Two step anodization and effect of alternating current in electrodeposited Nickel tin (NiSn) nanowires

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FORWARDING SHEET BY RESEARCH SUPERVISOR

The thesis entitled **"Two step anodization and effect of alternating current in electrodeposited Nickel tin (NiSn) nanowires"** submitted by **Usamah Bashir s/o Bashir Ahmad** Registration Number: 273-FBAS/MSPHY/S-14 in partial fulfillment of M.S. degree in Physics has been completed under my guidance and supervision. I am satisfied with the quality of student's research work and allow him to submit this thesis for further process to graduate with Master of Science degree from Department of Physics, as per IIU rules and regulations.

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MS Physics

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For the award of the degree of

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بسم الله الرحمن الرحيم

O my Rabb (Cherisher and Sustainer)! Bestow wisdom on me, and join me with the righteous; grant me honorable mention on the tongue of truth among the latest (generations); make me one of the inheritors of the Garden of Bliss." Al-Quran (26:83-84)

DEDICATION

DEDICATED TO MY LOVING PARENTS AND ESPECIALLY TO MY Father WHO ALWAYS PRAYS FOR MY SUCCESS AND MY TEACHERS WHO ALWAYS INSPIRED ME TO EXPLORE IDEAS OF LIFE WITH MODEST VISION AND FOSTER ME THROUGH ODD AND EVEN SITUATIONS OF LIFE.

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(Usamah Bashir)

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Abbreviations

1D Nanomaterials: One dimensional Nanomaterials

2D Nanomaterials: Two dimensional Nanomaterials

NWs: Nanowires

NTs: Nanotubes

Ms: saturation Magnetization

Mr: Remittance Magnetization

AAO: Anodic Aluminum Oxide

XRD: X-ray Diffraction

SEM: Scanning electron microscope

EDX: Energy dispersive X-ray spectroscopy

EDS: Energy X-rays dispersive spectroscopy

Abstract

In this research, the $Ni_{1-x}Sn_x$ (x=0.05 –0.5) nanowires are fabricated in Anodized Aluminium Oxide (AAO) templates by AC electrodeposition at $16V_{AC}$. The AAO templates are prepared by anodization method in 5% solution of phosphoric acid at 60V. The average diameter and length of NW_s is found to be d = 150nm and L = 15μm respectively. The EDS reveals the compositional analysis of nickel and tin. The FTIR confirms the absorption bands of tin and nickel at (600-660) cm^{-1} and (680-750) cm^{-1} respectively. The XRD results confirm that the prepared samples are polycrystalline with tetragonal structure of Sn and FCC phase of Ni. This study is useful to tune the structural and morphological properties of $Ni_{1-x}Sn_x$ nanowires.

CHAPTER 1
INTRODUCTION TO NANOTECHNOLOGY

Nano materials had formed at the time of Bing bang, but the research on these materials is started decade ago. Nano materials are present all the time in our atmosphere and effect on living organisms. These materials have positive and negative effects. Now it is possible that these materials are fabricated in the laboratory by different methods.

Initially Michal Faraday prepared nanoparticles in 19th century by using the colloidal solution of Gold particles. After some years, nanocatalysis are formed by different scientists. In 1940's fumed silica nanoparticles were prepared by different methods. But the proper research was started in 1960's in all over the world. Initially different nanomaterials like nanotubes, nanorings or nanowires are formed by the different methods. It was the start of nanoscience and nanotechnology [1].

1.1 Nanoscience and nanotechnology

There is some difference between nanoscience and nanotechnology. At nano level the properties of the materials change due to increase in the surface to volume ratio, is called "nanoscience". In other words we can say that the manipulation of knowledge at nanolevel is called nanoscience. In nanotechnology the engineering and functioning of the nanomaterials or the study of structures between 1 to 100 nanometers are discussed. How the nanomaterials are handled or controlled by different methods is called nanotechnology. Nanotechnology has broad and useful properties to make the life better and comparatively easier. Nanomaterials are further divided into different categories according to their dimensions.

1.2 Nanomaterials

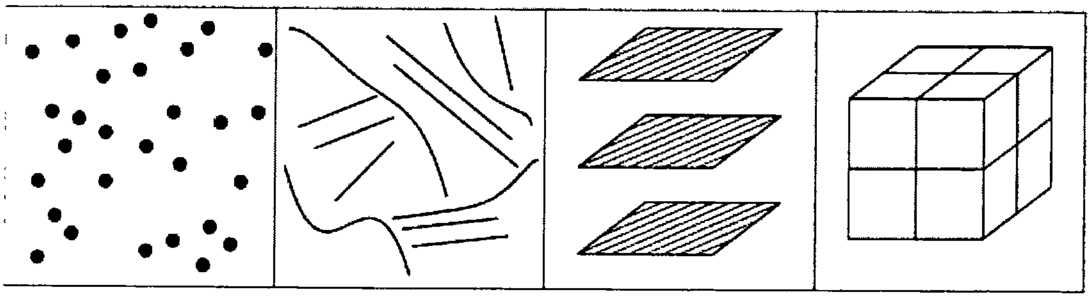
Nano level is very small and it is very difficult to see it with naked eye. Simply we can say that this level is 100,000 times smaller than human hair. As we discussed above that the nanomaterials are categorized according to their dimensions, these materials having one dimension are at nanometer range and the motion of the electron is confined in that dimensions. On the basis of these dimensions, nanomaterials are categorized in 0D, 1D and 2D materials. Now we discuss one by one.

1.2.1 Zero dimensional nanomaterials

These materials having all the dimensions are at nanometer (1-100nm) range and the motion of electron is confined in all three dimensions. Examples of these materials are quantum dots, nanoparticles or clusters etc. [2, 3].Figure 1.1 shows some nanomaterials.

1.2.2 One dimensional nanomaterials

These types of materials having two dimensions are at nanometer range and electron's motion is confined in two dimensions. The remaining dimension may be at micrometer range. Examples of these types of materials are nanowires, nanorods and nanotubes etc. [4, 5]. Following figure shows one dimensional materials.



Clusters (0D)

Nanotubes, filaments and rods (1D)

Films and layers (2D)

Polycrystals (3D)

Figure 1.1: 0D, 1D, 2D and 3D materials

1.2.3 Two dimensional nanomaterials

These types of materials having one dimension are at nanometer range and electron's motion is confined in single dimensions. Other two dimensions may be in micrometer range. Two dimensional nanomaterials have lot of varieties like nanosheets, thin films, graphene and quantum well etc. [6].

1.2.4 Three dimensional nanomaterials

That type of materials has three degree of freedom. These types of materials grow in three dimensions greater than the nanometer range. Some time they include in bulk or micro level. Also the motion of electron is not confine in any direction so the electron can move in any direction.

Table 1.1: Categorize of nanomaterials with respect to their dimensions

Nanomaterials	**Examples**
Zero dimensional materials	Quantum dots, nanoparticles etc.
One dimensional materials	Nanotubes, nanorings, nanobelts etc.
Two dimensional materials	Quantum well, thin films etc.

1.3 Magnetism and Magnetic Materials

Magnetism is the phenomena in which attractive or repulsive forces are experienced by specific materials when the magnetic field is applied. How much materials charged, this depends on the strength of the magnetic field and the materials. This leads to the major phenomena which are studied by the scientists. On the basis of magnetic properties, the materials are categorized in different kinds. Those materials can be ferromagnetic, anti-ferromagnetic, paramagnetic or diamagnetic. Some materials are strongly affected by the magnetic field while some materials are weakly affected [7].

Magnetism is produced by two phenomena. These two phenomena are motion of electron and the orbital and spinning motion of electron around nucleus. These two phenomena leads to the two branches of physics called “electromagnetism” and “permanent-magnetism” [8].

1.4 Origin of magnetism

Atomically the electron has not only spinning motion but it also revolves around the nucleus with specific velocity. Both spinning and orbiting motions produce the magnetic effect. Following figure 1.2 shows spinning and orbiting motion of the electron around the nucleus. Both motions of electrons produce the magnetic effects separately with magnetic moments. The net effect of magnetic moments can be obtained by taking the sum of both moments.

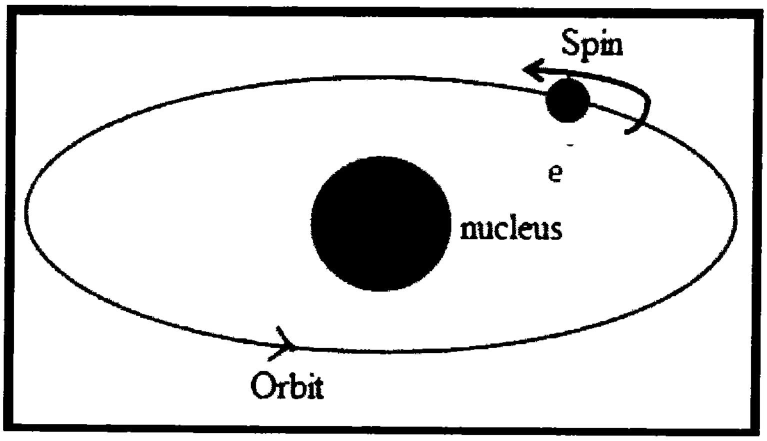


Figure 1.2: Spinning and orbital motion of electron around the nucleus

Magnetic moments behave differently in materials. In some materials, magnetic moments cancel each other due to opposite spins of electrons or pairing of electrons while in some materials magnetic moments do not cancel the effect of each other due to unpairing of electrons. That’s why net magnetic moment can be obtained [8-10].

On the basis of magnetism, all the materials are divided into different categories such as diamagnetism, paramagnetism, ferromagnetism, antiferromegnitism and ferrimagnetism [11]. From above types of magnetic materials, at least one type exists in material. So when the magnetic field is applied on the materials, the magnetic moment becomes responsible for the behaviour of magnetic materials.

1.5 Magnetic field B

Mathematically, the magnetic field is defined as

$$\mathbf{B} = \mu_o\mathbf{H} + \mu_o\mathbf{M} = \mu_o(\mathbf{H}+\mathbf{M}) \tag{1.1}$$

above equation describe as the sum of external magnetic field **H** and the magnetization **M** which is equal to the magnetic moment in per unit volume of magnetic material [12]. Where μ_o is constant of proportionality of free space and its value is 4π x 10-7 Wb/A-m. Wb/m^2 is SI unit of magnetic field **B** [12].

1.6 Magnetic Permeability

As we know that, the external magnetic field **H** affects the internal magnetic field **B** when the specific material is placed. The increment of magnetic field can be measure by μ which is known as magnetic permeability. The relation between **H** and **B** is

$$B = \mu H \tag{1.2}$$

From above equation μ can be defined as

$$\mu = B/H \tag{1.3}$$

(Wb/A-m) is SI unit of magnetic permeability (μ).

Another basic term is used to study the magnetic properties, which is known as relative permeability μ_r. Relative permeability is the ratio of μ/μ_o. This term gives the magnetization and demagnetization of the material [12].

When the external magnetic field **H** is applied, whole, material is aligned in the direction of magnetic field with the amplification of magnetic field by a factor of $\mu_o M$ as discussed in equation (1.1). This concept gives the proportional relation between magnetization **M** and magnetic field **B** as given below

$$M = \chi_m H \qquad (1.4)$$

In above equation χ_m is known as the magnetic susceptibility which is mathematically defined as

$$\chi_m = M/H \qquad (1.5)$$

Magnetic susceptibility has no unit because it is the ratio.

Also we can find the relation between the magnetic permeability and magnetic susceptibility from above equations, that is

$$\chi_m = \mu r - 1 \qquad (1.6)$$

1.7 Classification of magnetic materials

Magnetic materials are classified in different types such as diamagnetic, ferromagnetic etc. These classifications are on the basis of magnetic response of the materials. Magnetic response depends on the paired and unpaired spins of the electrons. Similarly it also depends on the spinning and orbiting motion of the electrons. The interactions of all magnetic fields produce the strengths of magnetic fields. At the same time some magnetic field lines cancel the effect of each other. This depends on the type of material [12].

In all classes of magnetic materials, antiferromagnetic materials are considered as subclass of magnetism. Periodic table (figure 1.3) shows classified magnetic materials.

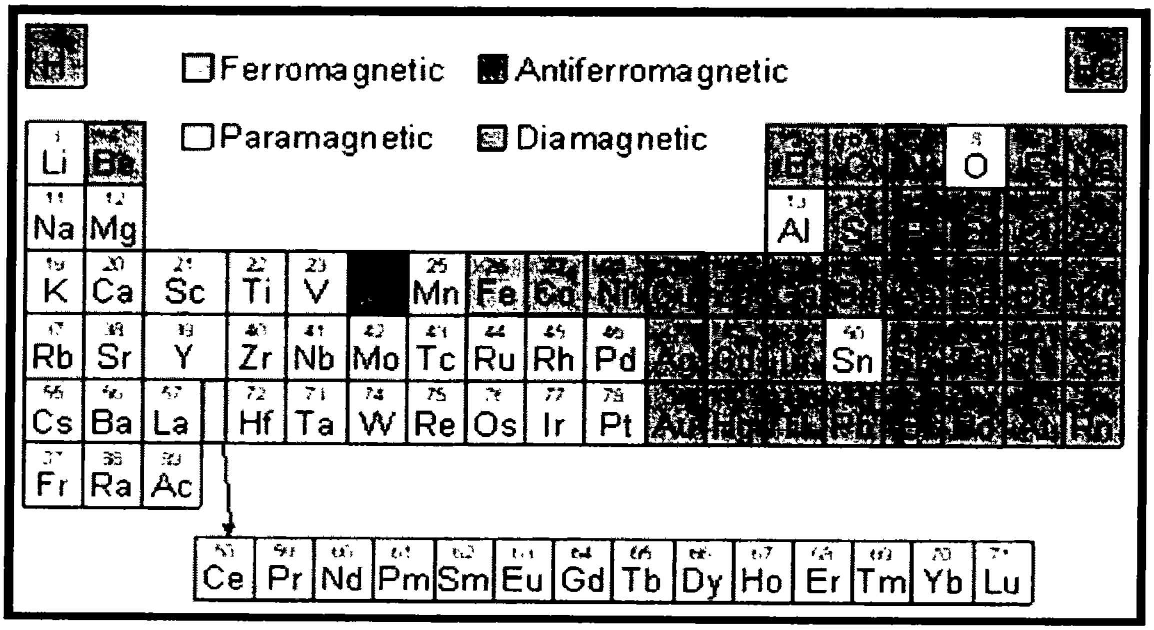


Figure 1.3: Periodic table shows the different magnetic materials

1.7.1 Diamagnetism

In all types of magnetism, diamagnetism is very weak form of magnetism as well as it is very short time phenomena. This phenomena produces when both types of electron's motion (spinning + orbiting) does not paired to each other, so the total magnetic moment become zero in this case. However when the magnetic field **H** is applied the magnetic moments align opposite to each other as shown in figure 1.4. Hence, magnetization **M** is zero when external field **H** is zero, and again zero when the material displaces under the magnetic field. So the basic terms relative permeability and magnetic susceptibility are less than one ($\mu_r<1$) and negative ($\chi_m<0$). The magnetic susceptibility will be in the order of 10^{-5} and in vacuum magnetic induction **B** will be very weak. The diamagnetic materials attracts towards weak field, when material is placed in strong magnetic field [9, 14].

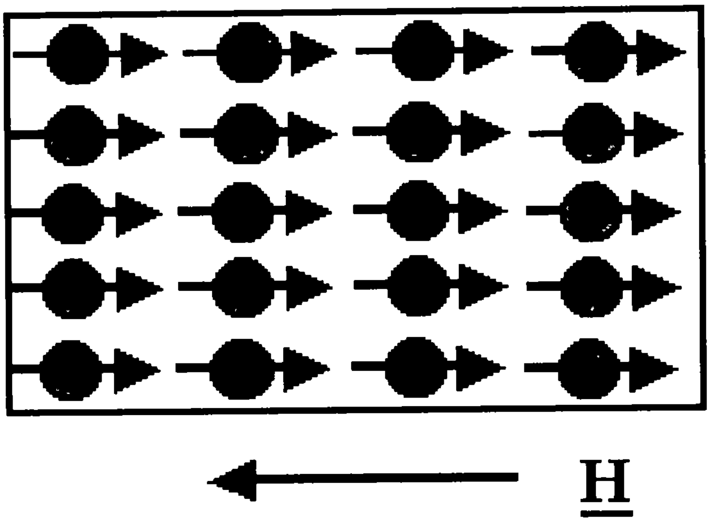
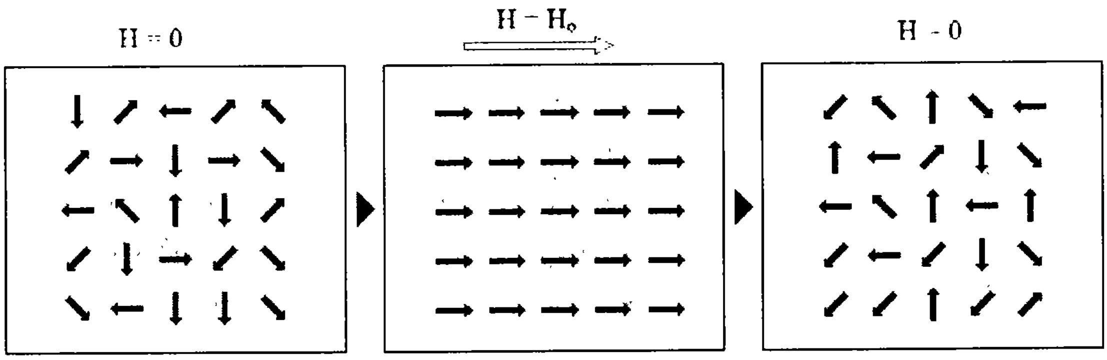


Figure 1.4: Behaviour of diamagnetic substance under the action of external magnetic field **H**.

1.7.2 Paramagnetism

Paramagnetic phenomenon produces when partially filled electrons exist in some materials. Also there is some difference in diamagnetic materials and paramagnetic materials, that is, the negative and positive susceptibility. Diamagnetic materials have negative susceptibility while paramagnetic materials have positive susceptibility as shown in figure 1.5. In these types of materials, the domains are aligned in the direction of magnetic field **H.** In that materials, the range of positive susceptibility is from 10^{-6} to 10^{-2} [9, 11].



M = 0 (a) M = +M₀ (b) M = 0 (c)

Figure 1.5: Behaviour of paramagnetic substance under the action of external magnetic field **H** also shows the positive susceptibility

1.7.3 Ferromagnetism

In first and second class of magnetism, the magnetization **M** is zero when the external magnetic field is removed, but in third class, it differs in this respect that is, the magnetization **M** exist even the magnetic field is removed. The magnetic moments are aligned permanently as shown in figure 1.6. initially the magnetization is zero due to randomly oriented moments of electrons, when the magnetic field is applied, the domains are arranged or aligned parallel to magnetic field and these domains stay aligned even the magnetic field is removed. Iron, nickel are the common examples of ferromagnetic materials. These types of materials have susceptibility in the order of 10^{-6} [9, 14].

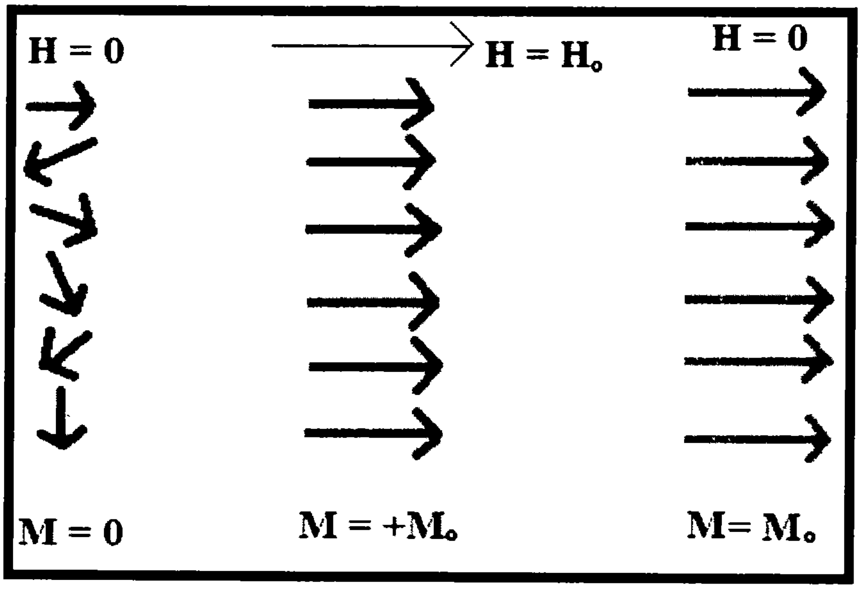


Figure 1.6: Ferromagnetic behaviour of material

1.7.4 Antiferromagnetism

Figure 1.7 shows the antiferromagnetic phenomena in which nearby atoms have opposite alignments. The net magnetic moments will be zero in these types of materials.

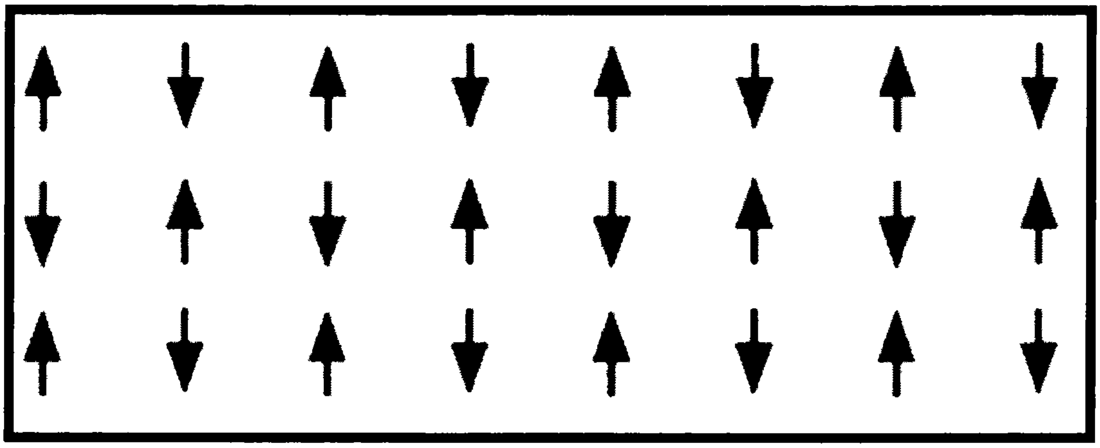


Figure 1.7: Antiferromagnetic behaviour of material

1.7.5 Ferrimagnetism

This class magnetism, approximately similar to antiferromagnitism with small effect that is, magnetization which is not zero in ferromagnetic materials. These types of materials have net magnetization because magnitudes are not equal of magnetic moments as shown in fig. 1.8. Fe_3O_4 is ferromagnetic material in which iron has two trivalent ions and oxygen has divalent ions. Both types of ions have different types of magnetic moments so cancel the effect of each other. Hence divalent ions possess the ferromagnetic materials also produces the magnetization [14].

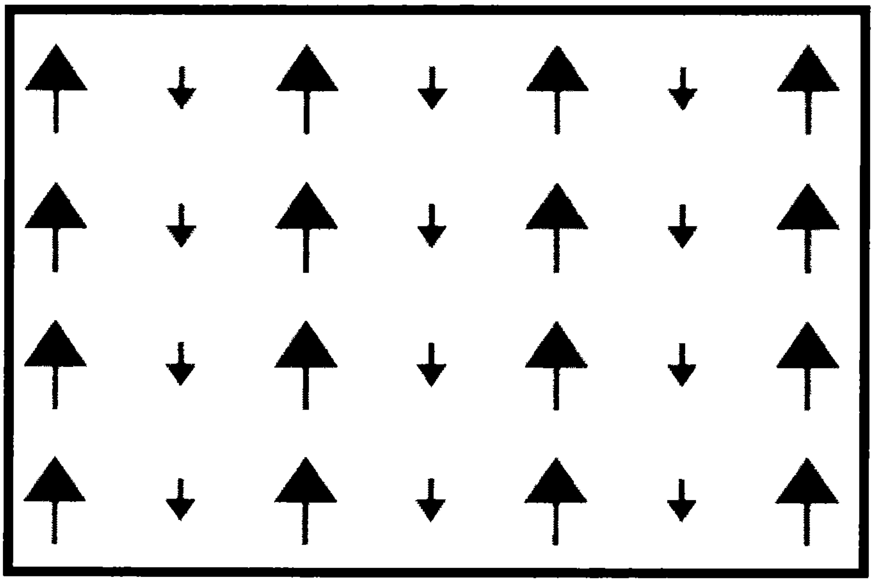


Figure 1.8: Ferrimagnetism

1.8 Magnetic hysteresis loop

Hysteresis loop is a basic source to study the magnetic properties of specific materials. Some basic terms like coercivity, retentivity, saturation points etc. can be study by hysteresis loop. The graph is in between magnetization **M** and external magnetic field **H**. initially the magnetization is zero when **H** is zero. When magnetic field is applied, the domains become aligned and saturation magnetization **Ms** (at point a) gained as shown in fig. 1.9. After that remanant magnetization (retentivity) is gained by applying field towards zero (at point b). To get coercivity, magnetic field again reduces to zero. By applying field continuously, this gives the saturation magnetization again but in opposite sense. Sqaureness of hysteresis loop can be define as ratio of M_R/M_S. Hysteresis loop depends on the shape, size of the material as well as the orientation of magnetic field.

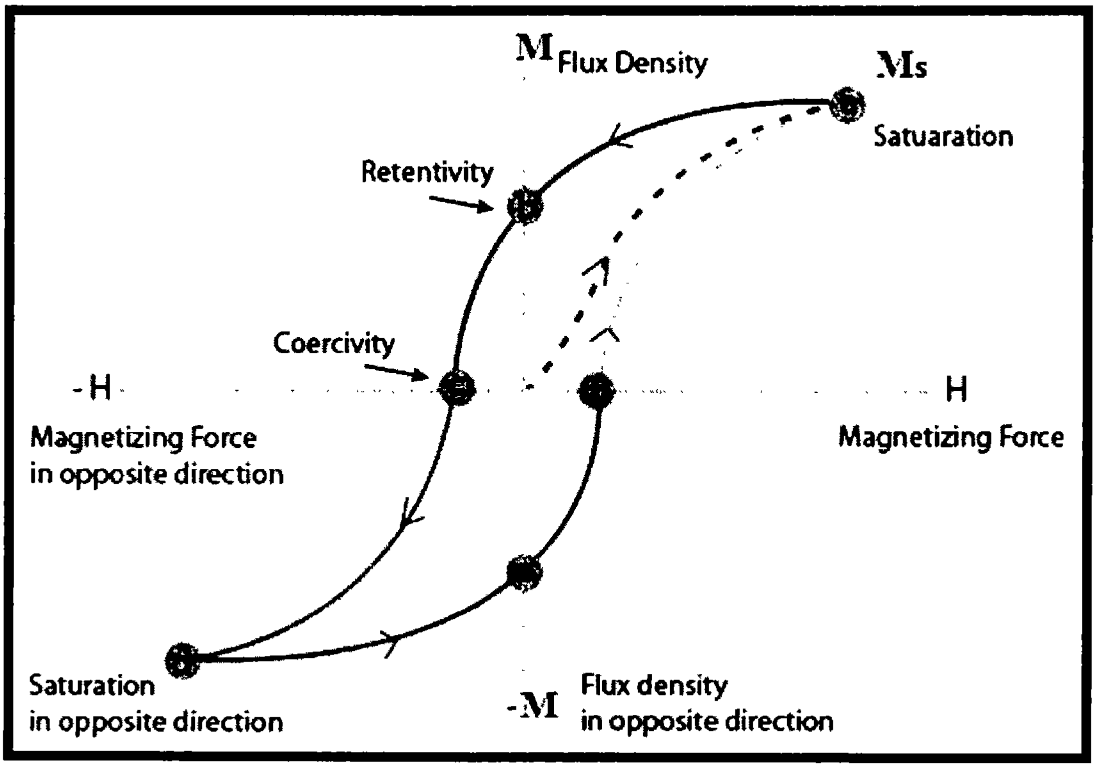


Figure 1.9: M-H loop

1.9 Nanowires

Nanowires have great importance in nanotechnological applications having one dimension at nano level. The motion of electrons in nanowires only in single direction, hence it is confined in other two directions. The uniqueness of nanowires is better electrical, magnetic and optical properties due to flow of electrons in single direction. There are many types of nanowires like cobalt, nickel, tin, chromium etc. [21]. But as we concern here, nickel and tin nanowires will be prepared. These nanowires are magnetic because tin is magnetic material. Semiconductor nanowires can also be fabricated with good applications. The focus of this discussion is to study the magnetic properties of Ni-Tin nanowires.

1.10 Magnetic nanowires

In the world of nanoscience and nanotechnology, nanowires have rare properties and broad use [21]. A big use of magnetic nanowires, i.e. commercial and laboratory level in all over the world. Many nanosensors and nanodevices are based on the magnetic nanowires.

1.11 Magnetic applications

The basic magnetic properties of nanowires such as coercivity, remenence and dipolar interactions can be controlled. This controlling can be take place by diameter domain of nanowires [22, 23]. A term that is, the aspect ratio has great importance by means of different applications in magnetic storage devices or medium. In storage devices, super paramagnetic limit can be controlled by nanowires which have large aspect ratio. Magnetic energy increases in a grain if the anisotropy increases or by increasing the grain's volume. The resolution depends on the particle size and decreases with increasing volume. The super paramagnetic limit reaches to 70 Gbit/in^2 at room temperature for spherical magnetized grain.

High aspect ratio required for magnetic data storage devices. Aspect ratio increases the coercivity of specific materials with packing density greater than 10^{11} wires/cm^2. Most important application of magnetic storage devices is "Racetrack memory" which has non-volatile and it is proposed by S. parlin. It is relevant to the domain wall in magnetic nanowires [24].

1.12 Motivation

There are many applications of one dimensional nanomaterials in the field of nanotechnology. Especially nanowires have lot of use in sensors, nanoelectronics etc. [60]. Comparatively as from bulk, the nanoscale has batter properties. Most of properties like electrical and optical can be enhanced at nanolevel. The cluster of atoms can be obtained by convenient way [15-18]. Magnetic storage densities with high value give the good recording densities in nanowires if the "Anodized aluminium" templates are used. In the whole world, nanowire's applications have lot of attention due to better and convenient use. Direct current (DC) electrodeposition is most preferable method to synthesize the metallic NWs [19]. This method is very cost effective and easily available in any laboratory. The basic use of this method is to easily control the size or diameter and length of the nanowires by controlling the template's size. AAO templates have great importance for the fabrication of nanowires due to high aspect ratio and batter pore distribution as well as high pore density [36-42]. Also to improve the performance of Li ion batteries such as in power sources and in cell phones, the nanowires are widely used now days [49-53].

Nickel (Ni) is a ferromagnetic material having important application in most of nano storage devices. Different types of electrodes by means of nanowires are also used such as TiO_2, V_2O_5, SnO_2, Fe_3O_4 and Co_3O_4 are used at large scale [54-59]. As we concerned in this project, we change the ratio of tin (Sn) by keeping the ratio of nickel constant. DC electrodeposition method will be used to make the nanowires by means of AAO templates.

CHAPTER 02
SYNTHETIC TECHNIQUES

Now a day's scientists take interest to make nanomaterials by different ways due to their big difference in bulk counterparts and obtain the different physical, electrical, chemical and magnetic properties comparatively. These materials can be prepared by different methods such as physical and chemical. This leads the preparation of different materials like zero dimensional (0D), one dimensional (1D) and two dimensional (2D) nanomaterials. Furthermore these methods are categorized in two ways. First is top down approach and second is bottom up approach. Usually physical techniques are considered as top down approach while chemical techniques are considered as bottom up approach.

The most common and convenient methods used in the world of science are chemical methods, vapour liquid-phase growth and hydrothermal process [33-35]. A brief discussion on top down and bottom up methods will be discussed next.

2.1 Physical method

This method is top down approach, usually starts from bulk and goes to nano level to prepare the nanomaterials. Normally bulk material is used at the start and processed it with different synthetic techniques and then ends it up at nano scale. Sputtering technique, Ball milling and lithography are the common examples of top down approach. Some techniques are discussed next.

2.1.1 Sputtering technique

This technique is very expensive that's why it is not common at laboratory level comparatively. Ions or atoms are deposited on the substrate's surface by focussing the ion beam. Usually helium or argon gas is used to generate the ions from specific materials. This sputtering technique also called magnetron sputtering because the magnets are used to attract the ions for deposition on the substrate. To sputter the desired materials highly energetic ion beam is used. This may depend on the nature of the material. Following figure (2.1) shows the sputtering technique.

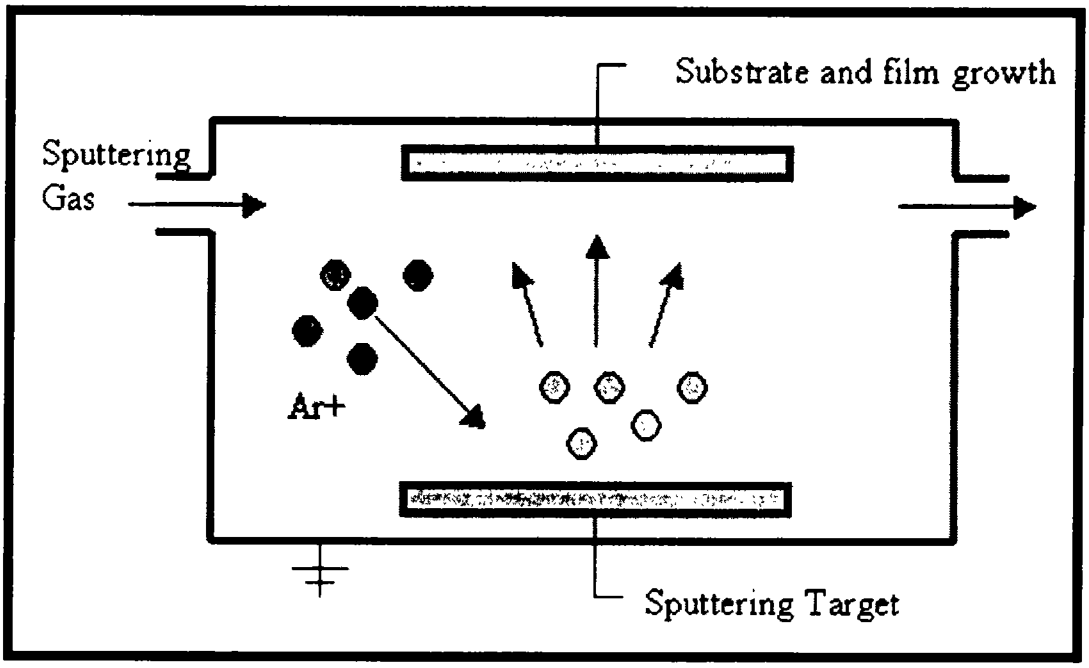


Figure 2.1: Sputtering technique [20]

2.1.2 Ball milling method

This method is not freely used at laboratory level because the size of the particles cannot be control easily. Usually 20 to 25 nm size particles are synthesized by this technique. Tungsten coating are used inside the mills, which is inserted inside the container. Hardened steel balls can also be used in the replacement of tungsten carbide as shown. Desired particles are milled inside the mills which gives the nanomaterials of different sizes.

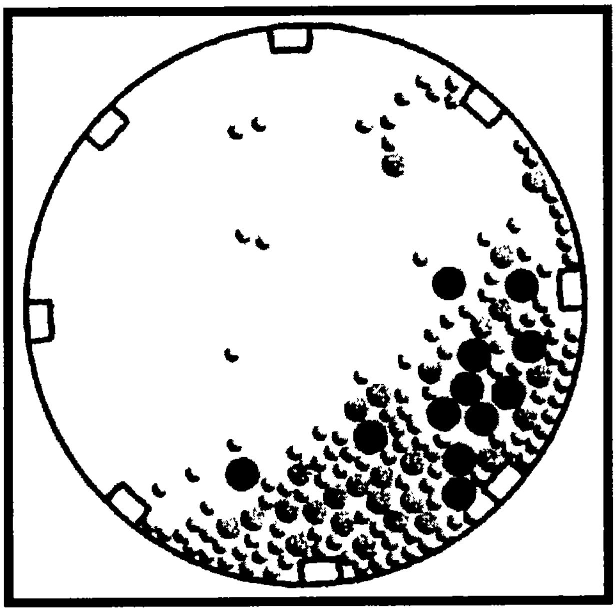


Figure 2.2: Ball milling technique

2.1.3 Inert gas phase condensation technique (IGC)

Usually this method is used to prepare the nanoparticles of semiconductor and metal oxides. At the start low pressure atmosphere environment is created and then inert gas is introduced inside. Condensation and evaporation processes happen to synthesise the nanoparticles. The precursors of materials are evaporated under the system as shown in figure 2.3. Collision processes starts with collector's atom and then lose energies. The homogeneous condensation becomes start for the deposition of atoms on a specific surface.

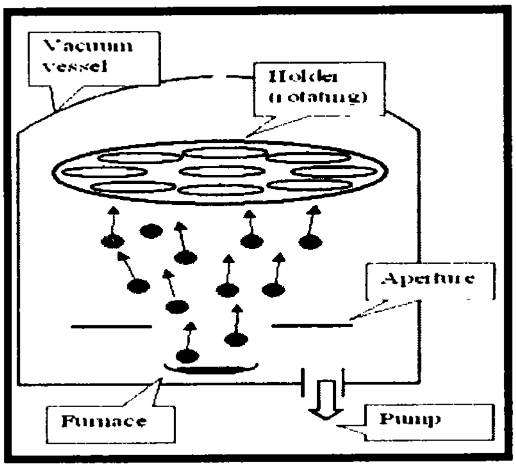


Figure 2.3: IGC technique

2.1.4 Pulse laser ablation

Pulse laser ablation method is very famous to synthesize the materials based on nanoparticles. A big advantage of this method is that, the desired yield is highly pure and ultra-fine. In this process a chamber is used and filled it with regent gas with known amount. Meanwhile evaporation process starts in the chamber by applying pulse laser. At the same time condensation of nanoparticles happens on the surface of the sample. Oxide compounds are formed when atoms are diffused on the sample and interaction with gas atoms take place. After diffusion, the nanoparticles (Np_s) are formed in the chamber. Np_s can be altered by altering the different parameters such as regent gas, temperature and inert gas composition.

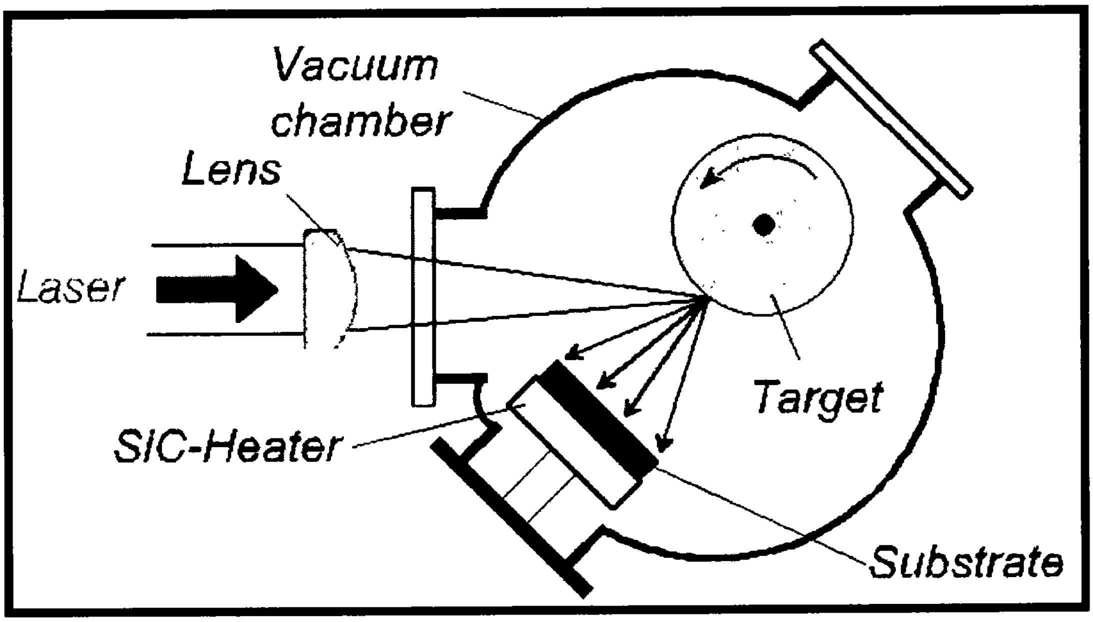


Figure 2.4: Schematic of pulse laser ablation

2.2 Chemical method

All the chemical processes are based on bottom up approach. These processes are the combination of same or different kind of atoms or molecules. These atoms and molecules combine together and form nano size materials. There are many draw backs of chemical processes like toxic effects, but a big advantage is that the require yield is ultra-fine, homogeneous and uniform. This leads a better characterization after sample preparation. Also the particle size by chemical methods can easily controllable which is very difficult in physical methods. Few examples of this approach are chemical vapour deposition (CVD), physical vapour deposition (PVD), sol-gel and electrodeposition processes. Some methods will be described next.

2.2.1 Sol-gel technique

The sol-gel is a bottom up approach. It is also called wet chemical process. This process is very cost effective and easily available in laboratories. The nanoparticles are prepared by gelatine and precipitation. Hydrothermal process takes place to get Nps. firstly chemical solution is taken to get a gel. Gel has highly viscous and solvent is trapped in it. Two basic processes take part; one is hydrolysis and second is condensation. Organic solvent is mixed in the gel for breaking the chemical bonds. In condensation water starts to release as the molecules combined. Size can be controlled by varying the ratios of hydrolysis and condensation. The whole process is shown in figure 2.5.

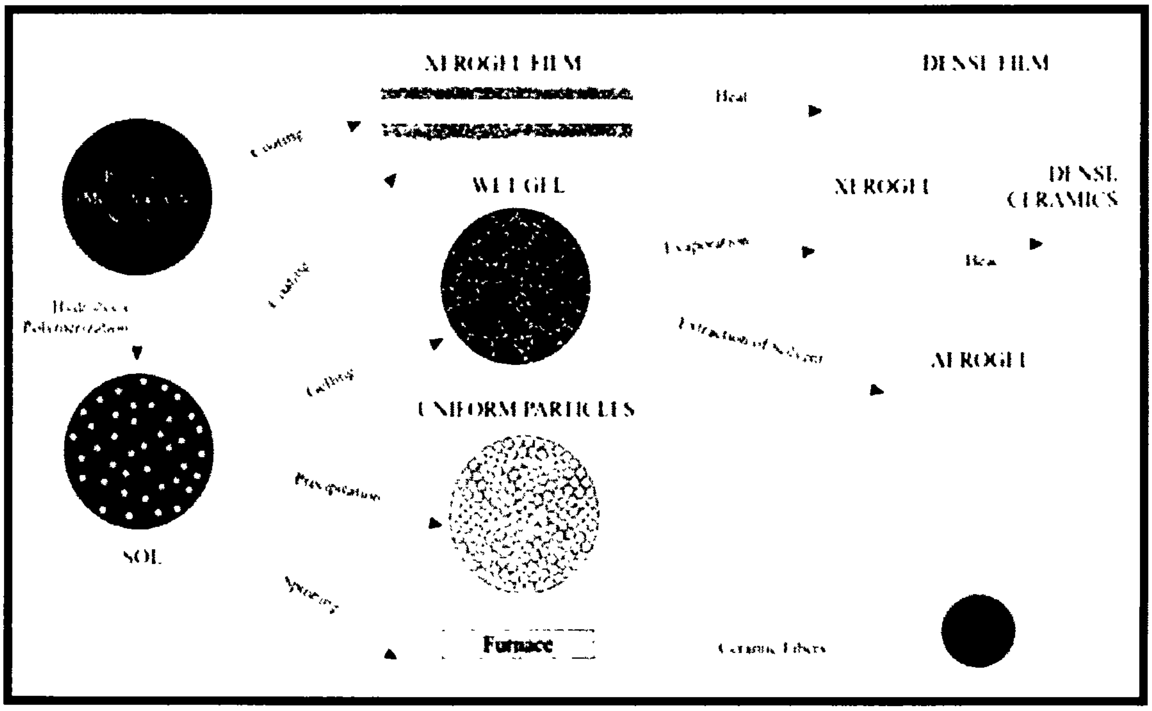


Figure 2.5: Sol-gel technique

2.2.2 Chemical vapour deposition (CVD)

In this process the nanomaterials are obtain in the form of thin film by transformation of gaseous state into solid. In this process highly heated substrate's surface is exposed and allows the volatile precursor to react with that surface to get desired particles. Two types of gases are introduced inside the chamber with specific flow that are, regent gasses and inert gasses. Now the reaction takes place on the surface as the gas atoms reached here and the gas atoms are absorbed by the surface. Chemical reaction gives the nanoparticles as it starts. By products starts to release and leaves the system (chamber). At the end, substrate goes to cool down gradually and the nanoparticles are obtained.

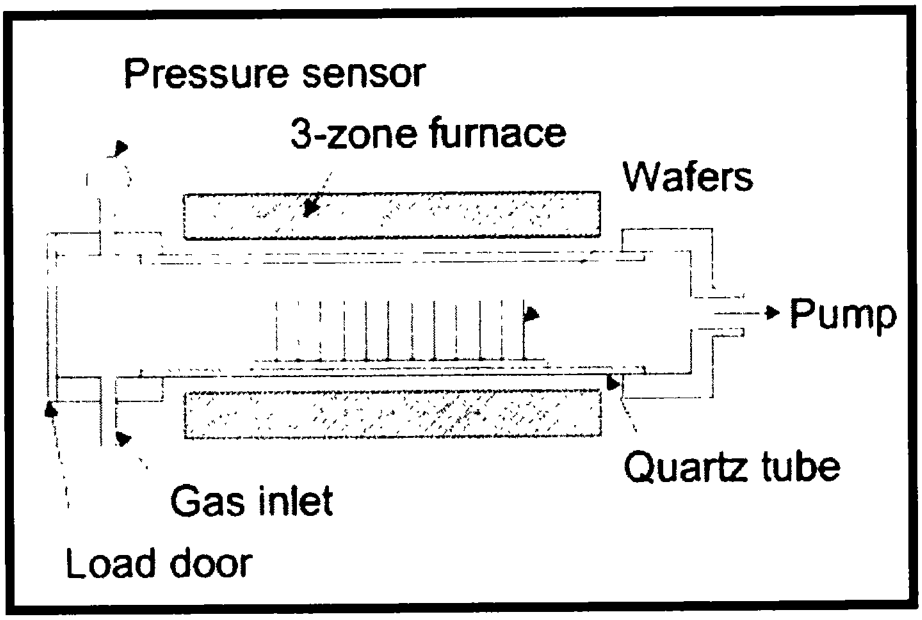


Figure 2.6: Chemical vapour deposition process

2.2.3 Electrodeposition method

Electrodeposition method of metals or its oxides is one of oldest process in electrochemical science [66-72].It is very unique and cost effective method in all bottom up approaches in which one material is deposited on the other. In this method electroplates are used for the resisting of corrosion. Whole process consists on the metal plates and acidic solution in a beaker. Usually the metal plates are of platinum as it has high melting point and other good parameters. A specific voltage is applied to the plates. Voltage depends on the acidic solution and the surface of the electrodes. Usually 60 volts are applied. 50 or 40 volts can also be applied but 60 volts gives the better results. Applied voltage directly depends on the pore diameter. If the voltage is low, the pore diameter will be small and if the voltage is large then the pore diameter will be large and gives the better results comparatively. Hence the voltage is directly proportional to the pore diameter [13]. Figure 2.7shows the electrodeposition process.

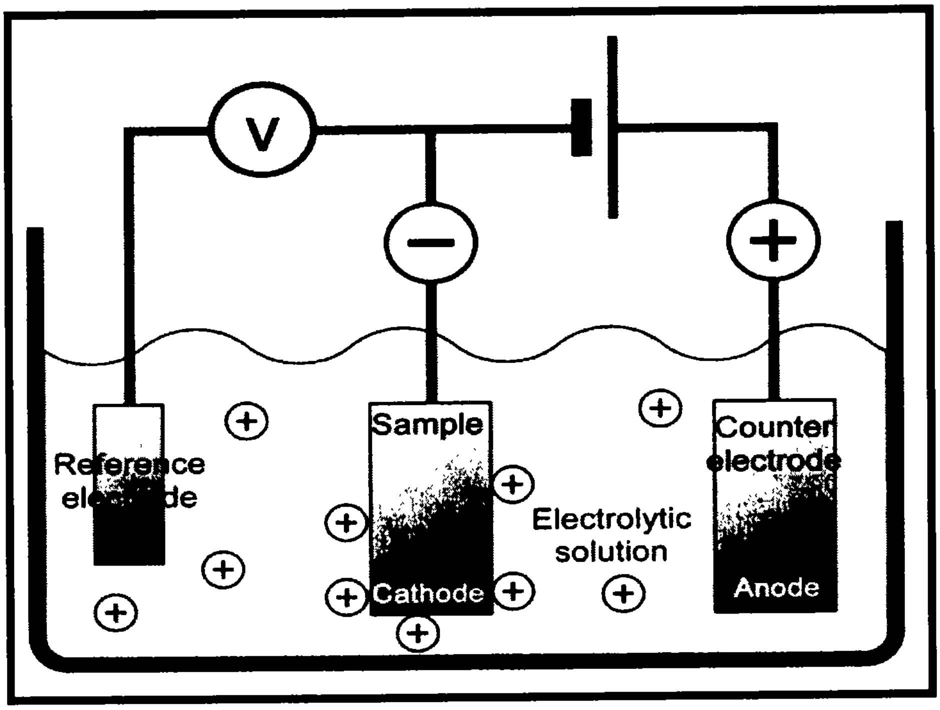


Figure 2.7: Electrodeposition process

There are different types of electrodeposition procedures to make nanowires. These are following,

- Direct current (DC) electrodeposition method
- Alternating current (AC) electrodeposition method [25, 26]
- Pulse current electrodeposition

At laboratory level DC and AC electrodeposition method is used but AC deposition is more convenient. In this method the aluminium foil is inserted at anode to fabricate the nanowires. Usually the anode is inserted in between two cathodes for dually sided deposition.

Subsequently, a chemical reaction take place as the voltage is applied. Positive ions go towards cathode and negative ions go towards anode and deposition occurred. Specific voltage is adjusted according to the material's nature. For DC deposition, conductive film is necessary because templates must have conduction with the aluminium substrate. This difficulty is not being face in AC deposition because deposition can occur directly without any conductive film. So the AC method is more popular method comparatively [27].

As we concern, we also used this (electrodeposition) process by means of anodization. Here anodization is of two steps that's why it is called two steps anodization. Usually first anodization has less time as compared to the 2nd anodization. The whole procedure will be described next.

2.2.3.1 Experimental procedure

The basic and important task is to make the templates for the fabrication of nanowires. For this, the templates have to make on the metal sheet. So the aluminium sheet is selected. The aluminium is a good conductor having high melting point, less corrosion resistance and easy to purchase. The bid advantage of using aluminium is that, the obtained nanowires are uniform and homogeneous so easy to observe and characterized. At the laboratory level it is very convenient. This aluminium sheet is processed with many steps for the growing of templates. These steps are given below

- Wash the metal sheet
- Electropolishing
- 1st anodization
- Annealing process or heat treatment
- 2nd anodization
- Removing the barrier layer
- Deposition of specific material

2.2.3.1.1 Wash the metal sheet

Metal sheet of the known size is rinsed with different liquids. Mostly ethanol or acetone is used in laboratories. Metal (aluminium) sheet is dipped in the acetone for 10 minutes. All waste materials or rust remove from the sheet. Now the sheet is washed with the distilled water. Sheet should not be washed with simple water due to impurities present in it, this makes the results bad. Above all the factors are necessary for the electropolishing.

2.2.3.1.2 Electropolishing

In this step aluminium sheet is attached to the anode. The anode is fixed in the holder, Also two cathodes are attached with the holder. Holder is dipped in the solution of ethanol and perchloric acid with the ratios of 4:1. 9 volt DC is applied to the holders which is optimized voltage for polishing as shown. After applying voltage the reaction becomes start and stay for 3 minutes. It is also observed that the oxide layer is removing from the sheet to make it conductor. As a result smooth and shine surface is obtain as shown in figure (2.8 (b)). Now this sheet is a conductor and ready for deposition in next step. At the end, again sheet is washed with the water for removing the solution from the surfaces.

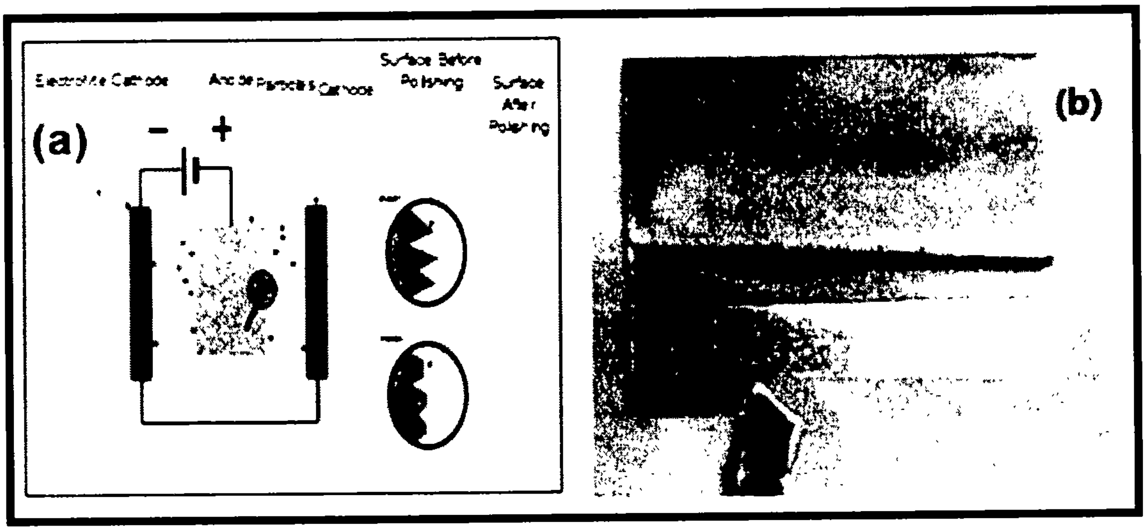


Figure 2.8: Schematic of electropolished process **(b)** Electropolished Al foil

2.2.3.1.3 First anodization

In this step, electrodes are dipped inside the anodic solution. The anodic solution is the 5% solution of phosphoric acid (0.5 molar solution of phosphoric acid) in distilled water. 60 volt DC is applied to the electrodes. Reaction continues to start for 3 to 4 hours. The temperature sets up 1 to -3 Celsius. The magnetic stirrer is used for stirring to keep the solution uniform. Continuously stirring is very important for the homogenous deposition on the sheets. Al_2O_3 layer grows on the surface of sheets. This grown layer is basically a template. Following reaction happens during anodization;

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$$

At the boundary of metal-oxide

$$2Al + 3O^{-2} \rightarrow Al_2O_3 + 6e^-$$

At the interface of oxide-electrolyte

$$2Al^{3+} + 3H_2O \rightarrow Al_2O_3 + 6H^+$$

Reaction, when the dissolution takes place

$$2Al \rightarrow 2Al^{3+} + 6e^-$$

Production of hydrogen gas

$$6H^+ + 6e^- \rightarrow 3H_2$$

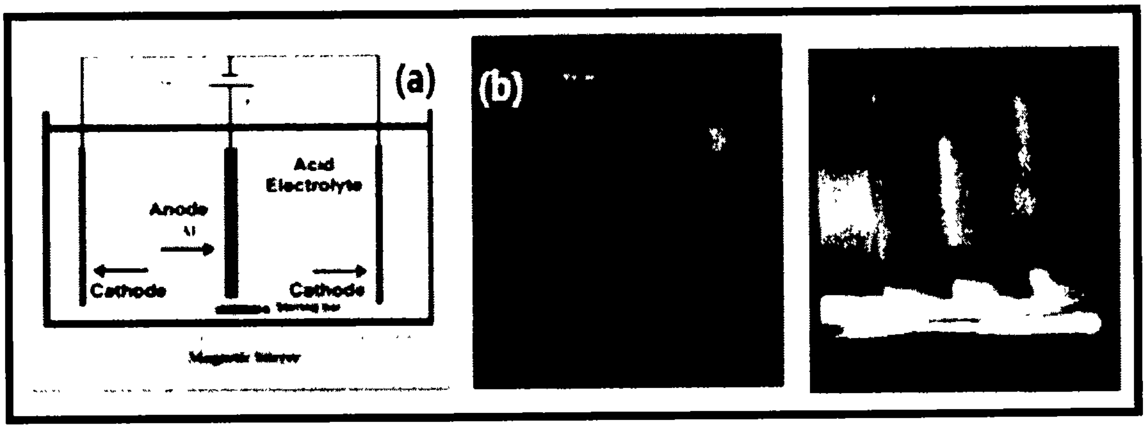


Figure 2.9: **(a)** Anodization process and **(b)** Al sheet after first anodization

2.2.3.1.4 Heat treatment or annealing process

After first anodization, the grown templates are ready to put in the oven. This is done in the yellow solution. The aluminium sheet (templates) is dipped in the yellow solution. The yellow solution is the mixture of chromium oxide and copper chloride ($cucl_2$). In the oven, the templates are kept for 2 hours at 60 Celsius. The reason is to anneal the templates, the initially grown templates are not uniform and have many directions. After the annealing, grown templates become align in single direction and uniform. S

2.2.3.1.5 Second anodization

After annealing, the samples are again inserted in the anodic solution. All parameters are same as in first anodization. 60 volt DC is applied under the environment below 0 Celsius for 9 to 10 hours. After this anodization the templates are obtain in micrometre range. These templates are now homogeneous and in single direction. After second anodization the templates are ready to remove the barrier layer.

The pH values strongly affect the diameter of pores. Three types of acids can be used for the anodization such as phosphoric acid (H_3PO_4), oxalic acid ($H_2C_2O_4$) and sulphuric acid (H_2SO_4). These three acids give the different diameters of the pores due to their different pH values [28]. Anodization in sulphuric acid gives small pore diameters while anodizations in oxalic acid, the pore diameters are comparatively large. The best diameter is obtained by phosphoric acid as anodic solution [29].

Time is important factor during anodization as the length of pores depends on it. If the time is increased the length will also increase, conversely the length will decrease as the anodization will decrease. Simply the pore length is controlled by time [30].

As we concerned, 0.5 M phosphoric acid is used as anodic solution. The anodization is done at 60 volts with the first and second anodization times 3 and 10 hours respectively. Following table shows the effectiveness of time on pore's length.

Table 2.1: Time dependent thickness

Anodization time (hours)	3	6	9	12	15
Thickness (μm)	40	60	78	110	122

Now we will describe that how the barrier layer is removed?

2.2.3.1.6 Removing barrier layer

The barrier layer is removed by decreasing the voltage from 60 to 0 volts. After every 3 minutes three volts are dropped. This will take 50 to 60 minutes. The dropped voltage and time can also be varying.

Actually there is aluminium conducting layer forms at the bottom of templates. This resists the deposition due to insulation of oxide layer. So the templates from the bottom must expose for the complete deposition. At the end the sheet (template) is washed with the distilled water. It is also observed that the colour of the sheet become change which shows the template formation. It has bluish like colour. Hence this was the whole procedure to make the templates.

2.4 Growth of nanowires

The nanowire's arrays are obtained by a narrow size distribution in the form of straight and cylindrical holes [31, 32]. When the reaction starts, the pores of templates start to fill which gives the nanowires. The voltage applied for nickel and tin nanowires is 16 volt which is found to be optimized.

2.5 Selection of material and deposition parameters

To get the nickel and tin nanowires, the nickel sulphate ($NiSO_4$) and tin sulphate ($SnSO_4$) material is selected. The reaction is done at 16V for 30 seconds. Each sample is prepared on same parameters. 0.1 gram sodium dodecyl sulphate (SDS) is used as buffer solution. To control the pH value, the same ratio (0.1g) boric acid is used for the dissolution. Following table contains the information about ratios and all other parameters;

Table 2.2: All parameters of deposition

	Sample 01	**Sample 02**	**Sample 03**	**Sample 04**	**Sample 05**	**Sample 06**
$NiSO_4$ (gram)	5	5	5	5	5	5
$SnSO_4$ (gram)	0.5	1.0	2.0	3.0	4.0	5.0
AC voltage (volt)	16	16	16	16	16	16
pH value	2	2	2	2	2	2
Time (second)	30	30	30	30	30	30

CHAPTER 03
EXPERIMENTAL TECHNIQUES

We prepared the samples by using the material $NiSO_4$ and $SnSO_4$ to obtain the nanowires at different voltages, so if these samples are characterized then lot of information are found. These properties can be physical or chemical. Some of techniques which are studied by us given below;

- Scanning electron microscope (SEM)
- Energy dispersive spectroscopy (EDS)
- Fourier transform infrared spectroscopy (FTIR)
- X-ray diffraction (XRD)

Scanning electron microscopy tells us about the surface topography and the morphology of the material. Energy dispersive spectroscopy investigates the compositional analysis of the sample. How much ratio contain the sample of other material, these are observed by EDS. Absorption and transmittance behaviour of the sample is studied by the Fourier transform infrared spectroscopy by bombarded the wide range of infrared radiation on it. X-ray diffraction tells us about the geometry of the material and also investigates either the given sample is crystalline or polycrystalline. All above techniques are being discussing now.

3.1 Scanning electron microscope (SEM)

Scanning electron microscope gives very fine image of the surface of the given sample as the electron's wavelength is very small. A beam of light is fallen on the surface and focusses over the whole area which gives the image on the computer through proper network. The beam interact with the sample's surface elastically or in elastically. As the beam moves over the sample, the image is obtained at every point. Initially the image is obtained with the help of cathode ray tube. Electron beam source is very important to discuss here.

3.1.1 Electron beam source

Electron beam is generated from the electron gun. Electron gun is the most important source in the scanning electron microscope. The generated electron beam is focussed on the sample and can be move over the sample to get the image point to point, required image is obtained on the computer. Different electron guns are used in microscope such as field emission gun and thermionic emission gun.

In thermionic gun, there is vacuum created inside the filament. The vacuum is of the order of 10^{-3} pa. Lanthanum boride is also used in thermionic emission instead of tungsten with the vacuum of 10^{-4}. So continuously supplied the direct current increase the temperature up to 2700 kelvin for tungsten filament. This temperature becomes different for different electron guns because it depends on the nature of material used. For lanthanum 2000 kelvin is achieved which is also very high temperature. This high temperature generates the highly energetic electrons which are targeted the sample with the accelerating voltage of approximately 1 to 50 kilovolts.

A gun having very small tip in the order of 0.1 micrometre is connected on the gun. A very strong electric field is applied on the tip which emits an electron. This electron strikes with the sample's electron and gives the image on the computer. This electron is independent of the temperature while it is depends on the electric field under the vacuum of the order of 10^{-6} pa. Due to independency of temperature, it is also called cold emission gun. Whole microscope with their parts is shown in figure 3.1.

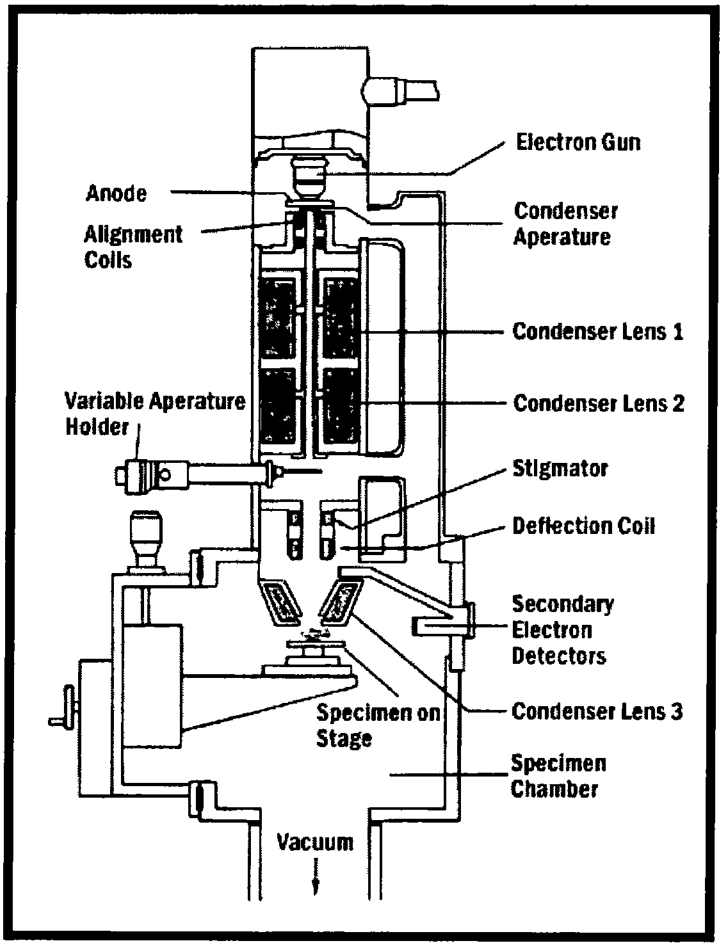


Figure 3.1: Scanning electron microscope

3.1.2 Spray aperture

Initially when the electrons shoot out from the electron gun, they have different energies, so they move in different directions and not to be focus easily on specific spot under consideration. Hence an aperture is inserted near the electron gun to make the beam focus in single direction. So after passing into the aperture, the electron beam easily focus on the sample. In this way the spray of beam can be controlled.

3.1.3 Focusing of electron beam

To focus the electron beam, a magnetic lens is inserted near the aperture which produces the magnetic flux. Magnetic flux focuses the beam on a sharp point on the sample. The magnetic flux and strength can be controlled by magnetic field which controlled by changing the current. In this way focal point of electron beam can be change.

3.1.4 Scanning coils and detectors

Scanning of whole the sample is not possible to itself, that's why two sets of coils are inserted in the microscope. These coils make the electron beam to be focus on the sample from one point to other point. Two knobs are fixed on the outer part of the microscope to control the plates which are controlled by the operator.

3.1.5 Detectors and image formation

Initially when the electron emits from the electron gun, it interacts with the sample's surface. For this purpose, the sample's surface must be conducting. There are two possibilities, the sample already conducting or it should make it conducting (if the sample is non-conducting) by coat it with the conducting layer for example the coating of gold or carbon. The image cannot be gain in case of non-conductive sample.

As the electron interacts with the atoms, two type of collision takes place. One is elastic and second is inelastic collision. Both collisions are relevant to the velocities and kinetic energies of the incident electron. If the velocity and kinetic energy change after collision then it will be called elastic collision, conversely it will be called inelastic collision. In scanning electron microscope, there is concern from the trajectory of incident electrons that's why inelastic collision under consideration. These incident electrons disturb the sample's atom. Two types of processes are observed after collision, the back scattered electron and secondary electrons. These two processes are responsible for image formation after forwarding the signals to the computer through the cathode ray tube. Hence a fine image is obtained on the screen.

3.2 Energy dispersive spectroscopy (EDS)

it is very convenient tool at laboratory level to help us for the composition of required samples. In this tool a source of x-rays such as electron gun is required. The x-rays then interact with the sample's atom and obtain an image. It gives very accurate image when the given result is characterized. The EDS tells us the specific and different structure of the material which is naturally exists that's why each element has its own emission spectrum due to different atomic arrangements.

Now as the x-rays fall on the sample and interact with the atoms of sample, the inner shell transitions become start. X-rays give the energy to the inner shell electrons or the electrons bounded near the nucleus, which excite the atoms. Electrons go from the ground state to the higher states and leave the vacancy called holes. Now the electrons at higher energy states fall down at the vacant place and release the specific rays. These specific rays are characteristics x-rays and are analysed by any energy dispersive spectroscopy (EDS). The energies of falling electrons become equal to the energy difference of two shells. Hence the atomic vibrations produce the characteristic x-rays. So continuously emission, determine the composition of the required materials.

3.2.1 Auger electron

Auger effect is basically relevant to the extra vacancy created by second knocked electron as the x-rays are fallen on the sample. This phenomena is observed as x-rays are directed towards the sample, an electron knocks out from the inner shell and leaves the hole. At the same time another electron of upper or higher shells fill this hole. As this electron fills the hole, it releases the energy which knocks out second electron as the second electron absorb the energy. This phenomenon is called the "Auger effect" and the secondly knocked out electron is called "Auger electron".

In this phenomenon emitted x-rays are called characteristic x-rays. Another phenomenon is under consideration that is the vacancy filling. Where the holes created and by which shell's electron these vacancies are filled? Normally K, L and M shells exist in the atom then obviously vacancies are filled by these shells. Further, different names are assign to these shells according to the filling as K alpha, K beta or L alpha.

If the vacancy created in K shell and filled by L shell electron then the emitted x-rays are K alpha. If the same vacancy is filled by L shell electron then emitted x-rays are called K beta. Similarly if the vacancy created in L shell and filled by M shell electron then emitted x-rays will be called L alpha. Hence the product of L shell transitions are called L series and product of M shell transitions will be called M series as shown.

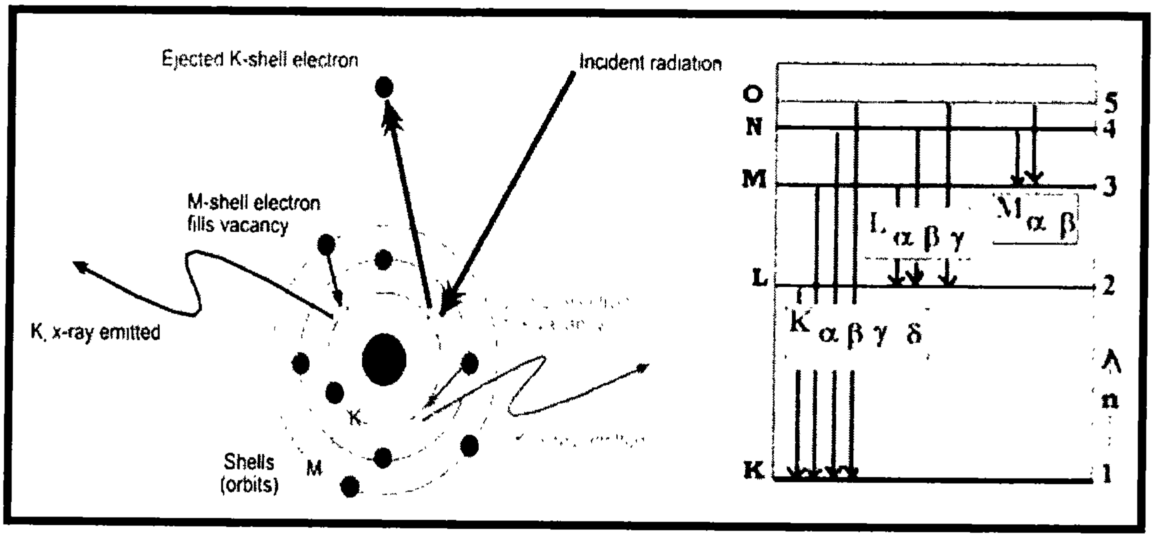


Figure 3.2: Schematic of inner shell transitions and K, L and M series

3.3 Fourier transformation infrared spectroscopy

Fourier transformation infrared spectroscopy (FTIR) is a very useful tool to determine the consistency and the components of a material as well as the unknown nature of a material. In this method, the spectrometer uses the infrared frequency to examine the material as the infrared radiation falls on the material. As the light shines on the material, absorption and transmission take place. Some part of light becomes absorb by the material while some transmits into the material. The detector is fixed in the way of light which reads the absorption and transmission radiations. On the same way these signals are read by computer which generates the spectrum of a specific material. The sample can be of different type such as it can be a mixture of different materials, so it is noted that the spectrum of material will be different if the materials are not same. So FTIR has unique property in this way.

Fourier transformation infrared spectroscopy (FTIR) is very convenient tool for the analysis of a material quantitatively by means of infrared spectrum. It represents the peaks of transmission and absorption signals which are formed when the frequencies of vibrations of atoms take place. It is possible that the sample is made up of different combinations of materials, so it is impossible that the given spectrums would be the same. Hence the infrared spectroscopy helps us to distinguish between the two different materials. Similarly the quantity of material can also be determined through the peaks. As the peaks are sharp the amount of material will be large, conversely if small peak is observed then the amount will also be small. The different parts of FTIR will be discussed next.

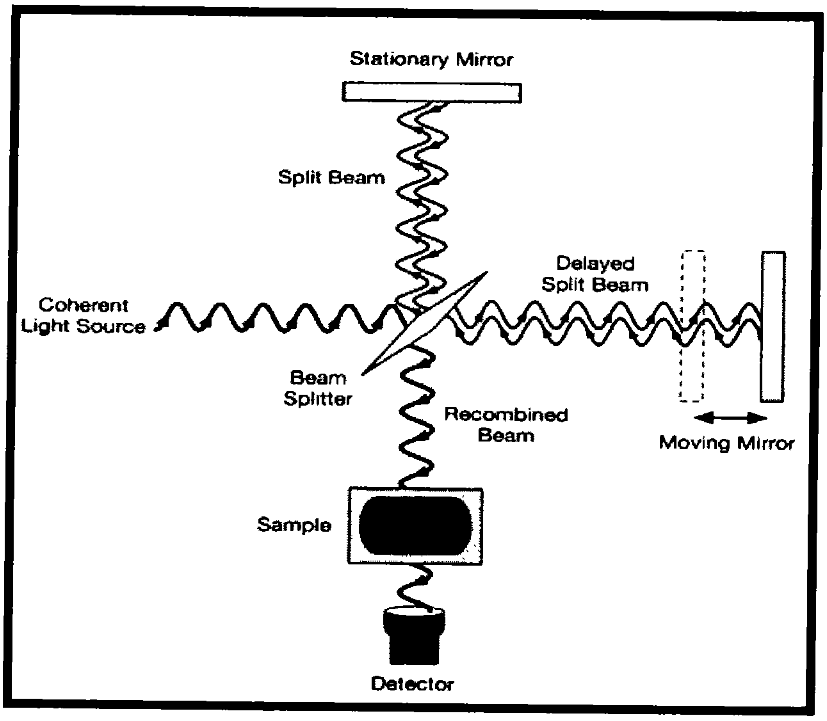


Figure 3.3: Schematic of FTIR

3.3.1 Source

Firstly the infrared radiations are produced from the source. Mostly black body is used as source. To control the radiation amount an aperture is inserted in the way radiations. These radiations pass through the sample which is under observation.

3.3.2 Interferometer

Secondly the infrared radiation then enters into the interferometer same as in the Michelson interferometer. After reflection from different planes, unique spectrum is obtained. Later on this beam goes towards the sample.

3.3.3 Sample

As the beam reaches near the sample and strike with it, absorption and transmission phenomena take place. Some radiations become absorb and some of them become transmit and reflected back. But specific range of frequencies absorb according to the characteristics of the samples.

3.3.4 Detectors

Here transmitted beam take under consideration. This beam is detected after passing through the sample. The detector reads these signals and passes the information away to the computer with the help of interferogram.

3.3.5 Computer software

At the last computer software reads the data and converts it to the actual data from the spectral data according to the Fourier transformation. Finally the plot (spectrum) is obtained.

3.4 X-ray diffraction (XRD)

A new and versatile technique called x-ray diffraction that is used for the crystal identification. Either given crystal is FCC, BCC or any other structure, these are analysed by x-ray diffraction (XRD). This technique firstly discovered by Van Laue in 1912. According to this technique the diffraction is possible only when the electromagnetic waves having wave length comparable to the interatomic distances of the material [43].

A lot of information such as lattice parameter, crystalline or polycrystalline or grain size investigates by XRD result [44].

A well-known law that is called Bragg's law is used for measuring the interatomic spacing as the x-rays hit the sample and produce diffraction phenomenon. By the diffraction of beam with the different angles, a regular pattern is obtained which is further analysed and specific peaks are obtained of specific materials.

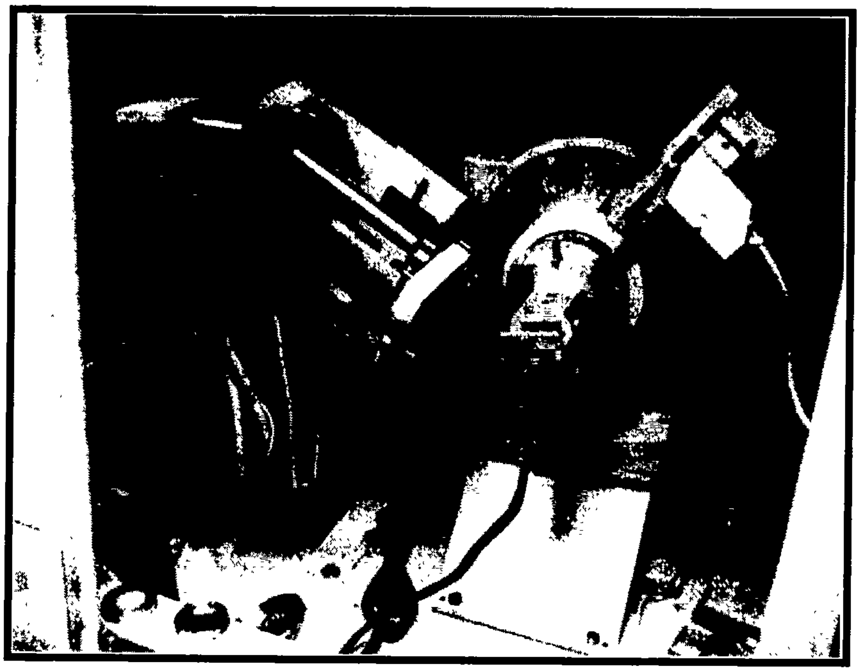


Figure 3.4: XRD schematic [45]

3.4.1 Bragg's law

As there are many planes in the crystal so the x-rays are diffracted at each plane. But every lower plane receives the x-ray with the path difference of 2dsinθ. Only those wavelengths of light are diffracted which are the integral multiple and in other words diffraction produce only when there is constructive interference, so we can say that constructive interference is produced when

$$2d\sin\theta = n\,\lambda \qquad (n = 1, 2 \ldots)$$

Above equation is Bragg's equation [46]. Here d, θ, n and λ are the interatomic spacing, angle, order and wavelength respectively. Following fig. shows the rays and planes by means of Bragg's law.

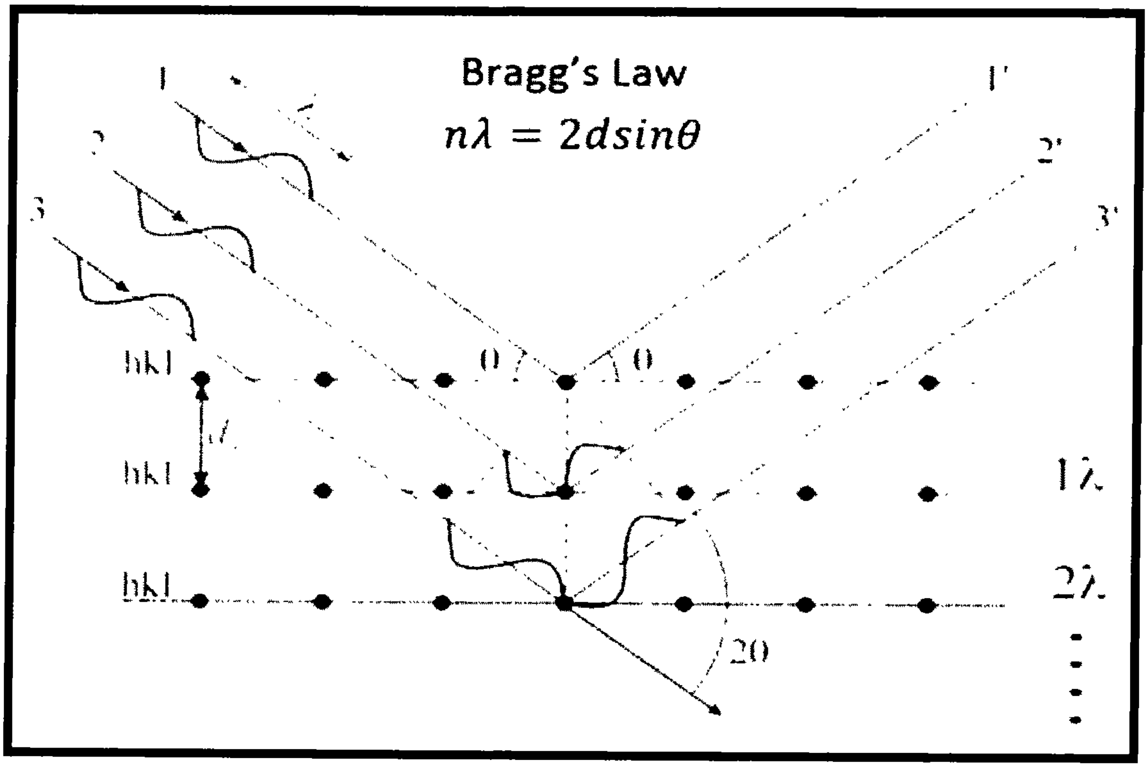


Figure 3.5: Schematic of Bragg's law

There are different methods to obtain the diffraction pattern such as Laue method, powder method and rotating crystal method.

3.4.2 Laue method

In Laue method the sample is fixed while angle is variable. Hence by Laue method the crystal orientation can be find as well as it is also found from this method that, either given sample is single crystal or poly crystal [47].

3.4.3 Powder method

Powder crystal method is used when the sample is not in pallet form but it is available in powder form. Other parameters are same as in Laue method. The powder sample will be fixed by keeping θ° variable. With the help of this method, the lattice parameters and miller indices can be found accurately.

3.4.4 Rotating crystal method

In rotating crystal method the sample can be rotate while keeping wavelength constant. It does not matter either the crystal in powder form or in pallet form. Also we can find the grain size from all above methods but with not accurately. So to find the grain size with high precision we use Scherer formula [48].

CHAPTER 04
RESULTS AND DISCUSSION

We have prepared six samples in which $NiSO_4$ is kept constant (5g) and $SnSO_4$ is varied (0.05g – 0.5g). All the samples are characterized by the SEM, EDS, FTIR and XRD as well as current verses time graph is analysed during fabrication of AAO templates in 5% phosphoric acid at 60V. The AAO templates are grown on the aluminium sheet during first and second anodization. The relevant graphs are given below.

4.1 First anodization I-T graph

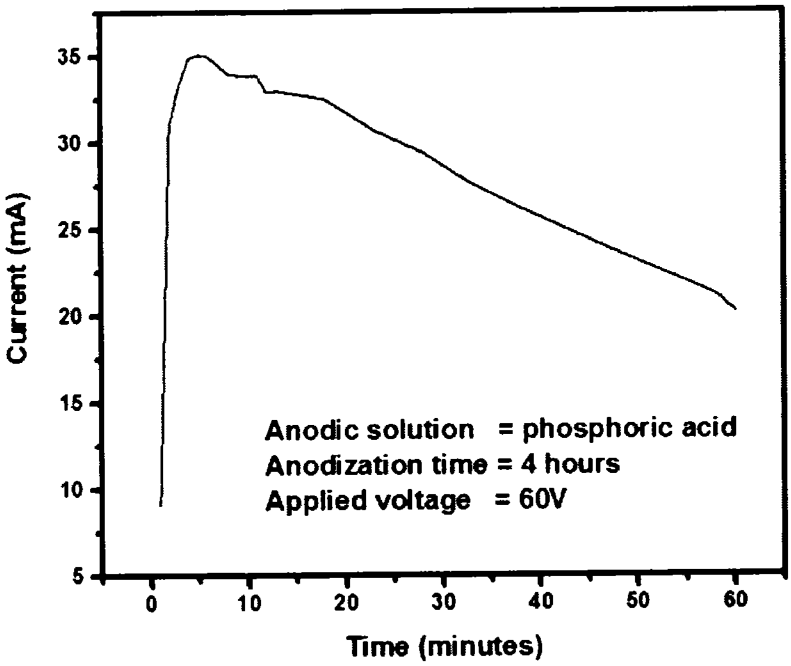


Figure 4.1: First anodization I-T graph

As the graph is showing that there is a sharp increase in current initially due to large area (sheet) is faced by ions. So at the start, a large number of ions are available to deposit on the sheet. Hence the current rises suddenly as shown. After some time, the current goes to decrease gradually due to formation of Al_2O_3 layer at the bottom of the sheet. This layer is insulating so the graph becomes straight after specific time. At the same time, this typical behaviour of current verses time shows that uniform growth of templates has started. We did the first anodization for 4 hours at 60 volt in 0.3M solution of phosphoric acid.

4.2 Second anodization I-T graph

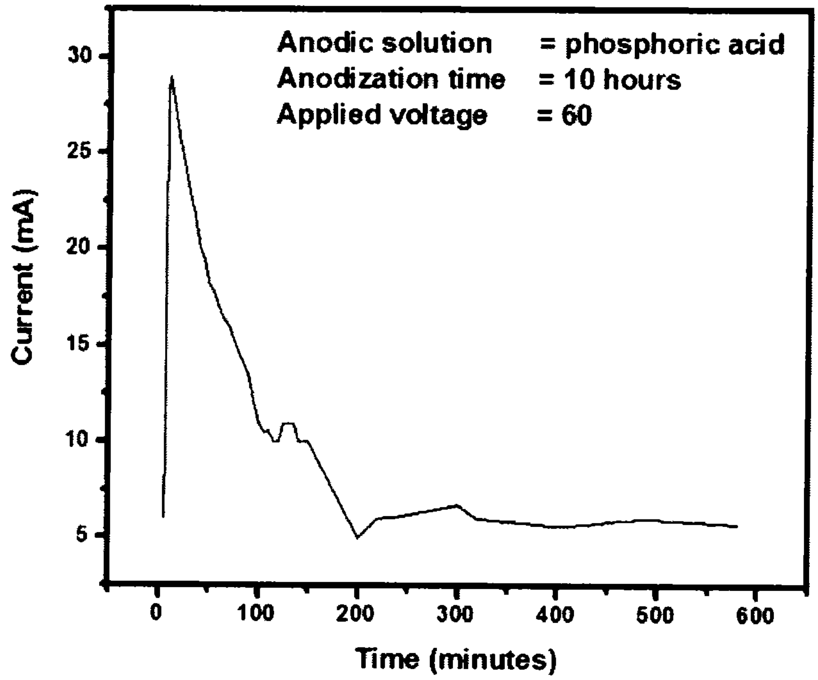


Figure 4.2: Second anodization I-T graph

Above graph shows the sharp change in the current at the initial. Actually, initially there is maximum area of the sheet is faced by electric charges also these charges are attracted by the metal sheet acting as anode. Subsequently the decrease in current is due to the increment in thickness of Al_2O_3 layer which repels the ions. So the I-t graph confirms that the templates have started to grow in length. We did the second anodization up to 10 hours by keeping all the parameters constant as in first anodization.

4.3 SEM of $Ni_{1-x}Sn_x$ nanostructure

The SEM images are shown in figures 4.3 and 4.4. Here we got very clear images of $Ni_{1-x}Sn_x$ nanowires after the dissolution of templates in 0.01 molar solution of NaOH and annealed at 60 Celsius for one half an hour. We select two samples (3 and 4) out of six having ratios 2.0 g and 3.0g of $SnSO_4$ respectively in 5.0g $NiSO_4$. Samples are magnified up to 50,000x. The average diameter of nanowire observed is 150nm with length 15μm.

There are three regions light black, pure black and white observed in following figures. Light black region confirms the nanowires formation while pure black is the region where there is no growth of nanowires. The irregular region can be NaOH or dissolved templates or the mixture of both.

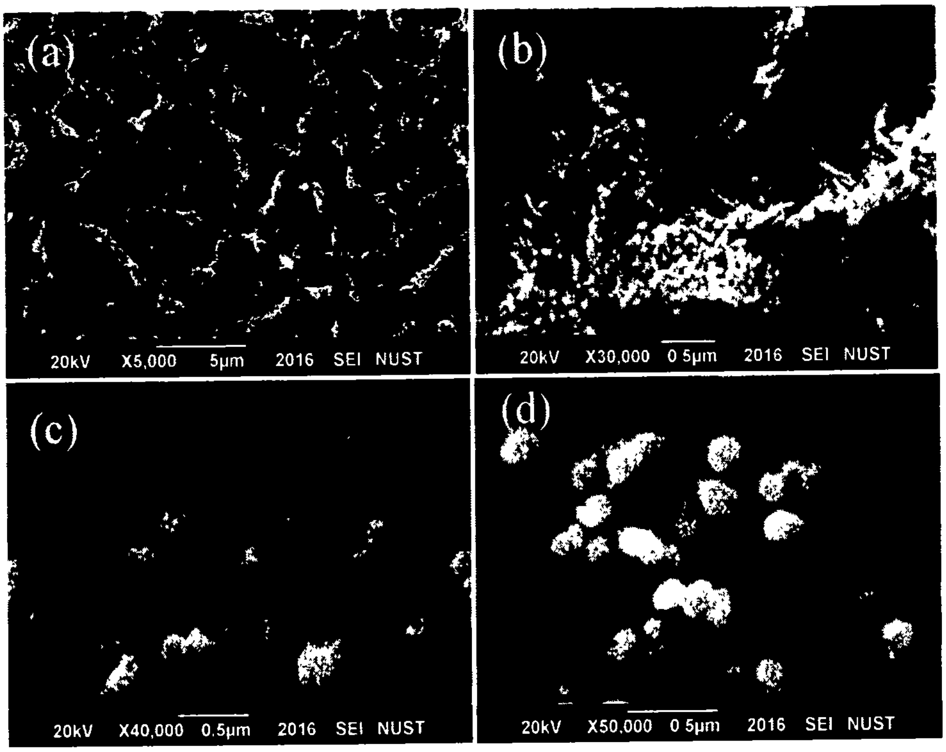


Figure 4.3: The SEM images of nanowires of sample 3 with magnifications **(a)** 5,000x, **(b)** 30,000x, **(c)** 40,000x and **(d)** 50,000x

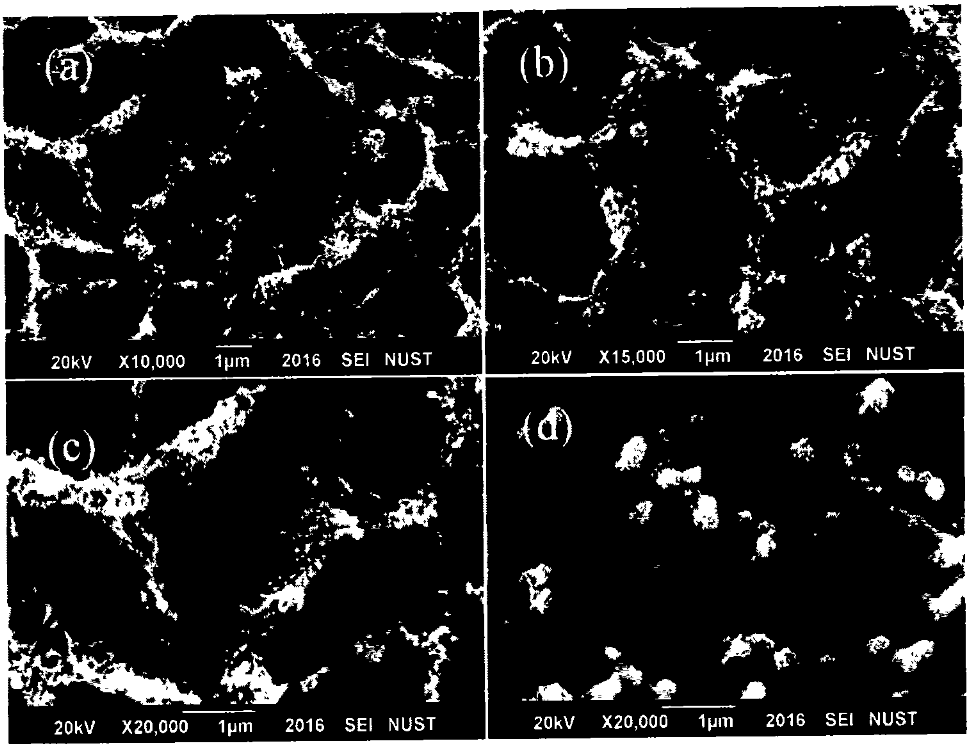


Figure 4.4: The SEM images of nanowires of sample 4 with magnifications **(a)** 10,000x,**(b)** 15,000x, **(c)** 20,000x and **(d)** 20,000x

4.4 Energy dispersive X-Ray spectroscopy (EDS) Results

Energy dispersive x-ray spectroscopy (EDS) confirms the composition of the sample as well as the ratio of the different materials in samples. We get the graph with high and low peaks of the materials involved. This shows that, our material is nickel and tin, so we got the peaks of required materials as well as aluminium oxides (Al_2O_3) peaks are also obtained as shown in figures 4.5 and 4.6. Some impurities are also obtained in the EDS pattern but we excluded them and take only relevant peaks. Hence, the EDS confirms that highly homogeneous and uniform nickel and tin nanowires are formed into AAO templates.

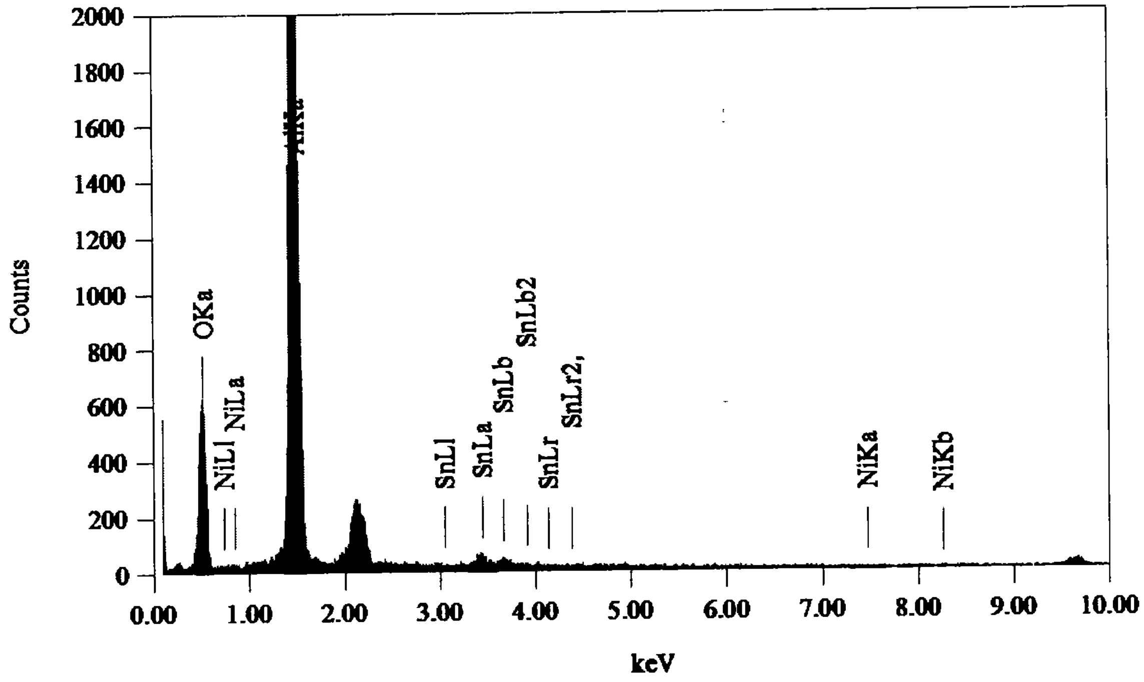


Figure 4.5: EDS pattern and compositional analysis of sample 3

The quantitative analysis evaluates the ratios of samples. Similarly it confirms the increment of Sn which is varied. The ratios of all materials are tabulated as below.

Table 4.1: Quantitative analysis of sample 3

ZAF Method Standardless Quantitative Analysis

Fitting Coefficient : 0.5366

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
O K	0.525	36.03	1.29	49.43				38.1803
Al K	1.486	61.59	0.69	50.11				59.6861
Ni K	7.471	0.07	3.98	0.02				0.0713
Sn L	3.442	2.31	2.85	0.43				2.0623
Total		100.00		100.00				

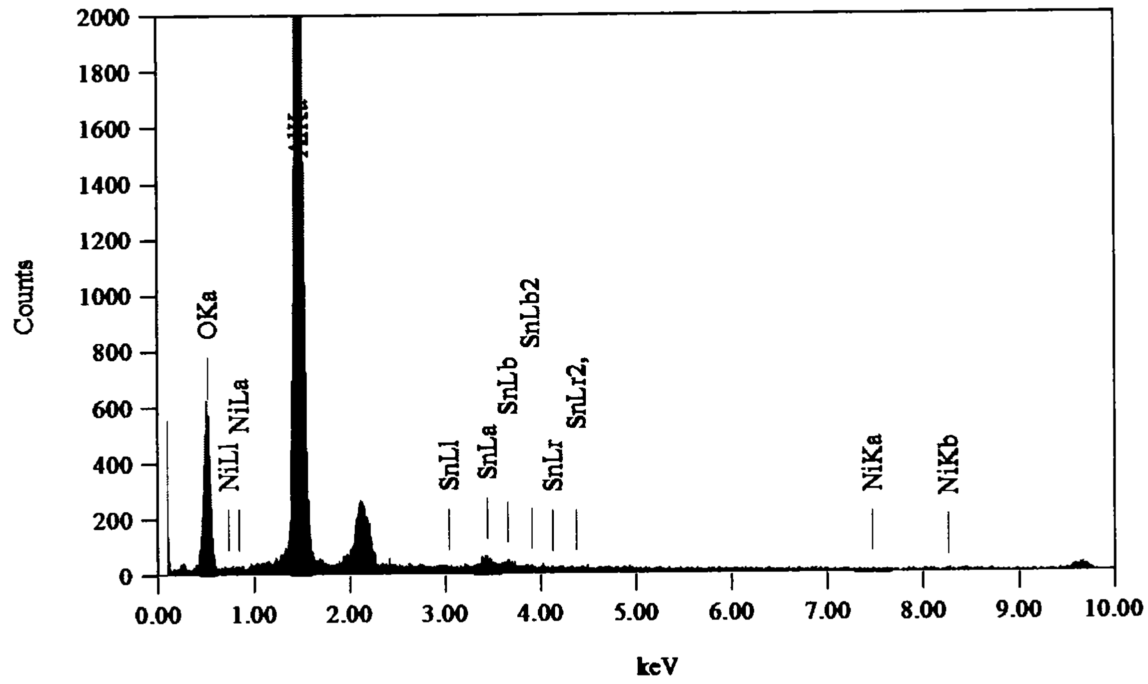


Figure 4.6: EDS pattern and compositional analysis of sample 4

The quantitative analysis of sample 4, which shows the increased ratio of tin as compared to sample 3.

Table 4.2: Quantitative analysis of sample 4

ZAF Method Standardless Quantitative Analysis

Fitting Coefficient : 0.5138

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
O K	0.525	36.35	1.15	50.52				38.3782
Al K	1.486	58.83	0.61	48.48				57.0502
Ni K*	7.471	0.53	3.39	0.20				0.5915
Sn L*	3.442	4.29	2.42	0.80				3.9801
Total		100.00		100.00				

4.5 Fourier transforms infrared spectroscopy (FTIR) Results

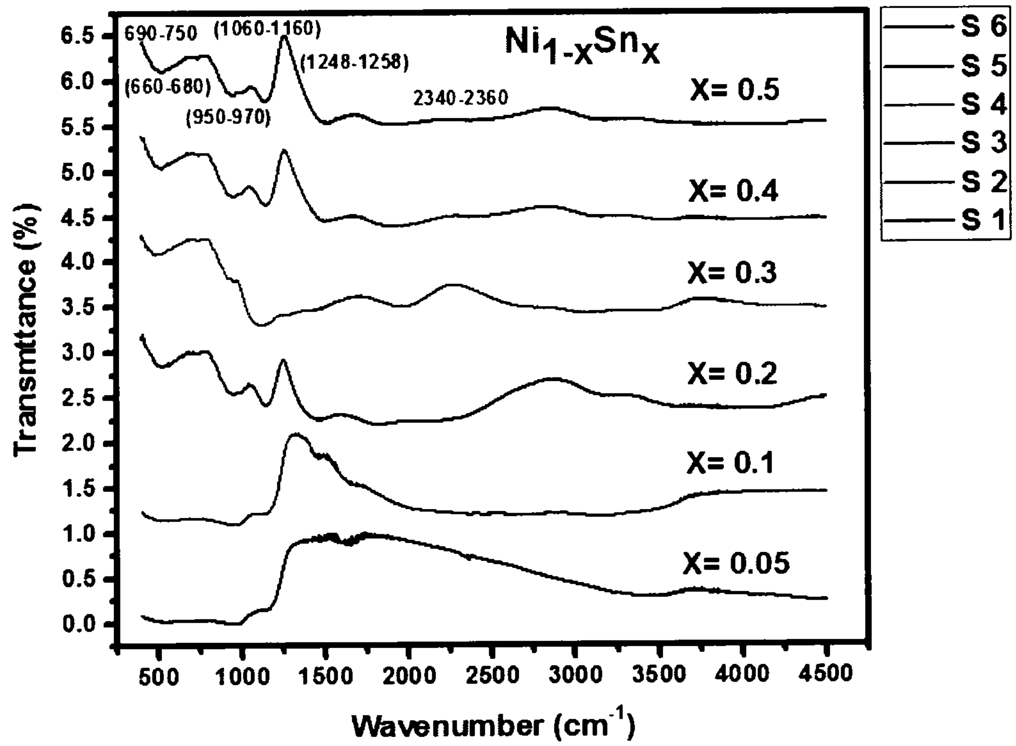


Figure 4.7: FTIR spectrum of 6 samples

In order to see the types of bonds in $Ni_{1-x}Sn_x$ NWs, the Fourier transform infrared spectroscopy (FTIR) technique is used. Different peaks are observed as shown by above figures with different ratios of tin (Sn) while keeping the ratio of nickel (Ni) constant.

The peaks at (660-680) cm^{-1} region correspond to the stretching modes of the Sn-O-Sn while the absorption at peaks (680-750) cm^{-1} is due to the Ni-OH bending vibration [64, 65]. Similarly the wavenumbers in the ranges of (950-970) cm^{-1} are stretching vibrations modes of alumina bands [61]. The ranges (1248-1258) cm^{-1} and (2340-2360) cm^{-1} are the stretching modes of carbon dioxide. Similarly the wavenumbers obtained are the stretching band of C-OH at peaks (1100-1025) cm^{-1} [65].

4.6 X-ray structure investigation

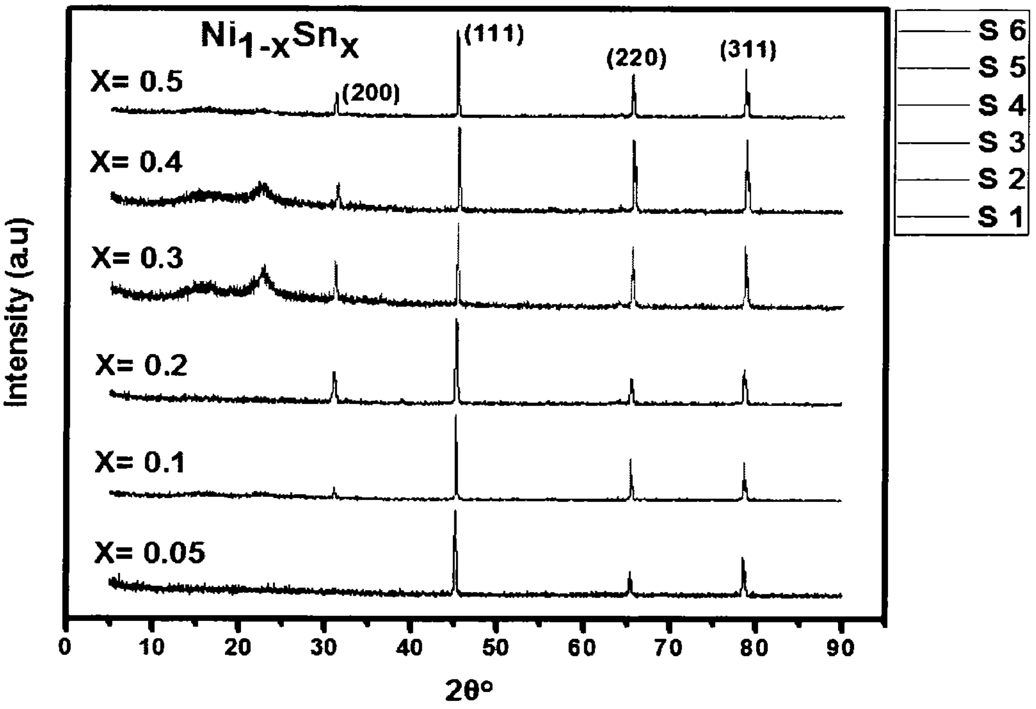


Figure 4.8: XRD pattern of 6 samples

The diffraction angles 2θ° =31°, 45°confirm the tin and nickel structure with the planes of (200) and (111) respectively. Also the tin has tetragonal structure while nickel posses FCC lattice structure [63, 65]. The plane at angles 2θ° = 66°, 78°confirm the Al_2O_3 structure having planes (220) and (311) [63]. Different indexes or planes also confirm that the materials are polycrystalline. In sample with x=0.05, the diffraction peak corresponds to Sn tetragonal structure is not clearly visible due to extreme low amount of Sn in the solution.

Conclusion

The magnetic nanowires are fabricated very easily at laboratory level by electrodeposition method. It is proved that electrodeposition method is very cost effective to make the AAO templates and these templates fulfil the requirements. The nickel and tin materials are chosen due to their large use in storage devices. The basic purpose of this project is to fabricate the nanowires on the aluminium sheet and this is done with proper way. The self-synthesized AAO templates are fabricated by applying 60 volts at temperature less than $0^{o}C$. The scanning electron microscopy (SEM) images confirm the nanowires. The average diameter of the obtained nanowire is 150nm. The EDS analysis proved that the nanowires are of desired materials with large ratio of tin and small ratio of nickel deposited on the aluminium sheet. The FTIR graphs give the detail structure of samples by mean of transmittance. The peaks at (660-680) cm^{-1} region correspond to the stretching modes of the Sn-O-Sn and the absorption at peaks (680-750) cm^{-1} is due to the Ni-OH bending vibration. The XRD results confirm that the prepared samples are polycrystalline with tetragonal structure of Sn and FCC phase of Ni.

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Abstract In this research, the NiSnx nanowires are fabricated by means of AAO templates. The AAO templates are prepared by DC Electrodepostion method in 5% solution of phosphoric acid at 60V. The NiSnx solution is deposited on the templates by applying 16 volts. The SEM image confirms the nanowire's fabrication and the diameter lie in between 100 and 300 nm. The EDS reveal the compositional analysis of nickel and tin. FTIR confirms the absorption bands of tin and nickel at (600-660)

26cm-1 and (680-750) cm-1 respectively. The XRD peaks