn vapour

possibly went out of the vessel and only a small amount of the Zn vapour condensed and solidified on the metallic Zn substrate. This resulted in lesser amount of Zn reacting with the oxygen and forming ZnO on the Zn substrate. This is the reason why in Fig. 4.11(a-b) we see only a few ZnO structures.

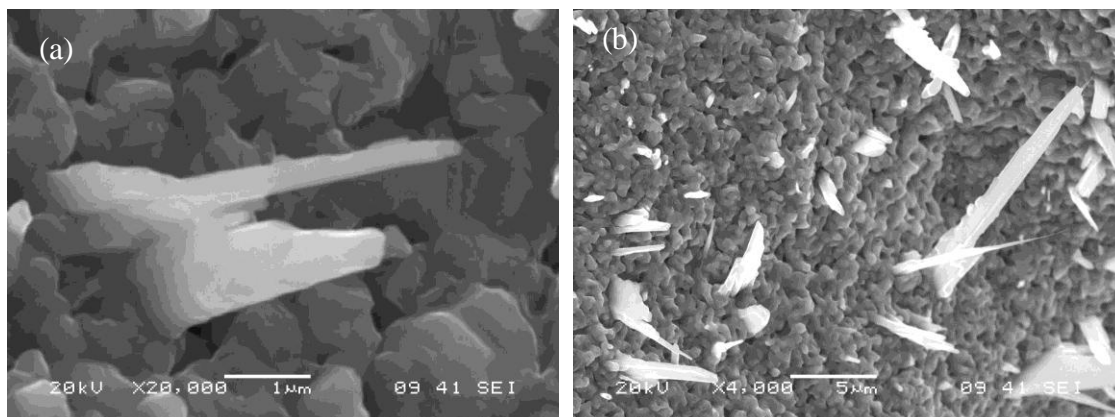


Fig. 4.11(a-b): SEM images showing the microstructures obtained on holding Zn at 1000 °C for 2 h.

5.0 Conclusion

In summary, this simple technique of oxidation of metallic Zn in air has been demonstrated as a very economical and effective technique for the synthesis of ZnO nanostructures on metallic Zn. The ZnO nanostructures were successfully synthesized by oxidizing pure metallic Zn in the temperature range 400-600°C. The structure and size of ZnO nanostructures strongly depends on the oxidizing temperatures. This is an economical route for the synthesis of ZnO on a pure metallic Zn substrate. It is found that the size of ZnO structures increases with increasing temperature of oxidation.

The scanning electron microscopy observation shows that needle like or rod like structures of ZnO could be formed at temperatures above 700°C. Above the oxidizing temperature of 700°C the needle like or rod like structures of ZnO were very uniform in shape and size. The Zn surface was covered densely with the ZnO structures at oxidation temperatures above 700°C. On the other hand at oxidizing temperatures between 400-600°C the nanostructured ZnO were nonuniform in size and structure and were less dense and more scattered on the metallic Zn surface.

6.0 References

- [1] Zhong Lin Wang, Zinc oxide nanostructures: growth, properties and applications, *Journal of Physics: Condensed Matter*. Vol. 16 (2004), R829- R858
- [2] <http://www.chemistry.ohio-state.edu/~woodward/ch754/struct/ZnO.htm>
- [3] Zhiyong Fan and Jia G. Lu, Zinc Oxide Nanostructures: Synthesis and Properties, *Journal of Nanoscience and Nanotechnology*. Vol. 5 (2005) (10), pp. 1561-1573.
- [4] S Baruah and J Dutta, Hydrothermal growth of ZnO nanostructures, *Sci. Technol. Adv. Mater*. Vol. 10 (2009) (1).
- [5] Hernandezbattez, A; Gonzalez, R; Viesca, J; Fernandez, J; Diazfernandez, J; MacHado, A; Chou, R; Riba, J; CuO, ZrO₂ and ZnO nanoparticles as antiwear additive in oil lubricants. (2008), pp. 265.
- [6] Porter, F, *Zinc Handbook: Properties, Processing, and Use in Design*, CRC Press. (1991).
- [7] Dapeng Wu, Zhengyu Bai, Kai Jiang, Temperature induced hierarchical growth of ZnO microcrystal, *Materials Letters*. Vol. 63 (2009), pp. 1057-1060.
- [8] Chen, Z., Z. Shan, S. Li, C.B. Liang, and S.X. Mao. 2004. A novel and simple growth route towards ultra-fine ZnO nanowires. *J. Cryst. Growth*. Vol. 265, pp. 482–486.
- [9] Sekar, A., S. H. Kim, A. Umar, and Y. B. Hahn. 2005. Catalyst-free synthesis of ZnO nanowires on Si by oxidation of Zn powders. *J. Cryst. Growth*. Vol. 277, pp. 471–478.
- [10] Zhang, J., Y. Yang, B. Xu, F. Jiang, and J. Li. 2005. Shape-controlled synthesis of ZnO nano and micro-structures. *J. Cryst. Growth*. Vol. 280, pp. 509–515.
- [11] T. K. Subramanyam, B. Srinivasulu Naidu, S. Uthanna, Physical Properties of Zinc Oxide Films Prepared by DC Reactive Magnetron Sputtering at Different Sputtering Pressures, *Cryst. Res. Technol*. Vol. 35 (2000) (10), pp. 1194-1202.
- [12] Wang, Zhong Lin, Zinc oxide nanostructures: Growth, properties and applications, *J. Phys.: Condens. Matter*. Vol. 16 (2004), pp. R829–R858.
- [13] Yang Liu, Jian-er Zhou, Andre Larbot, Michel Persin, Preparation and characterization of nano Zinc oxide, *Journal of Materials Processing Technology*. Vol. 189 (2007), pp. 379–383.
- [14] T. K. Subramanyam, B. Srinivasulu Naidu, S. Uthanna, Physical Properties of Zinc Oxide Films Prepared by dc Reactive Magnetron Sputtering at Different Sputtering Pressures, *Cryst. Res. Technol*. Vol. 35 (2000), pp. 1193–1202.

- [15] T.A. Polley, W.B. Carter, D.B. Poker, Deposition of Zinc oxide thin films by combustion CVD, *Thin Solid Films*. Vol. 357 (1999), pp. 132-136.
- [16] Ü. Özgür, Ya. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho, and H. Morkoç, A comprehensive review of ZnO materials and devices, *Journal of applied physics*. Vol. 98 (2005), pp. 041301.
- [17] B. Wang, E. Shi, W. Zhong, C. Xia, W. Li, Z. Yin, Growth habits and mechanism of ZnO, *Micro-Cryst. Hydrotherm. Cond.* Vol. 25 (1997) (2), pp. 223.
- [18] S.H. Jo, J.Y. Lao, Z.F. Ren, et al., Field-emission studies on thin films of Zinc oxide nanowires, *Appl. Phys. Lett.* Vol. 83 (2003) (23), pp. 4821.
- [19] P.X. Gao, Z.L.Wang, Nanopropeller arrays of zinc oxide, *Appl. Phys. Lett.* Vol. 84(2004) (15), pp. 2883.
- [20] Zhiyong Fan and Jia G. Lu, Zinc Oxide Nanostructures: Synthesis and Properties, *Journal of Nanoscience and Nanotechnology*. Vol. 5(2005) (10), pp. 1561-1573.
- [21] B. M. Ataev, I. K. Kamilov, A. M. Bagamadova, V. V. Mamedov, S. Sh. Makhmudov, A. K. Omaev, and Sh. O. Shakhshae, Controlled Growth of Quasibicrystal Zinc Oxide Structures. *Technical Physics Letters*. Vol. 26 (2000) (9), pp. 837–838.
- [22] INCAPentaFET-x3, (2008), Retrieved April 22 2010 from <http://www.oxford-instruments.com/products/microanalysis/eds/detectors/sili-detector/Pages/incapentafet-x3.aspx>
- [23] Raghu Viswanathan, Ram B. Gupta, Formation of zinc oxide nanoparticles in supercritical water, *J. of Supercritical Fluids*. Vol. 27 (2003), pp. 187-193.
- [24] Zhiyong Xu, Jiann-Yang Hwang, Bowen Li, Xiaodi Huang, and Howard Wang, The Characterization of Various ZnO Nanostructures Using Field-Emission SEM, Research summary (www.tms.org/jom.html).
- [25] K Sreenivas, Sanjeev Kumar, Jaya Choudhary and Vinay gupta, Growth of zinc oxide nanostructures. *Journal of Phy.* Vol. 65 (2005) (5), pp. 809-814.

- [26] A. N. Red'kin, Z. I. Makovei, A. N. Gruzintsev, E. E. Yakimov, O. V. Kononenko, and A. A. Firsov, Elemental Vapor-Phase Synthesis of Nanostructured Zinc Oxide. ISSN 0020-1685, Inorganic Materials. Vol. 45 (2009) (11), pp. 1246–1251.
- [27] S Roy and S Basu, Improved zinc oxide film for gas sensor applications. Bull. Mater. Sci. Vol. 25 (2002) (6), pp. 513–515.
- [28] Instrument Database:JEOL - JSM-6480LV, (2007), Retrieved April 22, 2010 from <http://www.speciation.net/App/Techniques/technique.html?id=47>
- [29] Zhong Lin Wang, Nanostructures of ZnO, Materials Today. Vol. 7 (2004) (6), pp. 26-33.
- [30] S. Music', S. Popovic', M. Maljkovic', D. Dragic'evic, Influence of synthesis procedure on the formation and properties of Zinc oxide. Journal of Alloys and Compounds. Vol. 347 (2002), pp. 324–332
- [31] Basics of X Ray Diffraction, Scintag Inc.,1999, Chapter 7, pp. 7.13-7.14.
- [32] T. K. Subramanyam, B. Srinivasulu Naidu, S. Uthanna, Structure and Optical Properties of DC Reactive Magnetron Sputtered Zinc Oxide Films. Cryst. Res. Technol. Vol. 34 (1999), pp. 981–988
- [33] Yousheng Zhang, Lisheng Wang, Xiaohua Liu, Yunjie Yan, Changqiang Chen, and Jing Zhu, Synthesis of Nano/Micro Zinc oxide Rods and Arrays by Thermal Evaporation Approach on Cylindrical Shape Substrate. J. Phys. Chem. B. Vol. 109 (2005) (27), pp. 13091-13093.
- [34] C.K.Yap, W.C.Tan, S.S.Alias, A.A.Mohamad, Synthesis of zinc oxide by zinc–air system. J. Alloys Compd. Journal of Alloys and Compounds. Vol. 484 (2009) (1-2), pp. 934-938.
- [35] Li ChenSha, Li YuNing, Wu YiLiang, Beng S. Ong & Rafik O. Loutfy, Synthesis of Zinc oxide nanocrystals by thermal decomposition of Zn-oleate in organic medium, Sci China Ser E-Tech Sci. Vol. 51 (2008) (12), pp. 2075-2079.
- [36] Dapeng Wu, Zhengyu Bai, Kai Jiang, Temperature induced hierarchical growth of ZnO microcrystal, Materials Letters. Vol. 63 (2009), pp. 1057–1060.
- [37] C.W. Yao, H.P. Wu, M.Y. Ge, L. Yang, Y.W. Zeng, Y.W. Wang, J.Z. Jiang, Triangle-shape ZnO prepared by thermal decomposition, Materials Letters. Vol. 61 (2007), pp. 3416–3420.
- [38] Orathai Yawong, Supab Choopun, Pongsri Mangkorntong and Nikorn Mangkorntong, Zinc Oxide Nanostructure by Oxidization of Zinc Thin Films. Chiang Mai University Journal Special Issue On Nanotechnology. Vol. 4 (2005) (1).

- [39] Industrial applications of ZnO, Retrieved April 22, 2010 from <http://navbharat.co.in/clients.htm>
- [40] Energy Dispersive X-ray Spectroscopy (EDS), John Goodge, University of Minnesota-Duluth, Retrieved April 22, 2010 from http://serc.carleton.edu/research_education/geochemsheets/eds.html
- [41] Scanning Electron Microscopy (SEM), Susan Swapp, University of Wyoming, Retrieved April 22 2010 from http://serc.carleton.edu/research_education/geochemsheets/techniques/SEM.html
- [42] Single Crystal X-ray Diffraction, Christine M. Clark, Eastern Michigan University, Barbara L. Dutrow, Louisiana State University, Retrieved April 22 2010 from http://serc.carleton.edu/research_education/geochemsheets/techniques/SXD.html
- [43] Regional Sophisticated Instrumentation Centre PU, Chd, Retrieved on May 4, 2010 from <http://rsic.puchd.ac.in/em.html>
- [44] What is SEM? Iowa State Varsity, MME dept., Retrieved on May 4, 2010 from <http://mse.iastate.edu/microscopy/whatsem.html>
- [45] Sato, H., Minami, T., Takata, S., Mouri, T., Ogawa, N. Thin Solid Films, Vol. 220 (1992), pp. 327 and Vol. 246 (1994), pp. 86.
- [46] Zinc oxide applications, Retrieved on May 4, 2010 from <http://www.stallonezincoxide.com/application.htm>
- [47] Zinc oxide (ZnO) – Properties and Applications, Retrieved on May 4, 2010 from <http://www.azom.com/details.asp?ArticleID=2357>
- [48] Zinc oxide applications, Retrieved on May 4, 2010 from <http://www.ucalanka.com/zinc-oxide-applications.html>
- [49] Zinc oxide application, Retrieved on May 4, 2010 from <http://www.numenor.com/application.asp>
- [50] Zinc oxide applications, Retrieved on May 4, 2010 from http://wopedia.mobi/en/Zinc_oxide?t=6.