

**Synthesis, Characterization and Functional properties of TMO's
(β -AgVO₃) nanowires with the affect of aniline.**



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This dissertation is dedicated to my mother and father.

No matter how far we come, our parents are always in us.

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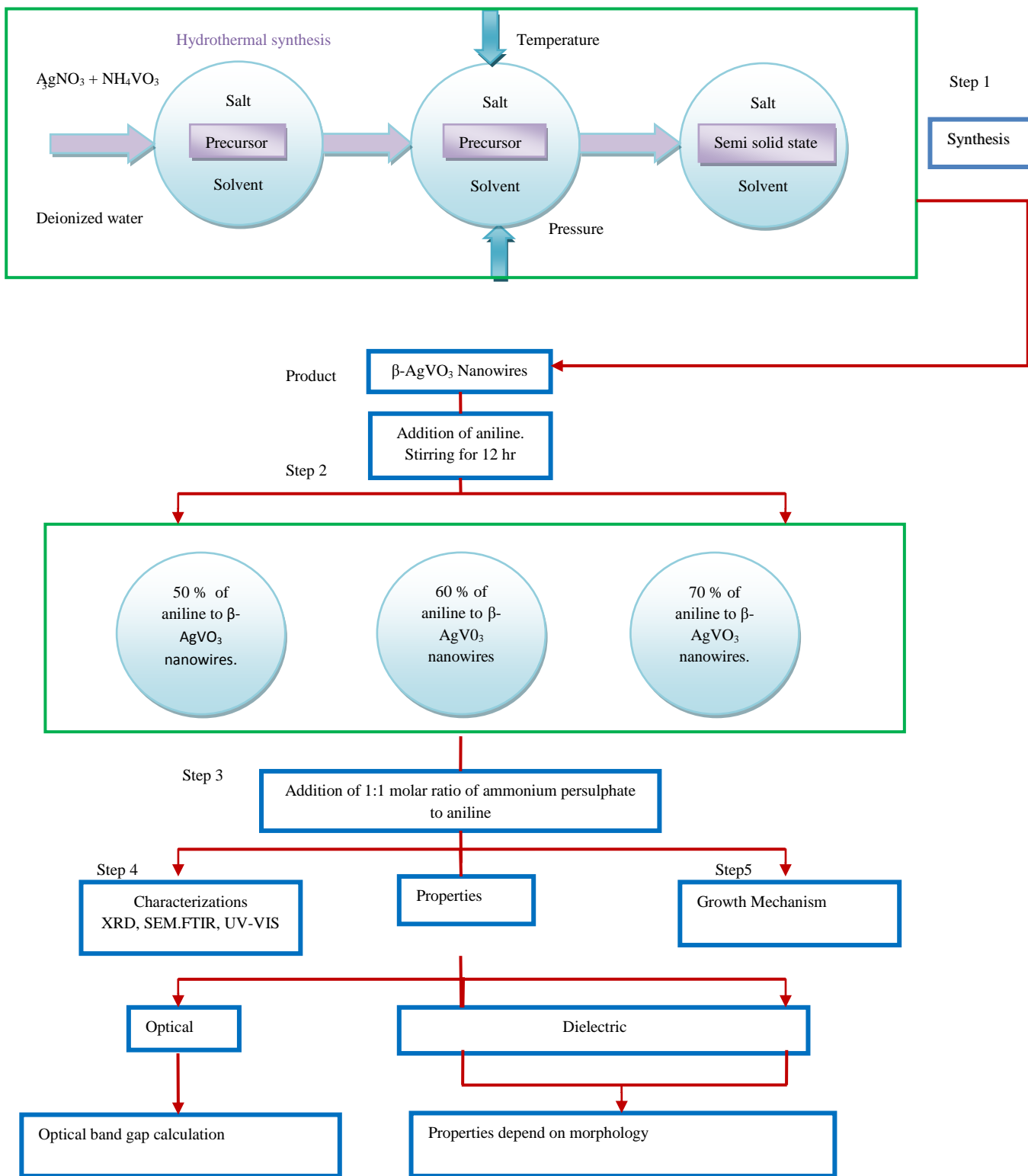
Abbreviations

SVO	Silver vanadium oxide
STM	Scanning tunneling microscope
SPR	Surface Plasmon resonance
CNT's	Carbon nanotubes
MWCNT's	Multi walled carbon nanotubes
CRT	Cathode ray tube
LED	Light emitting diode
TMO's	Transition metal oxides
k	Dielectric constant
E_0	Applied electric field
E_p	Electric field due tom polarization
χ_e	Electric susceptibility
SiO_2	Silicon dioxide
CMOS	Complementary Metal Oxide Silicon
β -AgVO ₃	Beta silver vanadium oxide
f.c.c.	Face centered cubic
b.c.c	Body centered cubic
(a,b,c)	Lattice parameters
eV	Electron volt
MHz	Mega hertz
XRD	X-ray diffraction
FTIR	Fourier transform infra red
SEM	Scanning electron microscope
UV,visible	Ultra violet visible
LCR meter	Inductance, capacitance and resistance meter
MOCVD	Metallo organic chemical vapour deposition
2D,3D	2 dimensional ,3 dimensional
PH	Potential of hydrogen
μ m	Micrometer
mm	Millimeter
PANI coating	Polyaniline coating

Abstract

β -AgVO₃ nanowires and polyaniline nanocomposites have been synthesized successfully by chemical oxidative reaction and redox reaction between Ag⁺ ions and aniline monomers by using hydrothermal process (temperature difference method). In these recent years their unique properties have been explored in different fields such as photonics, electronics, sensors and some other fields of life science. In this work the fabrication, characterization and functional properties of β -AgVO₃ nanowires and effect of aniline on nanowires is studied. X-ray diffraction peaks confirm the effect that how the addition of different weight percentage of conducting polymer (aniline) to pure β -AgVO₃ nanowires would increase the particle size. The crystal structure for β -AgVO₃ nanowires is single phase and monoclinic but after addition of aniline the crystal structure becomes cubic and it becomes more stable. The crystalline size is found from Debye Scherrer formula. Fourier Transform Infrared (FTIR) spectroscopy confirms the characteristic absorption peaks of β -AgVO₃ nanowires. The absorption peaks of aniline are shown which confirm the presence of aniline in polyaniline nanocomposites. The different morphology of controlled diameters are obtained that have been confirmed in scanning electron microscope (SEM). The size varies from 50nm to 82nm, 100nm and 152nm. The optical band gap of β -AgVO₃ nanowires is 2.2 eV and after addition of different weight percentages of aniline (polyaniline nanocomposites) β -AgVO₃ nanowires is decreased to 1.17eV, 1.13eV to 1.1eV. From Tauc Plot the optical band gap is measured. The absorption region of β -AgVO₃ nanowires lies in the UV-visible region after addition of different weight percentages of aniline the absorption region is shifted towards the infra red region. The Beer Lambert's law confirmed that absorption improves as the concentration of conducting polymer (absorbing species) is increased to the nanowires. The dielectric parameters such as dielectric loss and dielectric constant are studied for β -AgVO₃ nanowires. The AC conductivity is measured against the log F. The dielectric parameters and the AC conductivity are measured in this range of frequency 100 Hz to 5 MHz at standard temperature. By the controlled addition (from 50% to 70%) of conducting polymer to the β -AgVO₃ nanowires we get polyaniline nanocomposites with enhanced dielectric properties. Dielectric constant and dielectric loss is decreasing with increase in frequency of applied electric field because polarization mechanism fails to respond the electric field. The polyaniline nanocomposites showed an improvement in dielectric constant and dielectric loss as compared to β -AgVO₃ nanowires. The dielectric parameters decrease with increases in frequency. The phenomena of AC conductivity showed an increasing pattern with the increase in frequency. This phenomenon of AC conductivity can be understood by hopping mechanism.

GRAPHICAL ABSTRACT



Motivation

The social problem is to minimize the energy crises in the whole world at this present time.

1. The controlled morphology of TMO's nanowires would be obtained by using the hydrothermal process.
2. The addition of different weight percentages of aniline to TMO's nanowires would help us to synthesize the nanowires of reduced band gaps.
3. The reduced band gap would be very helpful in optoelectronic devices.
4. The varying amount of concentration of aniline to TMO's nanowires would help us to synthesize the nanostructures which would help in investigating the dielectric properties.

Objectives

1. To synthesize the TMO's nanowires and polyaniline nanocomposites, the reduced band gap would have better applications in optoelectronic devices especially in Solar cells.
2. By changing the amount of different percentages of aniline to the purely synthesized TMO's nanowires by hydrothermal process we would be able to synthesize the controlled morphology of nanowires which can be proved better material for high dielectric constant materials.
3. The addition of different weight percentages of aniline, speed of stirring, time duration and temperature would affect the morphology of nanowires.
4. The hot issue is to overcome the energy crises. The controlled synthesis of nanowires by using the bottom up approach would help us to contribute its role.

A bird's eye view of thesis

In the first chapter of this thesis, the basic theme of this research is introduced that describes the nanomaterials. By controlling the different parameters such as temperature, pressure, time duration, concentration of precursors, addition of oxidation agents would affect the morphology of nanostructures. The controlled morphology would affect the optical, electrical, magnetic and dielectric properties and these nanostructures have application in solar cells, LED, high dielectric constant materials.

In the second chapter of this research, the literature review of β -AgVO₃ and coating of aniline on β -AgVO₃ nanowires is introduced. An introduction of TMO's and transition metal elements with their

chemical and physical properties is also given. The TMO's β -AgVO₃ nanowires coated with aniline are studied for high dielectric constant materials.

In the third chapter of this thesis, the experimental setup and characterization techniques are discussed including X-ray diffraction (XRD), scanning electron microscope (SEM), ultraviolet visible (UV-visible), Fourier transform infrared spectroscopy (FTIR). The LCR meter is used to investigate the dielectric properties.

In the fourth chapter of this thesis, the successful synthesis of β -AgVO₃ nanowires by hydrothermal process at temperature of 180°C for 24 hr is studied. After addition of different concentrations of aniline to the as prepared nanowires it would change the diameter of nanowires. The diameter of prepared nanowires was 50nm but after addition of 50%, 60%, 70% of aniline the diameter is changed to 82nm, 100nm and 152nm. By controlling the parameter of time it would change the crystal structure from monoclinic to cubic structure. X-ray diffraction (XRD) is used to study the single phase of monoclinic structure of β -AgVO₃ nanowires prepared at temperature of 180°C for 24 hr. The as prepared nanowires are coated with aniline are reported to have single phase and cubic structure after controlling the parameter of time and concentration of aniline. Scanning electron microscope (SEM) is used to study the morphology of nanowires and nanocomposites. Fourier transform infra red spectroscopy (FTIR) is used to study the vibrational modes of β -AgVO₃ nanowires and Polyaniline nanocomposites(β -AgVO₃ nanowires/Aniline). The best absorption peaks for β -AgVO₃ nanowires lies in the range between 1000cm⁻¹ to 400cm⁻¹. The Polyaniline nanocomposites(β -AgVO₃ nanowires/Aniline) also show their absorption peaks in the range 1000cm⁻¹ to 400cm⁻¹. The four characteristics peak of aniline are obtained at 1150cm⁻¹, 1301cm⁻¹, 1501cm⁻¹, and 1585cm⁻¹, having C-H plane bending vibration, C-N stretching vibration, benzenoid ring stretching mode and quinoid ring stretching mode. Ultra violet visible (UV-visible) Spectroscopy is used to study the absorption region of β -AgVO₃ nanowires lies in UV-visible region and after addition of aniline it shifts towards the Infra red region. The band gap of β -AgVO₃ nanowires/Aniline is calculated and plotted by using Tauc Equation and Tauc Plot. The LCR meter is used to calculate the dielectric properties (Dielectric constant, Dielectric loss and AC.Conductivity) of samples at standard temperature and frequency ranges between 100Hz to 5MHz..

In chapter fifth of the thesis future recommendations and conclusions are given.

Chapter 1

Nanoscience and Nanotechnology

1.1: Nanotechnology

Why nanotechnology is preferred? and what are the pronounced factors which make the nano-world different from bulk materials?

Nanotechnology originates from the Greek word which means “dwarf”. Nanotechnology can be defined as “**It is the manipulation of matter on an atomic and molecular level**” [1][2]. There are many views that what nanotechnology includes. But in general these three things include

- A nanometer (nm) is one thousandth of a micron (μm) and it is one millionth of a meter.
- Surface to volume ratio is greater due to small sized, exhibits profound properties.
- Tailoring of controlled morphology and composition on nano scale exhibits different application due to its properties [3].

A classical system has two basic characteristics; length scales are larger than the atomic level and system move with speed less than the speed of light. In contrast a quantum mechanical system has length scales which are nearly equal to 10^{-9} and less than 10^{-9} and moves with speed which is comparable to the speed of light [4].

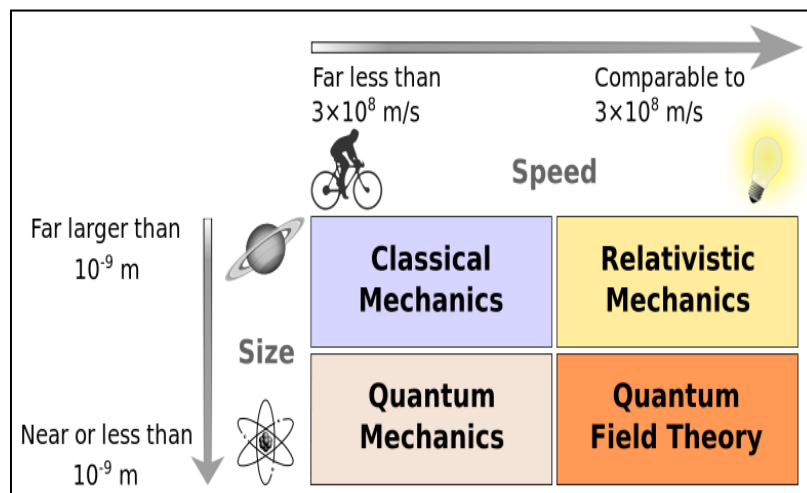


Figure 1.1: A comparison of classical and quantum mechanics on the basis of their sizes [4].

The physical properties of materials such as (gold) optical, electrical and magnetic at nano scale comes under the quantum mechanics regime and showed different behavior as compare to bulk material.

1.2: Nanoscience and Nanotechnology

The ideas and concepts included in nanoscience and nanotechnology lies on “**There is plenty of room at the bottom.**” according to Richard Feynman in 1959. According to him atoms can be arranged at atomic level so that arrangement would give property to the nanomaterials and resulting in we are able to construct nanodevices. As the size become smaller the surface properties becomes dominant and we are able to study phenomenon with the help of quantum mechanics. Due to this there is remarkable change in the properties of nanomaterials and we can use these materials in synthesizing the complex nano level circuits [5]. The term nanotechnology is an umbrella term under which many areas are covered. Nanomaterials can be used in a variety of ways in energy technologies to improve the efficiencies and low cost and open a door towards the microelectronic. The required functions can be improved by arranging these materials to complex nanostructures. The stability of nano devices depend on the technical and economical reliability.

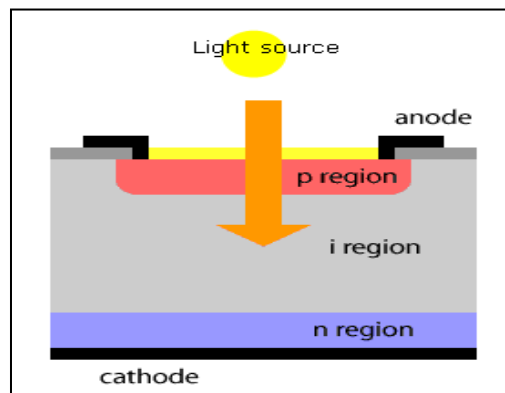


Figure 1.2: Nanomaterials in energy technologies, photodiode [6].

1.3: Nanomaterials

Generally, the materials which have at least one dimension in the range between 1 to 100nm

1.3.1: Categorization of Nanomaterials

1.3.1.1 :On the Basis of Occurance

(a) Natural Nanomaterials

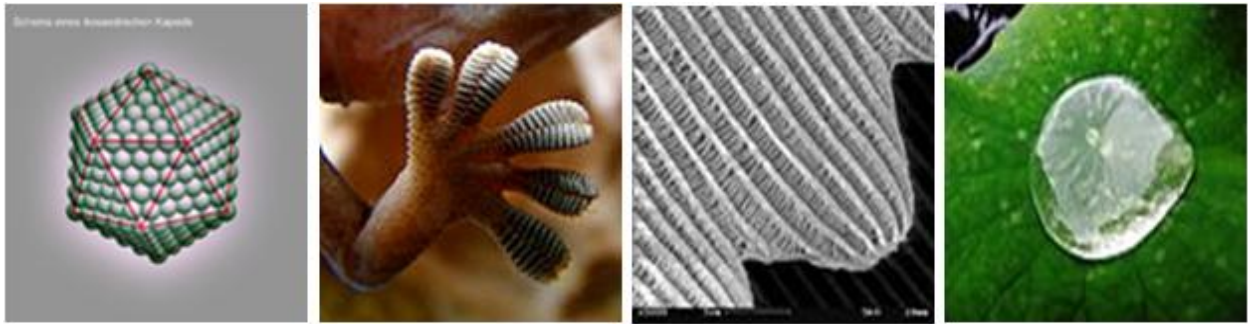
(b) Synthetic Nanomaterials

(a) Natural Nanomaterials

These nanomaterials can be categorized into two classes.

(i) Natural Organic Nanomaterials

On this planet there exist some naturally occurring nanomaterials such as fine structures of viruses (capsid), a lotus leaf having a wax crystal, a spider web shape, the spatula under the feet of gecko, some butterfly wings, natural colloids, horny materials and our bone matrix all these comes under the natural organic nanomaterials.



Virus (Capsid)

**Underside image
of gecko feet
(spatula 100
times 10-15 nm)**

**REM image of
butterfly wing
(100 times 500
nm)**

**Lotus Effect,
hydrophobic
effect.**

Figure1.3: Images of some natural organic nanomaterials [7].

(ii) Natural Inorganic Nanomaterials

Naturally inorganic nanoparticles formed from the some process which comes into existence due to naturally occurring process in nature such as erosion (clay), volcanic activities (opal) and from wildfire.

(b) Synthetic Nanomaterials

These can be categorized into two classes

(i) Fullerenes (ii) Inorganic Nanoparticles

(i) Fullerenes

As there are four allotropes of carbon diamond, graphite, graphene and fullerene. Fullerene is used because of its mechanical strength and electrical properties. Atomic arrangement leads to the spherical and cylindrical structures such as bucky balls and bucky nanotubes.

(ii) Inorganic Nanoparticles

By using the different synthetic routes we are able to fabricate the controlled diameter nanomaterials which improve the electrical and optical properties and enhance the efficiencies of optoelectronic devices e.g. quantum dot, nanowires, nanotubes. Nanoparticles act as a bridge between the bulk material and atom or molecules. Bulk materials have the same physical properties but at the nanolevel there is a difference in properties. Due to the difference in properties at the nanolevel quantum confinement in SPR in metal nanoparticles and superparamagnetism is observed in nanoparticles [8].

1.3.1.2: On the Basis of Dimensions

The nanomaterials are categorized into four classes on the basis of dimensions which are not in the allocation of the nanoscale range

1. Zero Dimensional 2. One Dimensional 3. Two Dimensional 4. Three Dimensional

1. Zero Dimensional Nanomaterials

Those materials in which all of the dimensions (x, y, z) are in this limit $d \leq 100\text{nm}$ are called zero-dimensional nanomaterials. It includes nanoparticles, quantum dots, core-shell nanoparticle, composite nanoparticles and nanoparticles encapsulated in hollow nanosphere.

2. One Dimensional Nanomaterials

Those materials in which two of the dimensions(x, y) are in the limit of nano level $d \leq 100\text{nm}$ and one dimension is at macroscopic level are called one dimensional nanomaterial. It includes the nanotubes, nanowires and nanofibres.

3. Two Dimensional Nanomaterials

Those materials in which one dimension (z) is in the limit of nano level and other two dimensions(x, y) are not in limit of nano level but at macroscopic level. It includes the nanofilms, nanoplates and nanobelts.

4. Three Dimensional Nanomaterials

Those materials in which all of the three dimensions are in the range of macroscopic level not in the level of nano scale is called three dimensional nanomaterials. It includes the clusters of nanowires, nanotubes and other nanostructures. So, these materials which are not in the limit of nano range ($\leq 100\text{nm}$) but still have properties like nanomaterials.

1.4: Pronounced Properties of Nanomaterials

Basically we would study fundamental aspects of nano affects which would assign the properties to nanomaterials. The physical properties are melting point, boiling point, conductivities etc. for the macroscopic materials which are measured in the laboratory in normal conditions. One mole has 6.022×10^{23} atoms but as we go on decreasing the size of bulk material it reaches at nano level regime and the same materials show remarkable change in the properties and these properties are totally different than melting point, boiling point, conductivity etc. of materials.

1.4.1: Physics of Nanomaterials

At nano scale the atoms took the size nearly equal to the single atom and their behaviour is studied by using the quantum mechanics. When the size is small then surface to volume ratio is increased and characteristic properties are observed for nano materials. Electromagnetic effect is observed rather than gravitational effects. The small mass is comparable to the size of electron and its behavior is wave like and position is determined by wave function. Tunnelling is a fundamental

concept of quantum effect used to study the surface images used in STM and is also used in nanofabrication tool. Quantum confinement effect in which electrons in nanomaterials are confined to specific area rather than bulk materials. Quantization of energy is observed in nanostructures which exist in discrete energy level such as quantum dot.

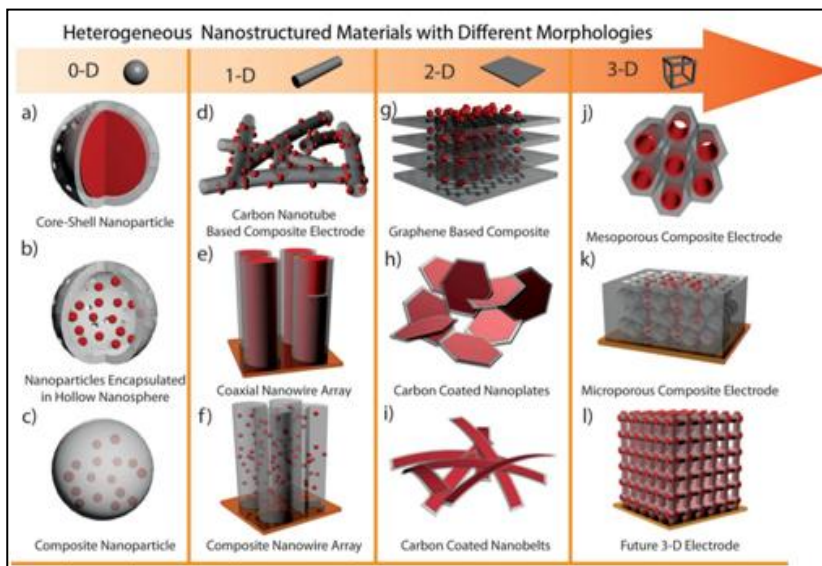


Figure 1.4: The 0-D, 1-D, 2-D and 3-D nanomaterials [9].

1.4.2: Chemistry of Nanomaterials

All types of bindings are important in bulk materials in chemistry as well as in nano scale. These can be classified further in to two classes. Intra molecular bonding and inter molecular bonding. It involves the chemical changes in the chemistry of atoms and molecules. e.g. ionic bonds, chemical bonds and metallic bond .Later involves only the interaction between the atoms and molecules.e.g.Vander walls interactions, hydrophobic interactions, repulsive forces, hydrogen bonding.

1.4.3: Optical Properties

According to Mie theory presented in 1908, he gives the concept of interaction of light with noble metal and he calculates the SPR by using the Maxwell equations for small interacting electromagnetic fields. Nano materials are engineered with enhancing optical properties including

reduction in band gaps. By using these properties we became able to construct solar cells, fiber optical sensors, Sensors for biomedical applications.

The absorption coefficient, band gap, size, shape and some other factors affect the optical properties of nanomaterials.

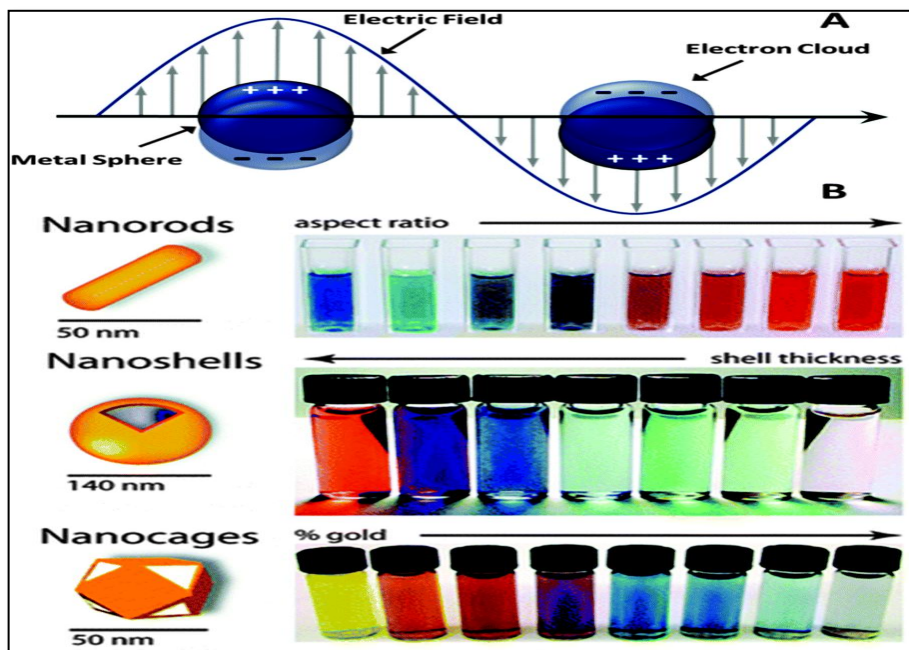


Figure 1.5: Different morphologies with different diameter and shows the plasmonic effect [10].

1.4.4: Electrical Properties

Electrical properties of nanomaterials shows enhanced effects due to its dimensions. The electrical resistivity of the metallic nanomaterials increases as dimension is decreased. At room temperature the grain boundary scattering and surface scattering are two important processes through which conductivity of metallic nanomaterials took place. At low temperature the electron-phonon, electron-electron interactions and localization took part in conduction [11]. In semiconductor nanomaterials behaviour of change of resistivity with temperature can be explained by Mott's variable range hopping mechanism. The resistivity of metallic nanowires which are temperature and size dependent are measured from the formula

$$\rho = R.A/l \quad (\text{Equ.1})$$

R: Resistance of material, A: Crosssectional area of metallic nanowires, l: Length of nanowires

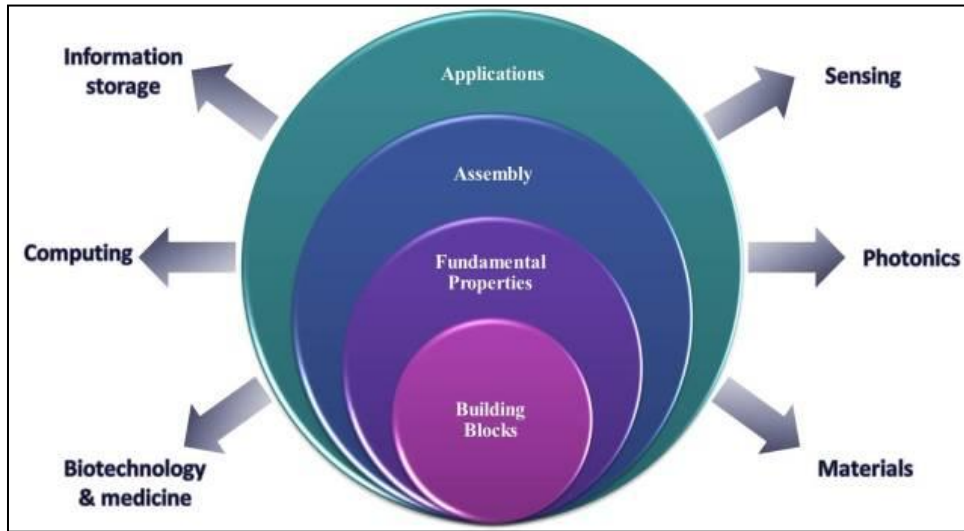


Figure 1.6: A flow chart showing how the assembling will give applications in electronics [12].

1.4.5: Magnetic Properties

Extremely interesting behaviour of magnetic properties for nanomaterials is observed on the basis of dimensions. On the basis of dimensions we can assign the different properties to nanomaterials such as in information technology (IT), medical engineering. We can categorize the magnetic nanomaterials into two classes.

(a) Systems with nanoscale dimensions.

(b) Systems with macroscopic dimensions having crystallites with dimensions of nanoscale [13]

As we know that size is important at nano level. The properties of bulk gold and Pt are non magnetic but at nanoscale they show magnetic properties. We can modify the surface atom by interaction with some other molecules. Nanoparticles' having magnetic properties is obtained by controlling the size of particles at nano scale such as Pt, Pd shows the ferromagnetic behaviour and Au shows the diamagnetic nature. We can modify the Au nanoparticles by wrapping up with different molecules and can obtained the ferromagnetic behaviour .Due to the charge localization at the particle surface would cause the ferromagnetic behaviour. The core and surface of Au

nanoparticles having diameter of 2 nm exhibits the ferromagnetic and paramagnetic nature. The permanent magnetism was viewed at room temperature for Au nanoparticles capped with thiol.

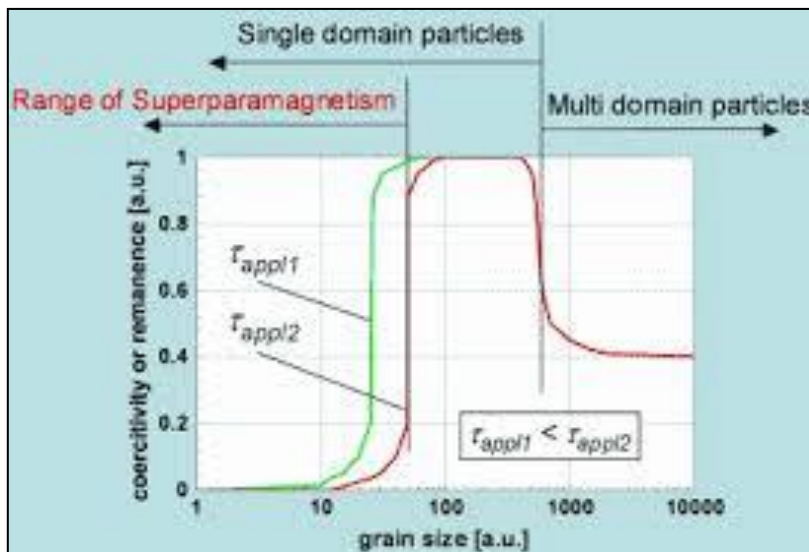


Figure 1.7: Magnetism in nanomaterials [14].

1.5: Tailoring of Nanomaterials and their Wide Applications

After the synthesis of nanomaterials there are wide applications in different fields of life such as in fuel cells, electronic agriculture. It is confirmed that the nanomaterials are divided in different applications due to physical, chemical and mechanical properties.

1.5.1: Fuel Cells

A fuel cell is a device which basically converts the electrochemical energy, which changes the chemical energy of fuel and oxidant into electricity. The electrodes are considered as the heart of fuel cells. The performance of electrode fuel cells can be enhanced by two ways, by optimizing the structure of fuel cell, by having electro active catalyst. The structures should be constructed in that way that loss should be reduced. This can be achieved by having the improved structure having the characteristics of broad surface area, reactant gas, electrolyte and helps in gas transport and having good electronic conduction.

1.5.1 .1: Microbial Fuel Cells

The microbial fuel cell is a device which converts the chemical energy stored in water soluble wastes into electrical energy with the catalytic action of microorganisms. The chemical energy is possessed by organic molecules present in water wastes which is released by changing the simple molecule to CO_2 .

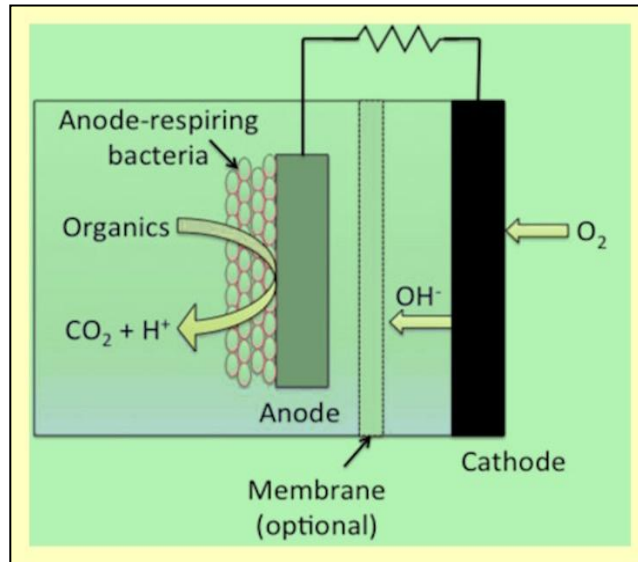


Figure 1.8: Basic structure of Microbial Fuel Cells[15].

1.5.1.2: Carbon Nanotubes

Carbon nanotubes are being extensively used because of their mechanical properties, chemical stability, and high surface area, are proved to be better for sensors and provide high surface area because of its structure. These have application in microbial fuel cells electrode and support for cell growth. Due to dimensional basis CNTs and MWCNTs have been reported as biocompatible material for eukaryotic cells. The efficient growth of the hydrogen producing bacteria throughout an electron conducting CNTs would give potential application as electrode in microbial fuel cells leading to high power performance.

1.5.2: Catalyst

Nanomaterials are characterized because of having large surface to volume ratio due to this these can be proved to be better applicable for catalysis.e.g. Bulk aluminum is used in utensils whereas the nano aluminum becomes so reactive that it can be used as fuel in rocket propulsion. Hence the catalysts supports or lessen the reaction rate depends on surface activity which could be helpful in controlling the rate controlling steps.

1.5.3:Nano Sensors

Sensors are based on the highly reactive surface to start a response by changing the minute concentration of species to be determined. By fabricating the monolayers on the surface of sensors and is exposed to environment and special functionality is used in sensing.

1.5.4: Nanomaterials in Microelectronic

Nanoelectronic term covers the devices and materials having same feature so that they are small and the inter atomic interaction and quantum mechanical properties should be studied in detail.

1.5.4.1: Approaches to Nanoelectronic

It includes different approaches such as nanofabrication, nanomaterial electronics, molecular electronics, nanoionic and nanophotonics. Nanofabrication involve the synthesis of ultra dense nanowires as compare to nanowires synthesized individually [16].e.g. It involves the single electron transistor, which operates on the basis of single electron.

1.5.4.2: Nanoelectronic Devices

Computers, memory storage, novel optoelectronic devices which include displays, quantum computers, radios, energy production which include the solar cells.

1.5.5: Photonic Devices

Photonic is a new emerging field that can rule over the semiconductor industry. The unique characteristics that would made photonic devices more favorable are large band gap, energy

saving larger communication distance, less sensitive to interference and have physical measuring characteristics [17].

1.5.6: Television Display

The resolution of computer's monitor and television highly depends on the size of the pixel. These pixels are made up of phosphors which shine when strike by a stream of electron in the CRT. The resolution can be improved by reduction of the size of pixel or phosphors. Nanocrystalline zinc selenide, zinc sulphide, cadmium sulphide and lead telluride fabricated by sol gel techniques and considered as best material for improving the resolution of pixels. The nanophosphor is used to minimize the cost of these displays to provide highly definition televisions (HDTV's) and PC's which are affordable.

Chapter 2

Literature Review

2.1: Transition Metal Elements

Transition metal elements are basically referred as the d block elements and these have great importance in our lives[18].The transition metal elements possess the electronic absorption spectrum lies in different ranges

1-Ultra-Violet (U.V.) between 200 to 380nm

2-visible region(vis.)between 380 to 780nm

3-Near infra red region (NIR) between 780 to 2000 nm [19] and these have applications in optoelectronic and electronic devices.

We can categorize the transition metal elements as paramagnetic and diamagnetic on the basis of absence and presence of unpaired electrons in the d orbital. The transition metals have 5d orbital. The d orbital's has a different no. of oxidation states. The s orbital does also contribute in determining the oxidation states. In the table, chromium (Cr) and copper (Cu) have $4s^1$ and $4s^2$. The stability of maximum oxidation state increases down the group. For example chromium is more stable at +3 oxidation state as compare to the +4 and +5 oxidation state [20].

2.2: Transition Metal Oxides

Transition metal oxides have valance electron in more than one shell and transition metals have more than one oxidation states. The number of properties exhibited by the transition metals that are not found in other metals, which are due to the partially filled d shell. The transition metal oxides have unique and profound magnetic and electric properties. The properties of TMO's depends strongly on the materials defects such as dislocations, stacking fault, vacancies and grain boundaries. Local oxygen bonding will be affected by these effects [21]. TMO's are used industrially in the catalytic processes.e.g. Used as selective oxidation, selective reduction and dehydrogenation [22].

Elements	Atomic Number(Z)	Common Oxidation States	Electronic Configuration
Scandium (Sc)	21	+3	Sc: [Ar] 4s ² 3d ¹ : ↑↓ ↑ _ _ _ _ 4s 3d
Titanium (Ti)	22	+4	Ti: [Ar] 4s ² 3d ² : ↑↓ ↑ ↑ _ _ _ 4s 3d
Vanadium (V)	23	+2, +3,+4,+5	V: [Ar] 4s ² 3d ³ : ↑↓ ↑ ↑ ↑ _ _ 4s 3d
Chromium (Cr)	24	+2, +3,+6	Cr: [Ar] 4s ¹ 3d ⁵ : ↑ ↑ ↑ ↑ ↑ ↑ 4s 3d
Manganese (Mn)	25	+2, +3,+4,+6,+7	Mn:[Ar] 4s ² 3d ⁵ : ↑↓ ↑ ↑ ↑ ↑ ↑ 4s 3d
Iron (Fe)	26	+2, +3	Fe: [Ar] 4s ² 3d ⁶ : ↑↓ ↑↓ ↑ ↑ ↑ ↑ 4s 3d
Cobalt (Co)	27	+2, +3	Co: [Ar] 4s ² 3d ⁶ : ↑↓ ↑↓ ↑↓ ↑ ↑ 4s 3d
Nickel (Ni)	28	+2	Ni: [Ar] 4s ² 3d ⁷ : ↑↓ ↑↓ ↑↓ ↑ ↑ ↑ 4s 3d
Copper (Cu)	29	+2	Cu: [Ar] 4s ¹ 3d ¹⁰ : ↑ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ 4s 3d
Zinc (Zn)	30	+2	Zn: [Ar] 4s ² 3d ¹⁰ : ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ 4s 3d

Table 2.1: Oxidation states of TMO's [20].

Large gap ^a insulators	Cr ₂ O ₃ , α-Fe ₂ O ₃ , NiO, CoO, MnO
Semiconductors	V ₂ O ₅ , Cu ₂ O, VO ₂ ^b , V ₂ O ₃ ^b , Fe ₃ O ₄ ^b , Ti ₂ O ₃ ^b
Metal	CrO ₂
High Tc superconductors	La _{2-x} Sr _x CuO ₄ , YBa ₂ Cu ₃ O ₇
Anti ferromagnetic	NiO, CoO, La ₂ CuO ₄ , Cr ₂ O ₃ , α-Fe ₂ O ₃
Ferrimagnetic	γ-Fe ₂ O ₃ , natural Fe ₃ O ₄
Ferromagnetic	CrO ₂ , K ₃ CuF ₄

a = referred as Mott insulator, b = Semiconductors via Mott transition

Table 2.2: The TMO's with ground state magnetic and electric properties [23].

2.2.1: Chemistry of Transition Metal Oxides

Transition metal oxides have their chemical properties based on the variable oxidation states have tendency to form complexes and used as a catalyst. Transition metal oxides are technologically important materials that have many applications. For example in chemical industry these oxides played a functional component in the catalyst used in a maximum processes to convert the hydrocarbon to other chemicals. These are also used as an electrode material as in electrochemical processes. In electronic field these are used in making conductors in films [24].

Process	Examples
Oxidation	Production of SO ₃ to SO ₂ CO oxidation in emission control
Dehydrogenation(non oxidative)	Production of styrene from ethyl benzene
Dehydrogenation(oxidative)	Production of formaldehyde from methanol and butadiene from butenes
Selective oxidation	Production of acrolein from propene and maleic anhydride from benzene and butane
Selective ammoxidation	Production of acrylonitrile from propene
Selective reduction	Reduction of NO, selective hydrogenation of unsaturated of unsaturated ketone.
Metathesis	Production of long chain alkenes

Table 2.3: The chemical processes in which the Transition metal oxides are Catalyst [24].

2.2.2: Physics of Transition Metal Oxides

Transition metal elements have large charge/radius ratios, hard due to that have high melting, boiling point and high densities form compounds which are paramagnetic in nature form compounds that have pronounced catalyst activity [25].

Elements	Group	Density (g/cm ³)	Melting point (°C)	Boiling point (°C)	Radius (pm)	Free atom configuration	Ionization energy (kJmol ⁻¹)
Sc	3	2.99	1541	2831	164	[Ar]3d1 4s2	631
Ti	4	4.50	1660	3287	147	[Ar]3d 24s2	658
V	5	5.96	1890	3380	135	[Ar]3d 34s2	650
Cr	6	7.20	1857	2670	129	[Ar]3d 54s1	653
Mn	7	7.20	1244	1962	137	[Ar]3d 54s2	717
Fe	8	7.86	1535	2750	126	[Ar]3d6 4s2	759
Co	9	8.90	1495	2870	125	[Ar]3d7 4s2	758
Ni	10	8.90	1455	2730	125	[Ar]3d8 4s2	737
Cu	11	8.92	1083	2567	128	[Ar]3d10 4s1	746
Zn	12	7.14	420	907	137	[Ar]3d10 4s2	906

Table 2.4: The physical properties of Transition metal elements [25].

2.2.3: High Dielectric Constant Materials

The present structure of Complementary Metal Oxide Silicon (CMOS) devices using SiO₂ gate oxide will change when thickness reaches at 15-20 °A and gate length around 0.1µm according to International Technology Roadmap for Semiconductors (ITRS). Rather by reducing the thickness of SiO₂ gate the scaling of SiO₂ can be completed by using the low frequency dielectric constant of gate material and thus increasing the capacitance. Any material that can replace the SiO₂ gate should have some characteristics these are given below:

- 1- The material should be thermodynamically stable (especially towards the reaction with Si or O) for proper processing of CMOS.
- 2- The material should be amorphous to control the diffusion of dopands along the grain boundaries.
- 3- A large band gap with band offsets is necessary as compare to the valance and conduction bands of Si.
- 4- The lattice polarizability of material should be large which is associated with soft phonon accelerating the transition between two crystalline phases.

The latest research on high dielectric is focused on the metal oxides and their silicates. These materials can replaced the SiO₂ because of the leakage of current due to the quantum tunneling effect of electrons in SiO₂. To overcome this issue SiO₂ is replaced by any other suitable material [26].

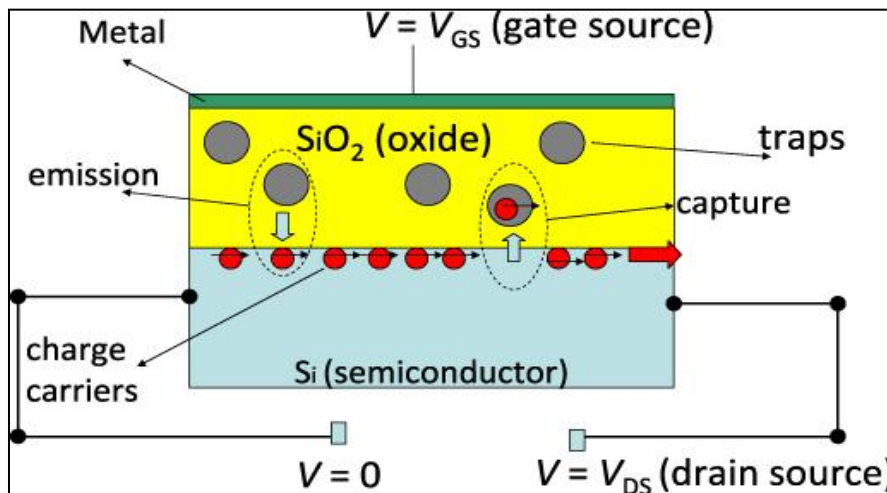


Figure 2.1: A block diagram for the metal oxide semiconductor (CMOS Transistor), composed of metal plate, an oxide SiO₂ and Si semiconductor. V_{GS} will attract the electron to the top of the semiconductor oxide near the oxide. V_{DS} will move the charge carrier that will generate the drain current [26].

2.2.4: Dielectric Constant

In the manufacturing of silicon integrated circuits (ICs), silicon based dielectrics (SiO₂, Si₃N₄, SiO_xN_y) are used as a key dielectric. The dielectric materials can be classified as high dielectric material and low dielectric material. The dielectric materials whose value of k is greater than

silicon nitride ($k > 7$) are classified as high dielectric constant material. The dielectric materials whose value of k is less than the silicon dioxide ($k < 3.9$) are classified as low dielectric constant material [27].

2.2.4.1: High Dielectric Constant Materials

High dielectric constant materials have their main applications in (a) memory cell dielectric (b) passive components (c) gate dielectric. Some important dielectric materials with their highly dielectric constant k are given below:

Dielectric Materials	Dielectric Constant	Applications
$\text{PbMgNbO}_3 + \text{PbTiO}_3$	22,600	B
PbLaZrTiO_3	1000	B
BaSrTiO_3	300	B
TiO_3	50	A,C
Ta_2O_5	25	A,B
CeO_2	20	A
BaZrTiO_3	17.3	E
AlO_3	9	B
$(\text{Bz, Ca, Sr})\text{F}_2$	3	D

A: Gate dielectrics, B: Capacitor dielectrics, C: Photoelectrochemical cells, D: Epitaxial dielectrics
E: Gate dielectrics for organic transistors on plastics.

Table 2.5: Some important high dielectric constant materials [27].

2.2.4.2: Low Dielectric Constant Materials

The revolution in communication (Microsystems operating at 1 Volt) and technologies thrusts towards the high circuit density and low powered electronic Microsystems has led the use of low k dielectric as interlevel dielectric materials (ILD). Only the use of Cu and low dielectric material are considered as best candidates because they can provide the lower delay time which is requirement for advance circuits.

Dielectric Material	Value of k(1 M Hz)
SiO _x F _y	3.2-3.5
Hydrogen silsesquioxane	3.0
Polysiloxane	2.89
Fluoropolyimide	2.8
Benzo-cyclo-butane	2.7
Black diamond	2.7
Polyethylene	2.4
Polypropylene	2.3
Fluoropolymer	2.24
Perylene	2.2
Dupont PTFE based copolymer AF 2400	2.06
Xerogels	1.2
Air	1.0
Carbon dioxide	1.0

Table 2.6: Some important low value dielectric constant materials [27].

2.3: Dielectric Polarization

When dielectric material is placed in an external electric field the movement of positive and negative charges in opposite direction in the dielectric is termed as dielectric polarization or the dielectric material is composed of small dipole and if electric field is applied to it then dipole moment per unit volume of dielectric is dielectric polarization. The dielectric material is comprised of small number of dipoles these will experience a torque that can be given as

$$\tau = \mathbf{p} \times \mathbf{E}_o \quad (\text{Equ. 2.1})$$

Torque will align the dipole vector p in the direction of E_o . Due to this effect there is a net polarization P parallel to E_o so the average electric field of dipoles is antiparallel to the E_o (that will try to reduce the total electric field strength E_o).

The total electric field is the sum of two fields that are given below:

$$E = E_o + E_p$$

$$E = E_o - P / \epsilon_o \quad (\text{Equ.2.2})$$

Polarization is proportional to the E_o and also is in the direction of E_o . This is suitable because in the absence of electric field E_o dipoles could not be aligned and no polarization. The linear relationship between the polarization and electric field can be written as:

$$P = \epsilon_o \chi_e E_o \quad (\text{Equ.2.3})$$

χ_e is the electric susceptibility. The materials that obey this linear relation are called linear dielectrics. By combining Equ.2.2 and Equ.2.3 we get:

$$E = (1 + \chi_e) E_o$$

$$E = K_e E_o \quad (\text{Equ.2.4})$$

$$K_e = (1 + \chi_e) \quad (\text{Equ.2.5})$$

where K_e is the dielectric constant. The dielectric constant K_e is greater than one and $\chi_e > 0$. So this implies that

$$E = E_o / K_e < E_o \quad (\text{Equ.2.6})$$

So, it is cleared from the above equation that effect of dielectric material is to minimize the effect of electric field [28]. The main purpose of dielectric polarization is to relate the macroscopic property such as dielectric constant to microscopic property such as polarization.

2.4: Mechanism of Polarization

We will discuss here some about some mechanisms in which dipoles or atoms or molecules would be polarized after the application of electric field.

(a) Electronic Polarization (b) Ionic Polarization (c) Dipolar Polarization (d) Maxwell-Wagner Polarization.

2.4.1: Electronic Polarization

It is sometimes called optical polarization. When dielectric material is placed in the electric field the electronic clouds relative to the nuclei of the atom will be displaced and forming the molecule of the dielectric. Induced dipole moment will be caused in the molecule. This process is called electronic polarization.

After the application of electric field there is a displacement of the centre of negatively charged electronic cloud relative to the positive nucleus of the atom. The displacement of electronic clouds results in dipole moment. Dipole moment is defined as “**The product of the charge and shift distance**” [17].

$$P = q \times d \quad (2.7)$$

2.4.2: Ionic Polarization

A polyatomic compound consists of ions and atoms when these are placed in the electric field these are arranged according to each other. This will create the distortion of the normal lattice vibration.

For example: Consider the ionic crystal structure of NaCl. The lattice will be consisted of Na⁺, Cl⁻ dipoles. The polarization in the natural dipole will be zero because for every dipole there is neighboring dipole which is equal in magnitude but opposite direction. When electric field is applied the Na⁺ and Cl⁻ ions moved towards each other. The dipole moments between the adjacent NaCl pair are different as compare to the applied electric field direction and there will be an existence of net dipole moment [17].

2.4.3: Dipolar Polarization

In materials this kind of polarization would take place and material is composed of molecules and particles with permanent dipole moment. When these materials are placed in the electric field the

randomly distributed dipoles will align themselves with the applied electric field. The orientation of the dipole along the direction of electric field is called dipolar polarization [29].

The dipolar polarization depends on the frequency and temperature. A large time would be required to align with the electric field. For example, the linear arrangement of O-C-O in CO₂ is consequence of non polar molecule. The dipole moment of non polar molecules depends on the direction of electric field and on the shape of molecule [30].

The dipole moment of polar molecules is greater as compared to the induced polarization of atoms. The polar molecules have greater value of dielectric constant. The material having polar molecules possesses the permanent dipole moments which can be oriented randomly in any position in the absence of electric field.

2.4.4: Maxwell Wagner Polarization

The colossal dielectric constant arises due to the non intrinsic effect. For example Maxwell Wagner polarization which begins with the charge accumulation at interfaces. There are different kinds of interfaces and each one generate the high value of dielectric constant because these can act as parallel plate capacitor with the very small distance between the plates in a result having high value of capacitance.

1-It can occurs at surface of the sample. e.g. formation of Schottky diode at the interface of sample/electrode.

2-At internal interface it can occur. e.g. grain boundaries in ceramic samples, planar crystal defects

3-Due to some spontaneous processes via electronic phase separation. e.g. charge stripe ordering and some other mechanisms. Quasi intrinsic effects are very important and interesting for applications.

Maxwell Wagner relaxation will lead towards the strongly frequency dependence of the dielectric properties which are used in modeling the equivalent circuits [17]

2.5: Dielectric Constant Dependence on Frequency

The mechanism of polarization involves movement of electronic clouds, dipoles, ions. These movements take very small time. We will consider the dependence of dielectric constant on frequency for covalent and ionic bonds respectively. For the covalent bonded materials the electronic polarization would take (10^{-14} seconds). Induced dipoles can align themselves according to the change of direction of field. The field switches back and forth in (10^6 times per seconds) for 1MHz. For covalently bonded solids the dielectric constant is considered to be constant up to 10^{14} Hz. Electronic polarization is the only polarization mechanism that will exist for high frequency others will not survive.

In materials in which ionic bond exist such as SiO_2 , ionic and electronic polarization contribute towards the dielectric constant. So, electronic and ionic polarization mechanisms contribute in dielectric constant in the range of 10^{12} - 10^{13} Hz. So, dielectric constant of SiO_2 would become smaller as we move from low to high frequency.

Frequency dispersion and dielectric relaxation is defined as the lowering of dielectric constant with increasing frequency. The dielectric constant at larger frequency is termed as optical frequency dielectric constant while at lower frequency is termed as static dielectric constant [17].

2.6: Silver Vanadium Oxide

Silver vanadium oxide (AgVO_3) is TMO's which has monoclinic crystal structure. The material is prepared by using the silver nitrate as precursor and ammonium vanadate as catalyst [21] having f.c.c. cubic structure with packing factor of 0.74 and having b.c.c. cubic crystal structure with packing factor of 0.64 [31] then obtained material having primitive b.c.c. crystal structure with packing factor of 0.68 [32]. The volume of the cell is $504.22 \times 10^6 \text{ pm}^3$ and the dimension of monoclinic crystal are ($a=17.87$, $b=3.58$, $c=8.0$) having density of 5.45 g/cm^3 . The space group is $12/m$. The band gap of the silver vanadium oxide is 2.20 eV. It possess some profound chemical, electrical and magnetic properties. Silver vanadium oxide is used as a cathode material in Li ion batteries and some other applications.

2.6.1: Literature Survey

Silver vanadium oxides (SVO) have drawn much attention as $\text{Ag}_2\text{V}_4\text{O}_{11}$ was used as an active cathode material in batteries due to its long term stability and high energy density [33]. $\beta\text{-AgVO}_3$

has a higher molar ratio, which is supposed to have better application in electrochemical performance [34]. However few researchers have focused on its electrochemical performance.

Nanowires have attracted the increasing interest because nanowires can offer a range of unique advantages in energy related field and electrochemical [35-37]. Inorganic nanostructures, nanoparticles, nanorods and nanowires are under extensive study. The active investigation as component for Photovoltaic devices because of the potential for exploring the new device concepts and increasing the efficiency at low cost [38].

Most previous research has focused on the Silicon nanowires whose doping and morphology can easily be controlled [38-40] although the indirect band gap of silicon can limit the light absorption in nanoscale measurement. In contrast inorganic β -AgVO₃ nanowires have attracted more attention as PV material, since the band gap of β -AgVO₃ nanowires be tuned to span nearly the spectrum from UV.Visible region to infra red region.

This work has focused on the successful synthesis of β -AgVO₃ nanowires by hydrothermal process at temperature 180 °C for 24 hr. By adjusting the concentration of precursors and temperature the desired morphology can be controlled. In literature study, β -AgVO₃ nanorods are obtained at 180 °C for 12 hr but after increasing the time nanowires can be obtained.

Polyaniline (PANI) is one of the most important conducting polymers because of its high conductivity, low cost and chemical stability. Recently aniline is used to fabricate the PANI/silver nanocomposites through a redox reaction between Ag⁺ ion and aniline which have potential applications. In this work a rational method is used to synthesize the β -AgVO₃ nanowires/Polyaniline with enhanced functional properties. Control experiments with varied amount of aniline have been carried out. By keeping other parameters unchanged the weight percentage of aniline is changed from 50%, 60% to 70%.

An X-ray diffraction (XRD), Scanning electron microscope (SEM), Fourier transformed infrared (FTIR) and UV.Visible are used to study the optical property of β -AgVO₃ nanowires and after the affect of aniline. This investigation confirms the tuning a band gap with size of particles of β -AgVO₃ nanowires after the affect of aniline from UV.visible region to infrared region.

β -AgVO₃ nanowires / Polyaniline nanocomposites have been fabricated in laboratory successfully by chemical oxidation polymerization and redox reaction between the Ag⁺ ions and aniline monomers. The pellets of β -AgVO₃ nanowires and polyaniline nanocomposites based on β -AgVO₃ nanowires are used to study the dielectric properties of the material at room temperature in the frequency range of 100 Hz to 5 MHz. The optical properties are explored by studying the reduced band gap of these materials.

The XRD analysis for pellets (for dielectric properties) and powder form (for optical properties) of TMO's nanowires and polyaniline nanocomposites based on TMO's nanowires showed that all peaks are in consistent with the pure one sample. This confirms the successful coating as the size of particle increases. All peaks of pure sample β -AgVO₃ nanowires matches with the indexed β -AgVO₃. The crystal structure investigations inform the crystal structure of β -AgVO₃ nanowires is monoclinic with the cell parameters as $a = 17.875$, $b = 3.58$, $c = 8.036$ while after addition of different weight percentage of aniline from 50%, 60% and 70% to purely synthesized β -AgVO₃ nanowires cubic crystal structure is obtained.

To study the structural property of samples the FTIR spectra of samples were studied and on the basis of bond type we become able to determine the exact energy to be absorbed. The best absorption peaks are studied in the range of 400cm⁻¹ to 1000cm⁻¹ for β -AgVO₃ nanowires. All peaks which are observed for β -AgVO₃ nanowires are also observed for polyaniline nanocomposites in the range of 400cm⁻¹ to 1000cm⁻¹. Four characteristics peaks are observed at 1147cm⁻¹, 1304cm⁻¹, 1503cm⁻¹, 1589cm⁻¹ after the addition of aniline.

The properties of dielectric material (in the form of pellets) are evaluated by measuring the dielectric constant ϵ , dielectric loss $\tan\delta$ and ac conductivity as a function of frequency at room temperature. All pellets are of same diameter 13.35mm and thickness is changed for each sample, for pure sample thickness is 0.55mm, for 50% by weight of aniline 0.59mm, for 60% by weight of aniline 0.59mm, for 70% by weight of aniline 0.89mm. The dielectric constant is measured as a function of $\log F$ at room temperature. The dielectric constant, dielectric loss is maximum at low frequency but minimum with the increase in frequency due to decrease in polarization. The ac conductivity is measured and it decreases when frequency is minimum and increases when frequency is maximum. The graphical results shows as we increases the amount of conducting polymer the ac conduction decreases can be explained by hopping mechanism.

Generally, in the case of band conduction the ac conductivity increases as frequency is increased but ac conduction increases when the frequency increases due to hopping conduction. The ac conductivity is frequency dependent have confirmed the similarity of wide range materials, conduction by ions, electrons and holes. Ordered and disordered involve different types of chemical bonding and different energy level structures. It becomes easier in hopping mechanism that we can distinguish different regions of frequencies. The ac conductivity is almost constant at low value of frequencies. At larger value of frequency the ac conductivity is larger and then finally a region is encountered where cut off starts at higher frequency and then becomes zero [41].

The optical properties for samples are studied by measuring the absorption peaks and activation energy of direct band gap. The β -AgVO₃ nanowires without addition of aniline has characteristics like semiconductor, its value of direct band gap is 2.20eV and absorption is reported 41%.After the coating of β -AgVO₃ nanowires with different amount (wt%) of conducting polymer it shows its characteristics like semiconductors its absorption increases from 10 % to 13 %.The values of direct band gap lies in the range of 1.17eV, 1.13eV, 1.11eV. By using the Beer Lambert Law we can calculate the concentration of absorbing species would increase the absorption. The direct band gap is measured and it decreases when size of polyaniline nanocomposites increases [42].

2.7: Methods and Apparatus for the Fabrication of Silver Vanadium Oxide Nanowires

2.7.1: Description of Apparatus

The following apparatus is used for fabrication of nanowires and nanocomposites based on these nanowires.

- Digital Analytical Balance
- Autoclave
- Hot Plate
- Filtration Pump
- Vacuum Oven

- Mortar Pestle
- Die
- Hydraulic press

Digital Analytical Balance

It is an important apparatus for weighing used in laboratory. It is used for weighing the mass of chemicals during preparation of samples.

Autoclave

It is a device used for the chemical reactions and other processes at high pressure and temperature. Hydrothermal and solvothermal reactions are carried out in autoclave.

Hot Plate

The hot plate is used to provide the required temperature for reaction. It may provide stirring for the reaction. For this work hot plate is used for stirring.

Filtration Pump

Filtration flask and vacuum pumps are used for filtration. Vacuum filtration works on the principle of pressure differential (atmosphere above the filter paper and vacuum in filtration flask) to push a solution through filter paper.

Vacuum Oven

A vacuum oven is used for drying, baking and curing the samples. The oven used at THERMAL TRANSPORT LAB in SCME can heat up to 300°C In this work it is used for drying the samples. It works on the principle of convection.

Mortar Pestle

Mortar is a bowl usually made up of ceramics or stone and pestle is club shaped object used for grinding the sample.

Die

For the preparation of pellet die is very important. Die are made up of usually very hard material. They are mostly available in circular shape having diameter from 5-15mm. A die used for preparation of samples in this work was having diameter of 13mm.

Hydraulic Press

Hydraulic press is a device used for the preparation of pellets by applying the required pressure. It works on the principle of pascal law. Hydraulic press uses both pressing and heating for the preparation of samples. In this work only pressing is used for the preparation of samples.

2.8: Approaches for Synthesis of Nanomaterials

There are two basic approaches for the synthesis of nanomaterials “Top down” and “Bottom up”. Top down approach means successive grinding or cutting of bulk material to nano scale by using the chemical, mechanical and other form of energy. Bottom up approach means to fabricate a nanomaterial from atomic or molecular level of precursor through chemical reaction and allowed to grow in size. A synthesis of nanomaterials require control on different parameters

- (a) particle shape
- (b) particle size
- (c) particle composition
- (d) size distribution
- (d) degree of particle agglomeration

2.8.1: Top down Approaches

There are different methods to prepare nanomaterials from bulk materials. It includes mechanical grinding, electro-explosion, etching, sputtering and laser ablation.

2.8.1.1: Mechanical Grinding

Mechanical milling is a process in which mixtures of elements and prealloyed powders are decomposed in a protective atmosphere in apparatus capable of high energy impact forces such as

shaker or attrition mills. One of the most important advantage of mechanical milling process is that it requires low temperature and newly formed grains size grow slowly .The range of obtained particle size is from 2nm to 35 nm.

2.8.1.2: Lithography

According to Marian Webster “**The process of introducing patterns on the semiconductor pattern and use as integrated circuit.**”

Lithography plays an important role in the modern age industry of semiconductor manufacturing. Modern lithography works well in the nano regime having features smaller than 100nm.Latest technique of modern lithography are enlisted below [43]:

- Photolithography (Optical ,U.V,EUV)
- X-Ray Lithography
- Ion beam Lithography
- Interference Lithography
- Scanning Probe Lithography
- Nanoimprinting Lithography

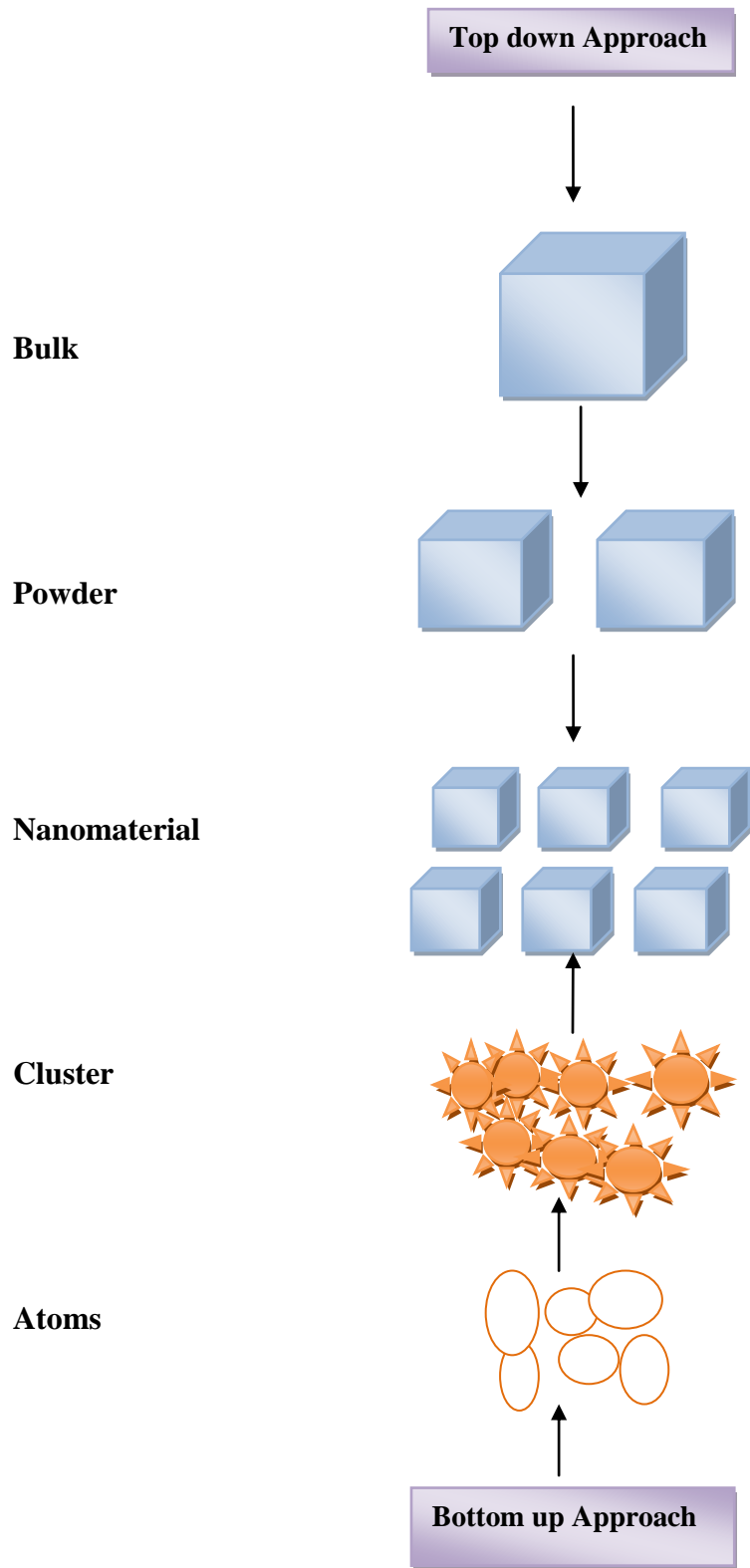


Figure 2.2: Schematic representation of approaches towards the synthesis of nanomaterials.

2.8.2: Bottom Up Approaches

In bottom up approach the reactants elements of system are first studied in detail, then these are reacted together to form a larger sub system, and then a complete complex system is formed. Bottom up approach includes different methods to synthesize the nanomaterials which are chemical vapour deposition, sol gel processing, plasma spraying synthesis, laser pyrolysis, atomic and molecular condensation.

Chemical Vapour Deposition

The CVD technique involves a number of chemical reactions such as reduction, hydrolysis, oxidation, carburization, thermal decomposition and nitridation. These reactions can be initiated by using different methods. Some of them are enlisted below:

Thermal activation occurs at high temperature greater than 900°C, by using the metallo organic precursors (MOCVD) the temperature can be lowered.

Photon activation uses shortwave ultraviolet radiation which can take place by using the direct activation of reactant and activation of intermediate.

Plasma activation takes place at lower temperature between 300°C – 500°C.

CVD technique uses the carbon source in gaseous form and by having the energy source medium such as plasma and resistively heated coil that will transfer energy to gaseous carbon molecules [44]

Sol Gel Process

Sol gel technique is a wet technique. In this technique we can synthesize the nanoparticles and nanostructures 2D and 3D materials. In this process we firstly prepare the colloidal suspension for these sol precursor mostly metal ions are used. Metal alkoxides are used for precursor because of its highly solubility in water. Titanates, Aluminates and borates are included in Metal alkoxides. If precursor is not soluble in water then another liquid alcohol is used for this.

This process involves the four steps.

1. In first step the hydrolysis of precursor is completed. The hydrolysis of precursor doesn't need catalyst but sometimes it needs some acidic and basic medium. as catalyst.
2. Sol will start to condense.
3. When sol will condense the particles started to grow and growth depends on different parameters such as temperature, pH of sol and pressure etc.
4. When particles grow they started agglomeration and whole liquid started to form network and gel is formed [45].

Hydrothermal Process

It is defined as “**Any heterogeneous reaction carried out in aqueous medium at temperature greater than at room temperature and at pressure greater than at 1 atm.**”

Mineralizes

In hydrothermal reaction or system confined in closed system, the solvent played an important role under the action of pressure and temperature .We can easily develop a hydrothermal process corresponding to the material synthesis and material process under a suitable solvent to increase the solubility of the desired compound. Water is an important solvent and it is used as mineralizer in experiments. Several compounds do not show high solubility to water even at elevated temperature so some other solvents are used such as ether ,alcohol etc

Advantages of Hydrothermal Reaction

In contrast to other conventional techniques, the hydrothermal technique has several advantages.(a)The compounds with elements in oxidation states that are very difficult to obtain ,especially for important transition metal compounds, can be obtained in closed system .e.g. ,ferromagnetic chromium oxide.(b)This method is also useful for the so called low temperature phases, e.g. α quartz etc.(c)The synthesis of metastable compounds, such as sub iodides of tellurium. An understanding of dynamics, structure and reactivity of water and other electrolyte solutions with the advancement in instrumentation like NMR, Raman, X-ray and Neutron Diffraction have contributed to the new branches of sciences that involve the hydrothermal technique. Water is considered as a safest and cheapest of all solvents. It can act both as catalyst

or mineralizer under elevated temperature and pressure conditions. The thermodynamic and transport properties of supercritical water are different from those of ambient water. The solubility of non polar species increases, while for ionic and polar species decreases. As a result the polarity of water decreases the mobility of molecules increases due to the decrease in solvent viscosity. The drastic changes in the ionic hydration are brought about due to decrease in the dielectric constant and density.

Autoclave

Why is it called autoclave? It is a device that automatically locks shut when pressure rises .The word is French, but its origin comes from Greek "auto" for automatic and the Latin "clevis" for key.

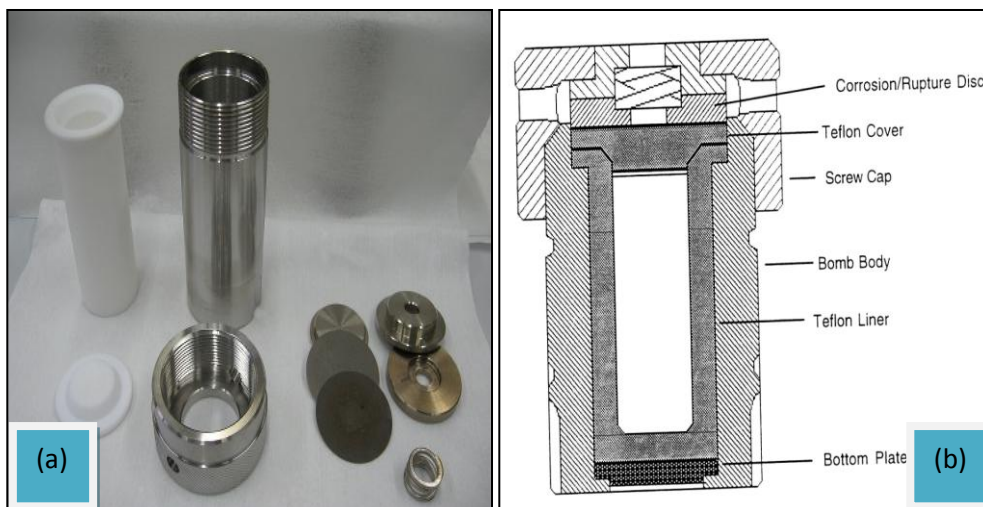
Theory of Operation

Why it is an effective sterilizer? An autoclave is a large pressure device that uses a steam under pressure as sterilizing agent. High pressures enable steam to react at high temperature and thus increasing its heat content. Most of the heating power of steam comes from its latent heat of vaporization. This is the amount of heat is required to convert boiling water to steam. This amount of heat is greater compared to that required to make water hot. By achieving high and even moisture content in the steam-air environment is important for effective autoclaving. The ability of air to carry heat is directly related to the amount of moisture present in air. The more moisture presents, more heat can be carried, so steam is one of the best effective carrier of heat.



(a) Image of autoclave.

Parts of autoclave



(a) Teflon cup with stainless steel body. (b) Description for parts of autoclave.

A reaction vessel is placed in autoclave and a removable teflon cup is placed, it exhibits a maximum operating temperature and pressure of 250 ° C and pressure of 1800psi. The thermal coefficient of teflon cup is greater than stainless steel. The capacity of teflon cup varies 50 to 100ml for synthesis of nanostructures. The starting material is added to the teflon cup. Different solvents are used as medium for the reactants to react after the completion of reaction the product is obtained. It is washed with deionized water and ethanol to remove further impurities [46].

2.9: Synthesis of Silver Vanadium Oxide Nanowires

Hydrothermal process is considered as one of the most important methods for the production of crystalline structure since 1970s. In this method precursor is mixed in aqueous solution and the mixture is placed in an autoclave at elevated temperature and pressure. A hydrothermal process is used for the synthesis of silver vanadium oxide by using silver nitrate as precursor [44]. Ammonium metavanadate 99%, ammonium persulfate 98% and aniline monomer 99.5% are purchased from Sigma Aldrich and used for the synthesis of silver vanadium oxide nanowires.

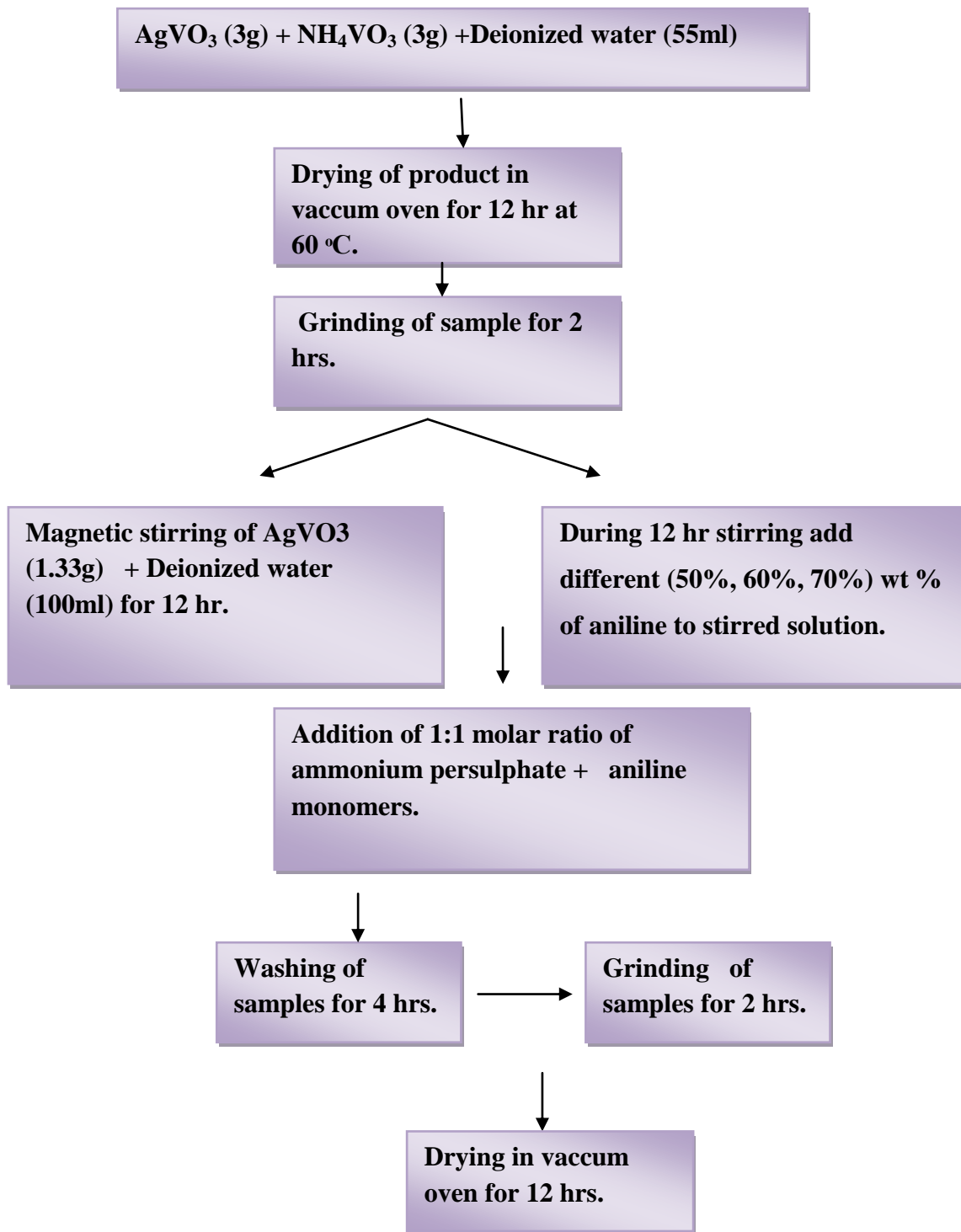


Figure 2.3: Flow chart diagram of synthesis of silver vanadium oxide nanowires and nanocomposites based on hydrothermal process.

Chapter 3

Experimental setup and measurements

3.1: Introduction

After the successful synthesis of Silver vanadium oxide nanowires and nanocomposites (coating with aniline) based on nanowires, next step is to characterize the material or sample. The morphology, composition and structural properties of materials or samples are studied. Each measuring technique has its own characteristics and working principles on which it work. We will discuss the characterization techniques one by one as used for examining the properties of samples. These techniques are given below:

- X-ray Crystallography
- Scanning Electron Microscopy (SEM)
- Fourier Transform Infrared Spectroscopy (FTIR)
- Ultraviolet visible Spectroscopy (UV.vis)
- Measurement of AC conductivity.
- Measurement of dielectric properties.

3.2:X-ray Crystallography

It is the basic tool for determining the atomic and molecular structure of materials. When an incident x-ray beam incident on the crystalline atom it will diffract in different directions. The diffraction pattern for sample can be obtained by using scattering of electron and neutron. The material under investigation gives us information about the crystal structure, crystal axis, cell volume, colour of that material.

3.2.1: Bragg's Law

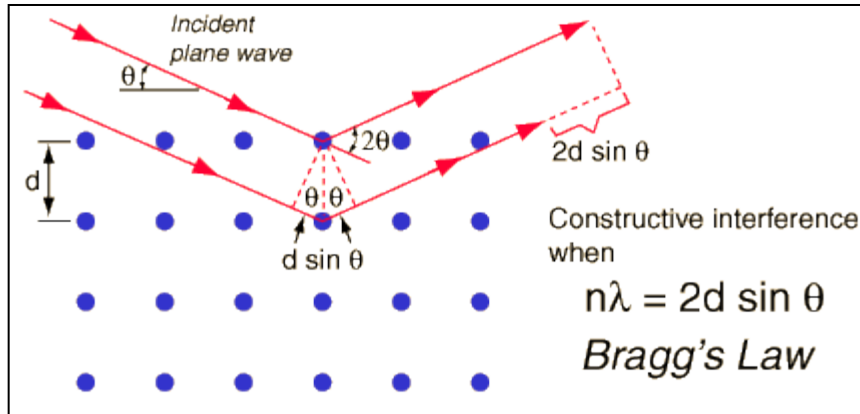


Figure 3.1: Representation of Bragg's Law [47].

A regular array of atoms defines a crystal. The X-rays are considered as electromagnetic wave and primarily the x- rays are scattered through the atoms. W. L. Bragg presented a model in which he explained a result by considering two planes having a distance of d between them. The incident beam is considered to be plane wave. Beam 1 is reflected from the surface 1 and respectively beam 2 is reflected from the surface 2. Both beams have same angle of incident and angle of reflection. Both the beams are in phase because incident beam is planar before reaching to the sample. After reflection beam 2 have to cover some extra distance. There is a need to maintain the in phase relation between beam 1 and beam 2 and should have constructive interference and the extra distance that the beam 2 will travel will be an integral multiple of wavelength or $n\lambda$. This is termed as Bragg's law [48].

$$2d \sin \theta = n \lambda \quad (3.1)$$

d = interatomic spacing

λ = wavelength of incident beam

θ = incident angle

n = integer

3.2.2: Scanning Electron Microscope (SEM)

Scanning electron microscope is considered to be a central to micro structural analysis. It shows the morphology, topographical features, compositional differences, crystal structure and crystal orientation of samples after scanning with focused beam of electrons. The magnification range for SEM is between 10 to 100,000 but the higher magnification of SEM can be achieved by using TEM.

Now we will discuss the structure of SEM. It consists of electron gun, condenser lens, apertures, deflecting coils and objective lens

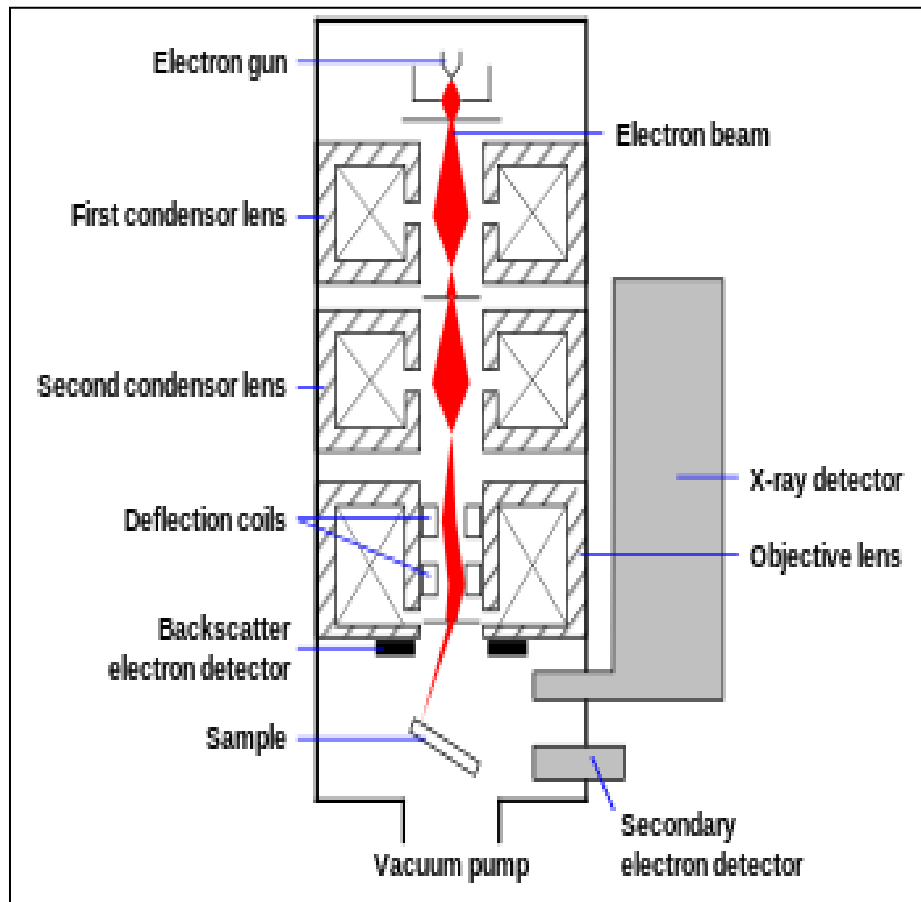


Figure 3.2: Schematic representation of Scanning Electron Microscope [49].

Electron Gun

The electron gun is a triode system; initially the electrons come across from filament because field is created by filament, grid cap and anode. The diameter of the initial beam can be reduced by using condenser and objective lenses. The accelerated electrons have energies in the range of 1-40keV. The SEM can produce the electron beam at the sample surface with spot size less than 10 nm in diameter .

Apertures

A size is varied for aperture and classified as (a) thick aperture discs and strips (b) thin foil aperture

- (a) Thick aperture discs and strips: For objective lens the size of hole is between 100-500 μm while for condenser lens it lies between 10-60 μm .
- (b) Thin foil aperture: The thickness of in gold foil is 0.5 μm .

The resolution and depth of focus are controlled by apertures

Lenses in SEM

SEM uses 1 or 3 condenser lenses to minimize the electron beam crossover diameter in the electron gun. The condenser lens will control the size of probe and the number of electron coming down. If we increase the strength of the condenser lens then it will decrease the diameter of probe or electron beam but it will decrease the probe current. A smaller diameter of probe will be produced by the objective lens due to the reduction in the working distance.

Deflecting Coil

The function of deflecting coil is to deflect the beam in x, y directions so beam of electron can move over the specific area of samples. The electron beams from the deflecting coil enter into the objective lens and converges to fine electron beam.

Objective Lens

There are three basic designs for the objective lens (a) pinhole lens (b) immersion lens (c) snorkel lens.

The focal length of pinhole lens is in the range of 5-40 mm. The specimen will be outside the lens and its magnetic field.

The focal length of immersion lens is between 2-5mm. The sample can easily be placed in the lens.

The snorkel lens is the combination of best features of pinhole lens and immersion lens. The sample is placed outside the lens but inside the magnetic field.

It will affect the final probe or beam in this way. The aperture angle should be optimum to reduce aberrations. A current can be controlled by the size of aperture. A convergence angle of probe should be small to control the depth of field [50].

Interaction of Electrons

Electrons can experience a multiple interactions such as elastic and inelastic interactions are experienced because interaction of beam of electrons in to the material.

Elastic Interaction

Elastic interaction is “**There is change in the path of beam of electrons without the loss of energy.**” Backscattered electrons are electrons from the incident beam that experience elastic interactions with the sample material and trajectory will be changed and escaped from sample.

Inelastic Interaction

Inelastic interaction is “**The energy is transferred from the beam to the sample.**” Secondary electrons are low energy and these come out from the outer shell of the sample atom.

Characteristic x-rays

Auger electrons are created due to the inelastic interaction of the beam electrons with sample and inner shell electron is emitted

3.2.3: Fourier Transform Infrared Spectroscopy (FTIR)

This technique investigates the structural property of the material such as which type of bonding exist in between the atoms. It is divided into three regions near, mid and far infrared regions.

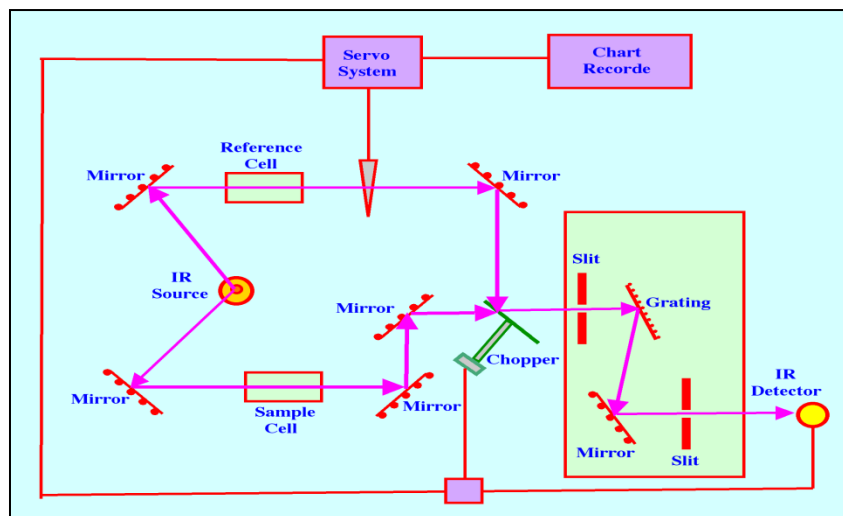


Figure 3.3: FTIR spectrum based on the Michelson interferometer [43].

Working

It works on the principle of the optical instrument interferometer. It consists of three components fixed and movable mirror and beam splitter. A beam splitter is used to divide the infra red beam into two beams half of the beams are reflected off towards the fixed mirror and half is transmitted towards the movable mirror. A light is recombined by two mirrors and send back to the beam splitter. Fixed mirror has fixed length and movable mirror has changing length due to which two beams can interfere each other. A signal is generated after interference and is called interferogram. A signal from interferogram is encoded with the information about every infrared frequency from source [52].

3.2.4: Ultraviolet Visible (UV-VIS) Spectroscopy

It an important technique used to examine the transmittance directly in percentage, this shows the percentage of incident beam of light is transmitted by sample. We may be able to calculate the absorbance.

$$\text{Abs} = \log (1/T) \tag{3.2}$$

T= transmittance

$$T = T / 100 \%$$

Absorbance is used to measure the concentration of liquid solutions according to the Beer Lambert Law [53]. The basic theory on which it works is “when light is absorbed by the sample the electrons moves from ground state to higher energy state

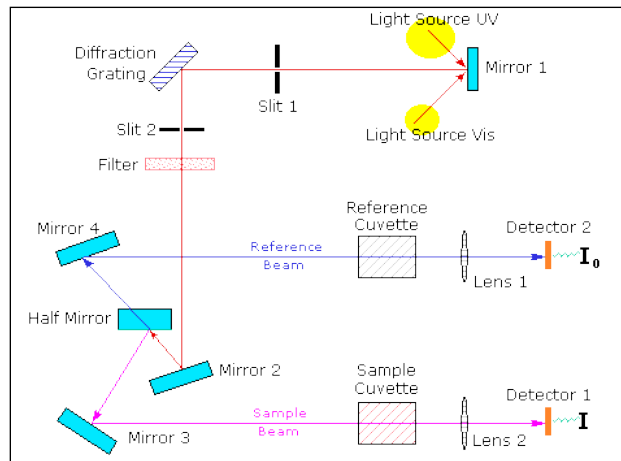


Figure 3.4: Working of Ultraviolet Visible Spectroscopy [54].

The absorption spectra can be studied by having information about source, monochromator, sample compartment and detection and measurement of light intensity.

Source

The source should be stable for duration of measurement. i.e. no fluctuation in the intensity of emitted radiation, should have maximum intensity over a large range of wavelength region.

Monochromator

Its function is to produce a beam of monochromatic light that can be selected from large number of wavelengths. Its important components are (a) entrance slit (b) collimating device (c) dispersing system (d) mirror or focusing mirror (e) exit slit.

The wavelength can be selected by these two methods (a) filters (b) dispersing medium.

Sample Handling

Samples can be solid, gas and in liquid form. Solid and gaseous form of samples can be adjusted but for liquid form we need special instrument a cuvette. It is made up of U.V. grade silica or glass.

A cuvette should have these characteristics:

- (a) The optical windows should be highly polished, flat and parallel. (b)
- (b) The entrance and exit surface should be parallel and orthogonal.
- (c) The light path should be controlled and cuvette should be placed in its path.

Detector

There are four type of detectors used in the spectrophotometer.(a) photoconductive cell (b) photomultiplier (c) diode array (d) silicon diode. The radiations passes through sample can be detected by detectors. It will convert the photon inside the radiation into small electrical current [55].The spectrum is obtained by comparing the current generated by sample and reference beam.

3.2.5: LCR Meter

It is a device used for the direct measurement of inductance (L), capacitance (C) and Resistance (R) of measuring device.

Basics of LCR meter:

LCR meter uses different techniques including in which bridge method and current voltage measurement are important.

Bridge Method:

This method is used for the measurement of lower frequency usually up to 100 kHz. The bridge method uses a balanced bridge. The position of components of bridge can be used for determining the value of components under examining at balancing point. This method works on the principle of wheat stone bridge configuration in which device, unknown resistance, under test is placed in bridge circuit.

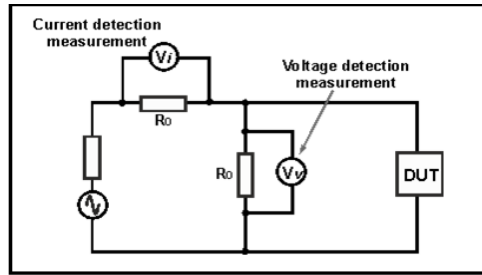


Figure 3.5: Representation of LCR measurement for low impedance circuit [56].

Current Voltage Method

This method is used for measurement of higher frequency. A current voltage measurement is used for the components which have application at high frequency

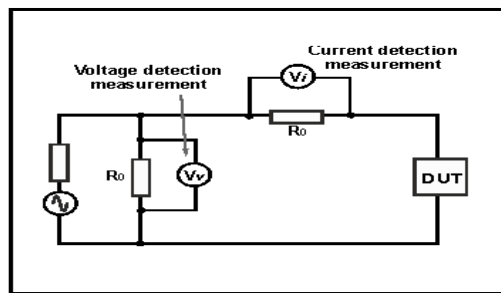


Figure 3.6: Representation of LCR measurement of high impedance circuit [56].

Chapter 4:

Results and Discussion

4.1: Introduction

β -AgVO₃ nanowires are laboratory synthesized through hydrothermal process. It has monoclinic structure having primitive b.c.c structure. After addition of aniline to these β -AgVO₃ nanowires we get polyaniline nanocomposites having cubic structure. Transition metal oxides are considered as one of the most important material because it exhibits the novel properties so it is studied widely. The hydrothermally synthesized β -AgVO₃ nanowires are of 50nm in diameter after the addition of varied wt .percentages (50,60,70%) of aniline the diameter is changed to 82nm, 100nm, 152nm . The band gap is reduced from 2.20eV to 1.17eV, 1.13eV and 1.11eV. The obtained result is important because reduction in band gap and absorption would contribute towards the application in electronic devices. The dielectric properties are studied for these controlled morphology nanocomposites and these are proved to be good high dielectric materials. The electrical properties of oxides are improved by addition of metal ions, conducting polymers and impurities as doping. The intermediate energy levels between the β -AgVO₃ nanowires and polyaniline nanocomposites have made it for better application in electronic devices. There is a lot of need to do work on the transition metals and their functional properties should be explored.

4.2: X-ray Patterns

To investigate the information about the crystal structure of β -AgVO₃ nanowires and polyaniline nanocomposites with addition of different weight percentages of aniline synthesized in the laboratory, X-ray diffraction of powdered samples is examined. The spectra of β - AgVO₃ nanowires is highly purified and all other characteristics peaks of polyaniline nanocomposites are in consistent position to β -AgVO₃ nanowires. As we are going to increase the weight percentage of aniline from 50%, 60% and 70% the particle size enlarges. As we will increase the amount of aniline and reaction time then there will be change in structure of β -AgVO₃ nanowires the maximum no. of H⁺ ions (the no. of free H⁺ ions becomes greater from structure of aniline as we increases the amount of weight percentage of aniline to purely synthesized AgVO₃ nanowires) become free from the structure of aniline (conducting polymer) and attached to the structure of

AgVO₃ nanowires. All diffraction peaks of β- AgVO₃ nanowires matches with the indexed β- AgVO₃, having monoclinic structure and space group 12 / m (No12). While the samples with 50% ,60%,70% of aniline have cubic structure and stable with space group Fm-3m having space group number 225.

4.2.1: Study of the Structures of β-AgVO₃ Nanowires and Polyaniline Nanocomposites (β-AgVO₃ nanowires /Aniline)

X-ray diffraction (XRD) is used to study the crystal structure of synthesized nanowires using Model theta-theta, X-ray diffractometer with graphite monochromatized Cu K_α radiation (λ=1.5).The structural study involves the calculation of lattice parameters (a, b, c), bulk density and calculated density. The diffraction pattern is observed when condition of constructive interference for Bragg's Law is satisfied.

$$n\lambda = 2d\sin\theta \quad (\text{Equ.4.1})$$

where n = an integer, λ = wavelength of incident wave, d = spacing between the planes in atomic lattice, θ = angle between incident ray and scattered planes

In monoclinic crystal the lattice plane and lattice constant are related by equations

$$a = d_{hkl} / (h_2^2 + k_2^2 + l_2^2)^{1/2} \quad (\text{Equ.4.2})$$

$$b = d_{hkl} / (h_2^2 + k_2^2 + l_2^2)^{1/2} \quad (\text{Equ.4.3})$$

$$c = d_{hkl} / (h_2^2 + k_2^2 + l_2^2)^{1/2} \quad (\text{Equ.4.4})$$

By combining Equ.4.1 and Equ.4.2, Equ.4.3, Equ.4.4 we get a set of Equ.

The crystalline size of β-AgVO₃ nanowires and polyaniline nanowires measured by using the 2θ is 43nm and 44nm.

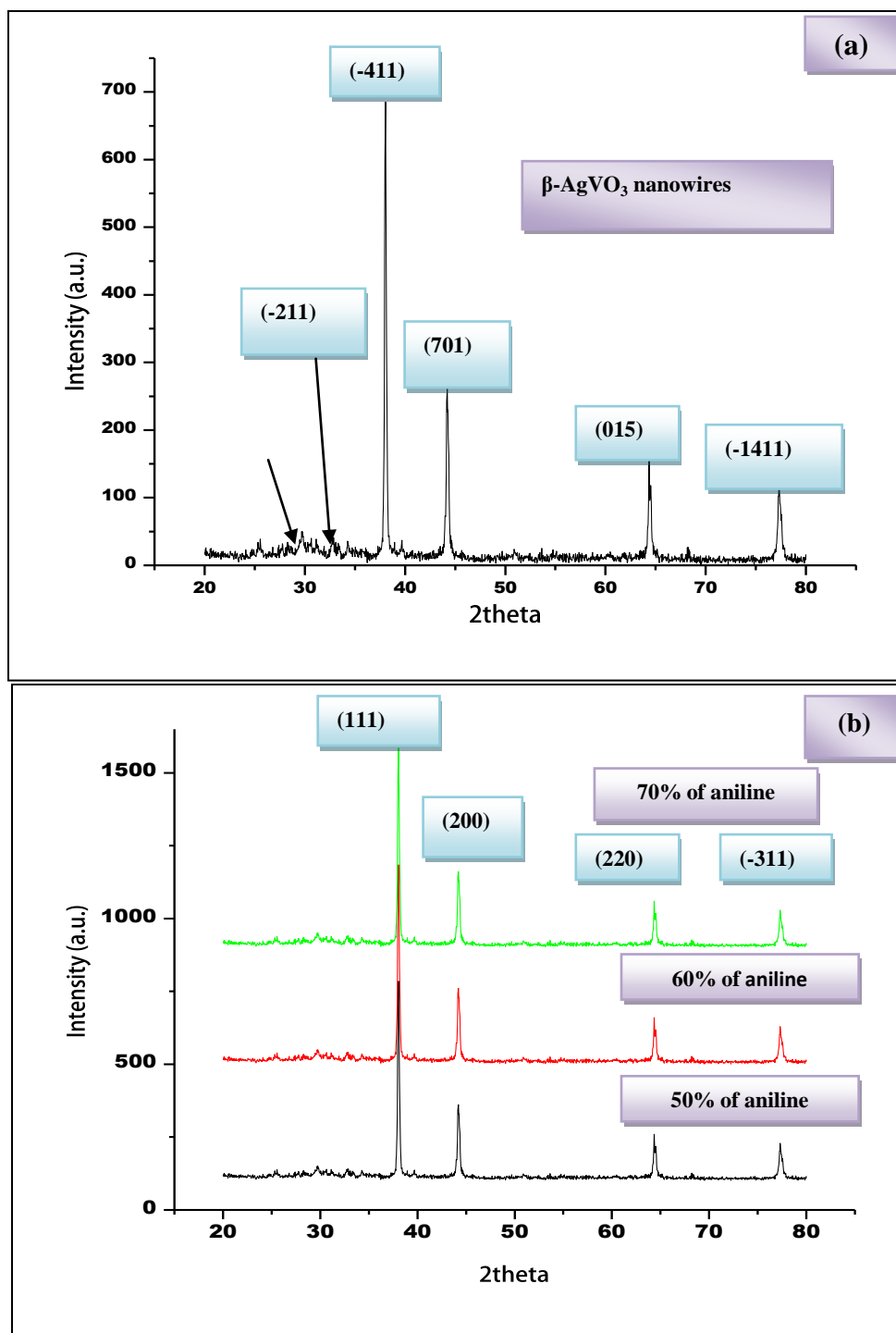


Figure 4.1: XRD spectra of β -AgVO₃ nanowire (a) nanocomposites after addition of different weight of aniline 50% (b), 60% (c), 70% (d).

Sr.No.	Sample Material	Crystal structure	Miller Indices	Lattice parameters
A	β -AgVO ₃	Monoclinic	-411	a = 17.875 , b = 3.58 ,c = 8.036
B	50% by wt. aniline	Cubic	111	a = 4.09 , b = 4.09 ,c = 4.09
C	60%by wt .aniline	Cubic	111	a = 4.09 , b = 4.09 ,c = 4.09
D	70%by wt. aniline	Cubic	111	a = 4.09 , b = 4.09 ,c = 4.09

Table 4. 1: Crystallographic information of sample materials.

4.3: Fourier Transform Infrared Spectroscopy (FTIR)

It Indicates the FTIR spectra of β -AgVO₃ nanowires and polyaniline /AgVO₃ nanocomposites with the addition of different weight% of aniline. It displays the bonding as well as functional groups attached during vibration. The dominant absorption peaks of β -AgVO₃ nanowires lies in the range of 400 to 1000cm⁻¹. The best absorption peaks are in the range of 965,828,752,691 and 518 cm⁻¹ (finger print region).The FTIR spectra indicates the peak at 1631 cm⁻¹ which show the functional group O-H having vibrations are stretch free[57].All peaks of polyaniline composites are in accordance to the β - AgVO₃ nanowires..By increasing amount from 50%, 60% and 70% of aniline to β - AgVO₃ nanowires four additional characteristic peaks are obtained at 1150 cm⁻¹, 1301 cm⁻¹, 1501 cm⁻¹, and 1585 cm⁻¹, having C-H plane bending vibration , C-N stretching vibration, benzenoid ring stretching mode and quinoid ring stretching mode. All these peaks confirm the successive coating of aniline on the β -AgVO₃ based nanowires.

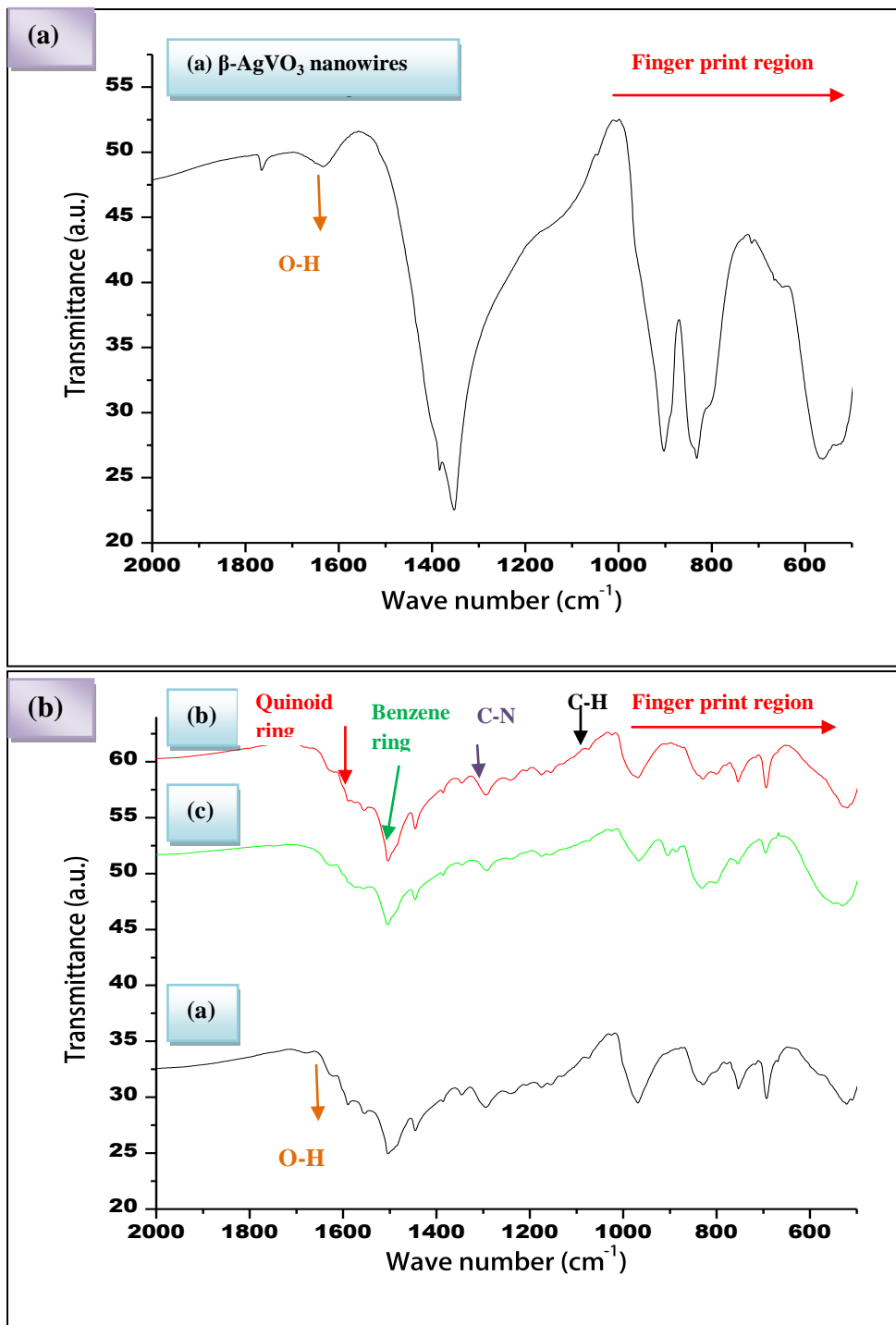


Figure 4.2: FTIR patterns of β -AgVO₃ nanowires (a) affect of adding different weight of aniline 50wt% (a), 60wt% (b), 70wt% (c).

4.4: AC. Electrical Conductivity

The electrical properties of nanomaterials depend upon the morphology, size of particles and method of preparation. The AC conductivity is measured from the dielectric parameters. A pure charge transport mechanism contributes towards the loss mechanism. The AC conductivity (σ_{AC}) is calculated using the relation.

$$\sigma_{AC} = \omega' \epsilon \epsilon_0 \tan \delta \quad (\text{Equ.4.5})$$

where ϵ_0 is the permittivity of the free space, ω the angular frequency and $\tan \delta$ is the loss tangent.

The ac conductivity is measured as a function of frequency at room temperature. The ac conductivity is minimum at low frequency but with the increase of frequency it goes on increasing and then comes a cutoff point at which conductivity becomes zero even at higher frequency. This type of behaviour confirms the semiconductor nature of $\beta\text{-AgVO}_3$ nanowires and polyaniline nanowires [58]. By adding different weight percentage of aniline to $\beta\text{-AgVO}_3$ nanowires the size of the coating increases and it will show the conductivity is decreased and is explained by hopping mechanism. The hopping mechanism is a type of conduction in which carrier transport took place through electrons and hopping takes place from one localized state to another. In semiconductor material the hopping takes place from between the localized states lies within the band gap. At room temperature the mechanism of exciton hopping occurs repeatedly and leading to large hopping distance [59].

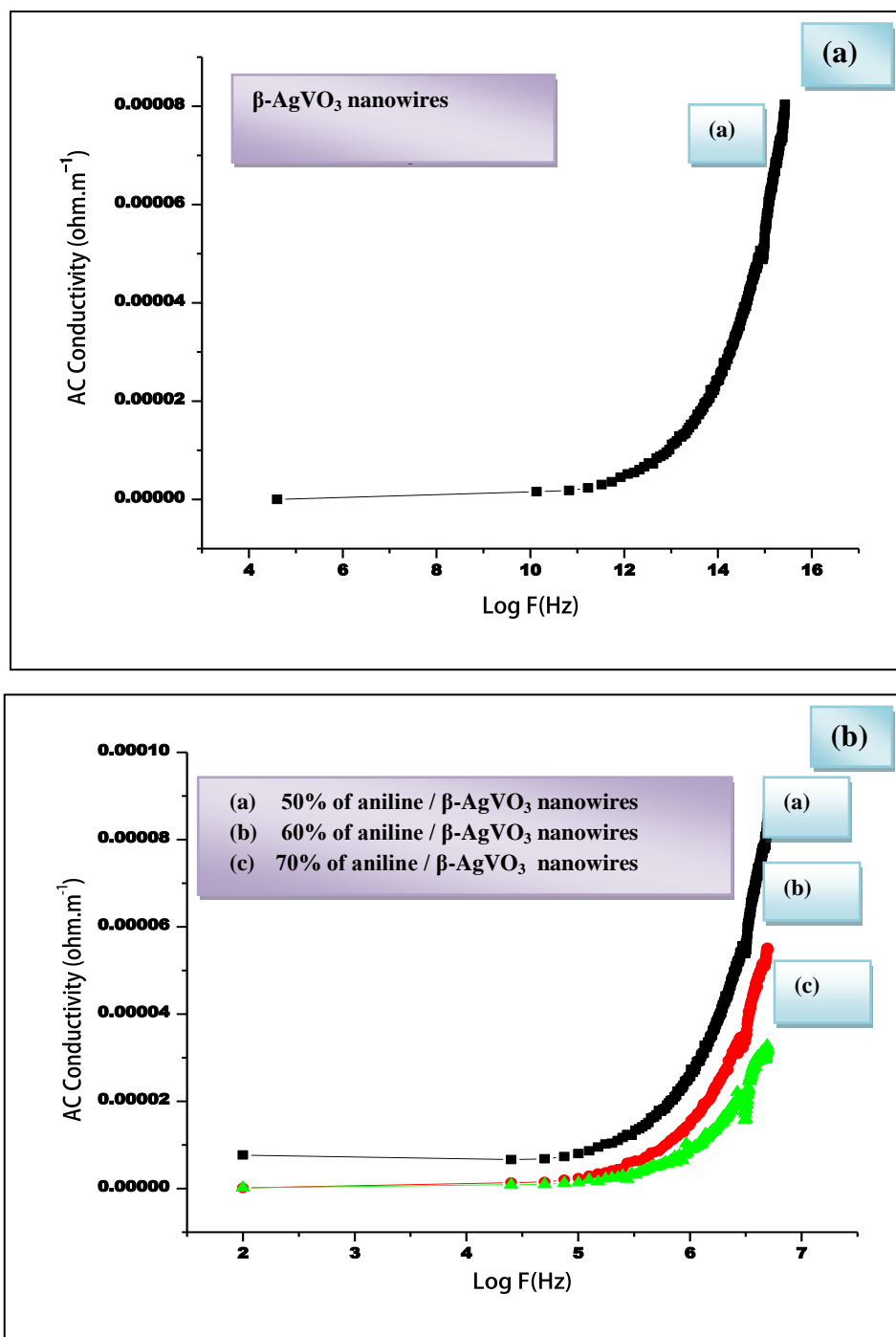


Figure 4.3: Variation of AC conductivity with frequency for β -AgVO₃ nanowires (a) addition of different weight percentage of aniline 50% (a), 60% (b), 70% (c).

4.5: Scanning Electron Microscope (SEM)

The synthesis of nanowires is very delicate and can be controlled by controlling parameters. The controlled morphology of nanowires can be obtained by selecting the method of preparation. The method of preparation and atmosphere affect the parameters of synthesis and properties can be changed. The SEM of prepared samples of silver vanadium oxide nanowires and polyaniline nanowires is done. The samples of silver vanadium oxide nanowires and polyaniline nanowires were dispersed in deionized water and sonicated for an hour. A drop of sample was taken and spread on the glass substrate and dried for fifteen minutes. A thin layer of gold particles was sprayed on the samples to make them conductive. The SEM images showed the controlled morphology with different diameter ranges from 50nm to 82nm, 100nm and 152nm.

Sr.No.	Addition of aniline to β -AgVO ₃ nanowires	Shapes of nanomaterials	Average diameter of nanowires (nm)
1	Without addition of aniline	Thin nanowires	50
2	50% of aniline	Flaky shaped	82
3	60% of aniline	Coral shaped	100
4	70% of aniline	leaf shaped	152

Table 4.2: Different sizes of nanowires with addition of different weight percentages of aniline.

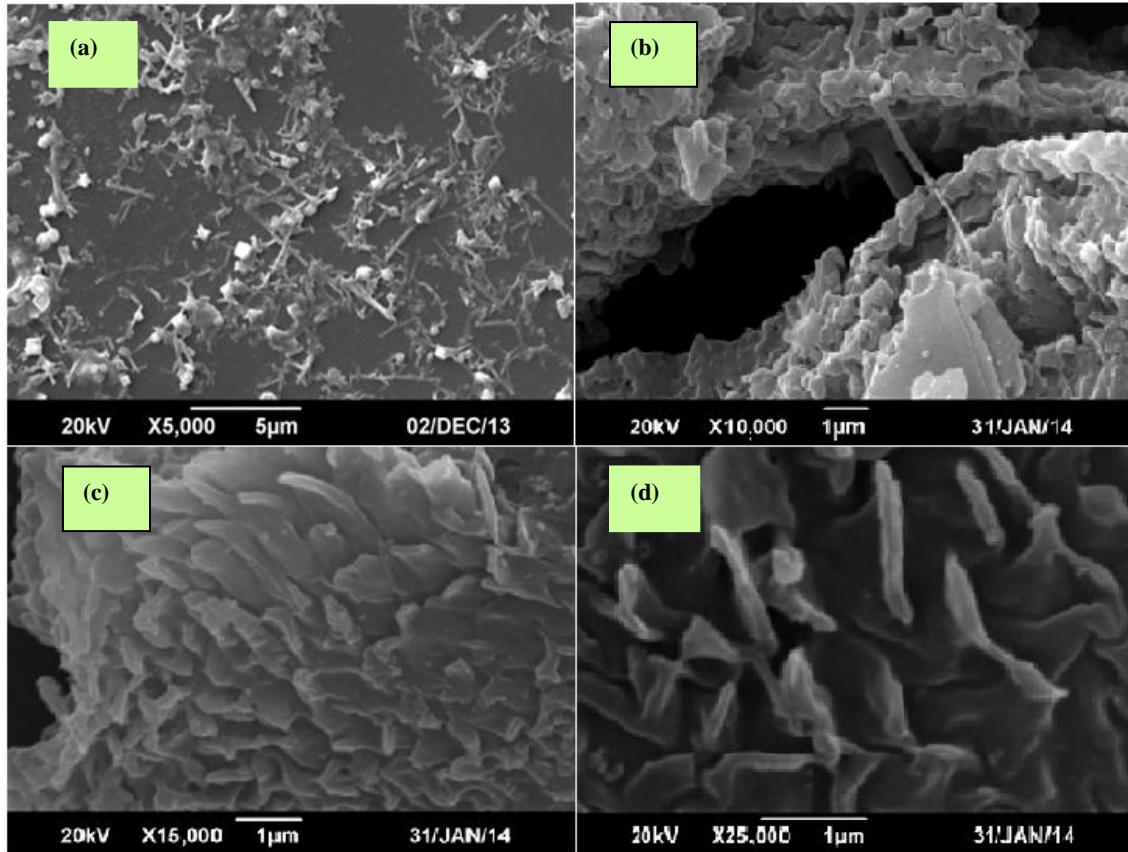


Figure 4.4: SEM morphology of silver vanadium oxide nanowires (a) after adding different weight of aniline 50% (b) 60% (c) 70% (d).

4.6: Dielectric Properties

The dielectric properties of β -AgVO₃ nanowires and polyaniline nanocomposites studied at room temperature as function of frequency. The dielectric properties of pellets were studied in the range of frequency from 100 Hz to 5MHz. The dielectric properties of material was showing its dependence on frequency, increase in frequency caused to reduce the dielectric constant because polarization is reduced at high frequency. This behaviour is in accordance with the Maxwell's Wagner Model. Figure 4.5 (a) plot shows the dielectric constant decreases with the increase in frequency. Figure 4.5(b) shows with the addition of different weight percentage of aniline from 70%, 60%, 50% to β -AgVO₃ nanowires the value of dielectric constant is decreased as 25, 24, 19 with increase in frequency. The material in which 50% of aniline is added has dielectric constant 19 which is less than as compare to material in which 60% and 70% of aniline is added.

Figure 4.6 It displays the plot of Dielectric loss as a function of frequency and shows a trend a dielectric loss is greater at lower frequency but shows loss is smaller at high frequency. This is due to the reason of high resistivity of materials. In Figure (a) the value of dielectric loss for beta AgVO₃ nanowires is 14.5 which decrease with the increase of frequency. In Figure 4.6(b) the pattern of decreased dielectric loss with increase in frequency is observed. As the amount of addition of aniline is changed there is a decrease in the value of dielectric loss. When we added 50%, 60%, 70% of aniline the value of dielectric loss is 0.36, 0.44, 0.45. By comparing the values of dielectric loss the material with addition of 50% of aniline has value of dielectric loss 0.36 as compare to 0.44 and 0.45. It shows material with 50% of aniline is more resistive than 60% and 70%.

At standard temperature 25 °C

Range of frequency (100Hz to 5 MHz)

Sample	Dielectric Constant	Dielectric Loss	AC Conductivity (ohm.m ⁻¹)
(a) β-AgVO ₃ nanowires	300	14	8.07E ⁻⁵

Table 4.3(a): The value of dielectric constant, dielectric loss and AC Conductivity for β-AgVO₃ nanowires(a).

Samples	Dielectric Constant	Dielectric Loss	AC Conductivity (ohm.m ⁻¹)
(a) 50% of aniline	19	0.36	8.57E ⁻⁵
(b) 60% of aniline	23	0.44	5.15E ⁻⁵
(c) 70% of aniline	24	0.45	3.34E ⁻⁵

Table 4.3(b): Affect of 50%(a), 60%(b), 70%(c) of aniline on dielectric constant, dielectric loss and AC Conductivity of β-AgVO₃ nanowires.

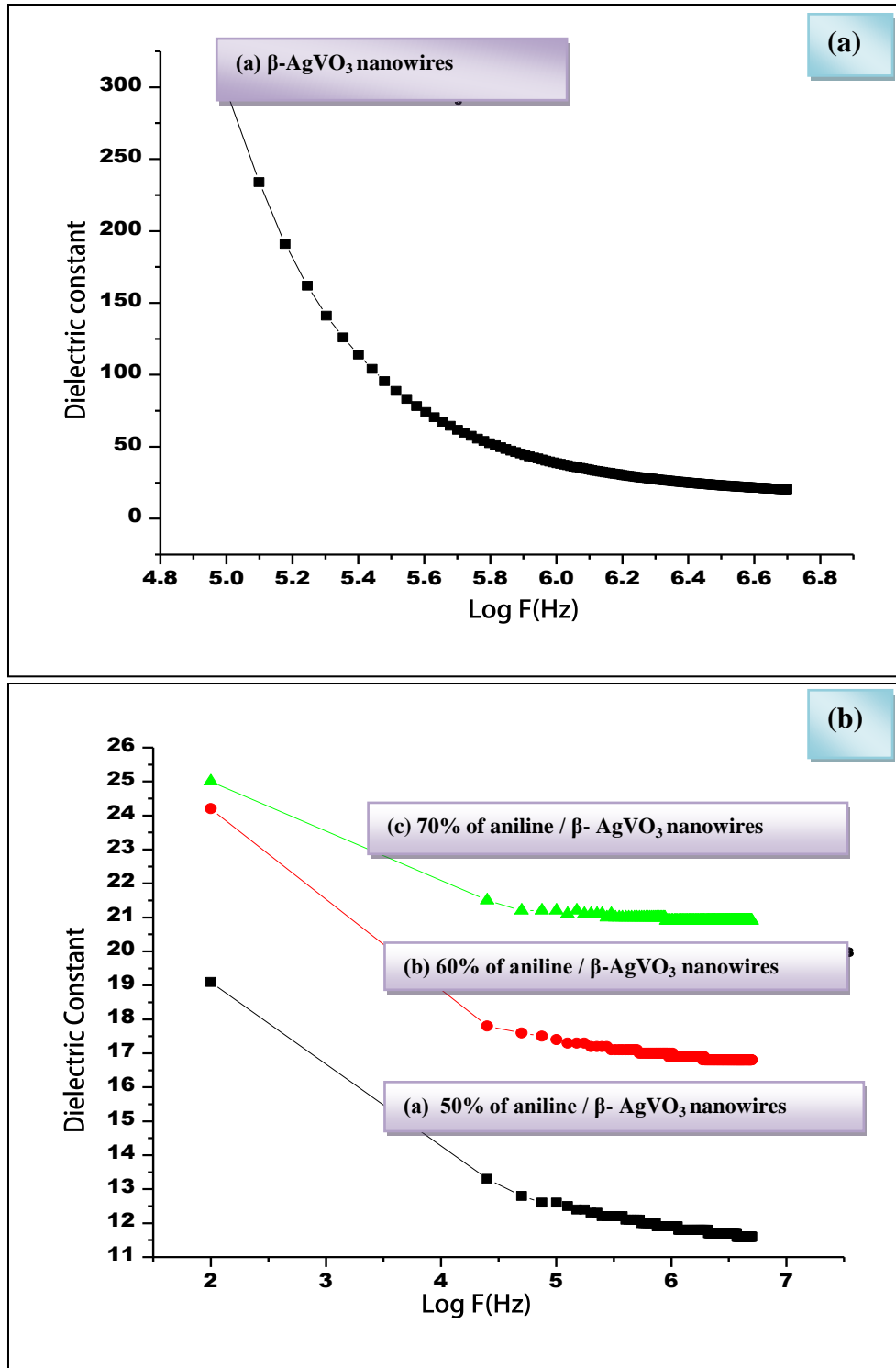


Figure 4.5:Plot of Dielectric Constant vs. Log F for β -AgVO₃ nanowires (a) affect of aniline with 50 % (a), 60 % (b) and 70 % (d).

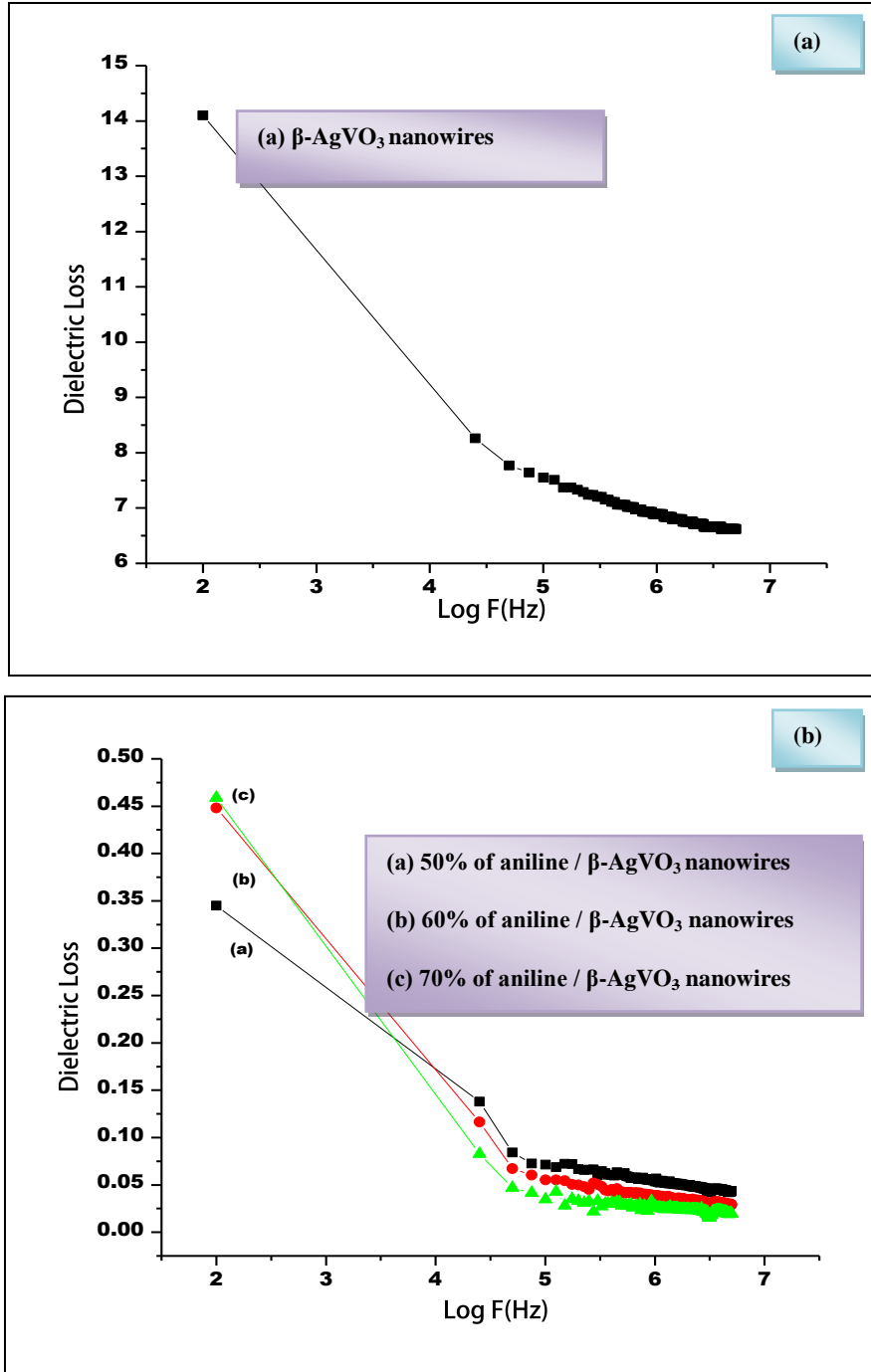


Figure 4.6: Plot of Dielectric Loss vs. Log F for beta AgVO₃ nanowires (a), after addition of aniline affect on dielectric loss ,70% (a) , 60% (b) , 50% (c).

4.7: Optical Properties

The graphical image in Figure 4.7 shows the absorption of β -AgVO₃ nanowires and result after adding aniline to β -AgVO₃ nanowires. The graph shows the absorption of β -AgVO₃ nanowires is 42% but as amount of aniline is changed from 70%,60%,50% to β -AgVO₃ nanowires the absorbance changes to 13%,11% and 10%.The reason for this is as the particle size increases and its band gap decreases due to the effect of polymerization and redox reaction so absorbance increases.

Sr. No.	Samples	Diameter (nm)	Band Gap (eV)
1-	β -AgVO ₃ nanowires	50	2.20
2-	50% of aniline	82	1.17
3-	60% of aniline	100	1.13
4-	70% of aniline	152	1.11

Table4.4 Direct Band gap of β -AgVO₃ nanowires and how it affect after the addition of different percentage of aniline.

Table 1. It shows that as we increases the amount of weight % of aniline to purely synthesized β -AgVO₃ nanowires absorbance is increased. This is confirmation of polymerization and redox reaction in which Ag⁺ ions becomes free and took part in oxidation reaction with aniline monomer[60].The difference between the conduction and valance band is defined by band gap Direct band gap contributes toward application in optoelectronic devices the gap decreases as we go on increasing the wt% of aniline(50%,60%,70%),the range of direct band gap given in the table confirm the successive oxidation reaction because maximum number of electron become free and band gap decreases[61-63].The concept of band gap helps us to understand the interaction of light with material. In case of semiconductor materials band gap is small and electrons can easily move from valance to conduction band at cost of low amount of energy. Similarly as we go in increasing the weight percentage of aniline we get narrow band gaps which would increase the absorption gradually because the particle size has increased. β - AgVO₃ nanowires are coated with layers of conducting polymers the maximum no. of H⁺ ions (No. of

free H⁺ ions becomes greater from structure of aniline as we increases the amount of weight percentage of aniline to purely synthesized β -AgVO₃ nanowires) become free from the structure of aniline(conducting polymer) and attached to the structure of β -AgVO₃ nanowires. From the Beer Lambert law, as the concentration of absorbing species increases absorption also increases. In this work aniline monomers attached to the β - AgVO₃ nanowires and leaving a H⁺ from every single monomer and these form a chain then layers of polyaniline monomers are formed on the β -AgVO₃ nanowires. As the weight percentage of aniline (act as absorbing species) is increased the structure becomes most delocalized due to pi delocalized electron in aniline structure. So, changing from 50wt.%,60wt.% to70wt.% of conducting polymer (aniline) absorption increases due to the delocalized structures from 10,11 to 13 percent.

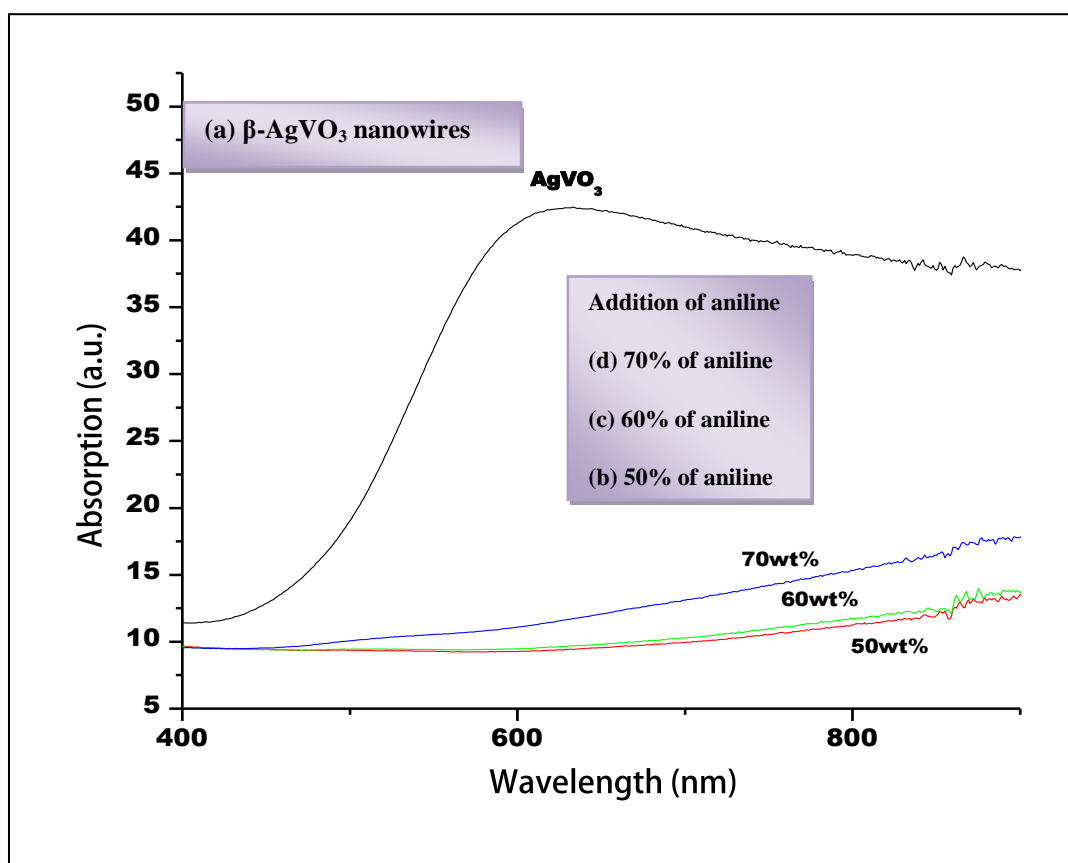


Figure 4.7: Absorption Spectra of β -AgVO₃ nanowires (a) with affect of 50wt%(b)60wt % (c)70wt % (d) of aniline.

4.8: Band Gap Analysis of β -AgVO₃ Nanowires and Polyaniline (β -AgVO₃ nanowires /Aniline Nanocomposites by UV-VIS Spectroscopy

There are two types of optical transition that can occur at the basic edges of crystalline semiconductor: direct and indirect transitions. Both involve the interaction of electromagnetic waves with an electron in the valance band which is raised across a forbidden gap to conduction band. If the exciton formation is neglected the forms of the absorption coefficient α as a function of photon energy $h\nu$ depends on the dependence on energy of $N(E)$ of the bands containing the initial and final stages. For simple parabolic band $N(E)$ is directly proportional to $E^{-1/2}$.

$$\alpha h\nu = (h\nu - E_g)^n \tag{4.5}$$

Where n is a constant of $1/2$ for allowed transitions and $3/2$ for forbidden transitions. $h\nu$ is photon energy and E_g is band gap energy [64].

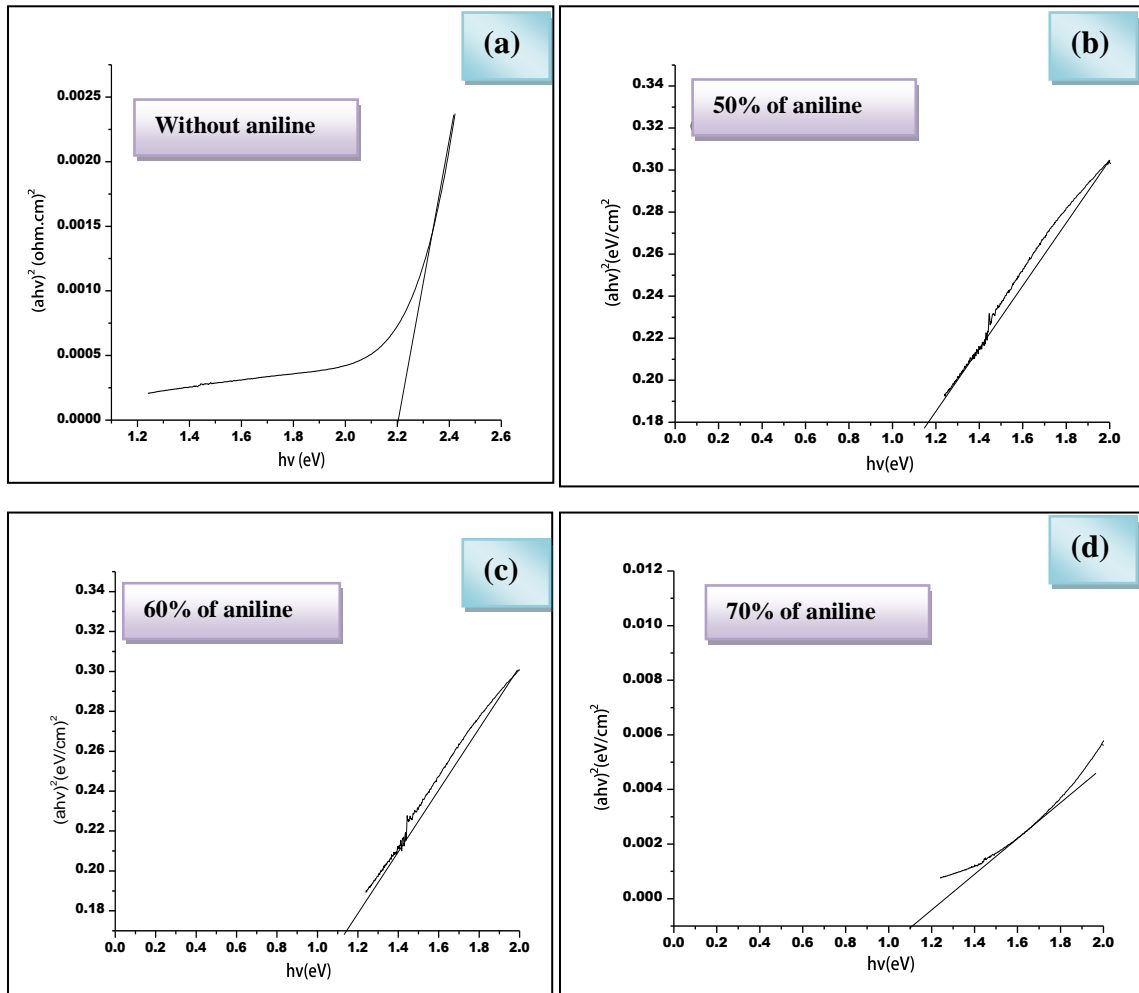


Figure 4.8: Tauc plot for analysis of band gap.

Chapter 5

Conclusions and Future Recommendations

The synthesis of silver vanadium oxide (β -AgVO₃) nanowires (TMO's oxides) are synthesized by hydrothermal reaction and the affect of addition of different weight percentage of aniline to silver vanadium oxide (β -AgVO₃) nanowires and stirring time would change the morphology to Polyaniline nanocomposites. After the addition of 50%, 60% and 70% of aniline to β -AgVO₃ nanowires the optical and dielectric properties are studied and compared to Polyaniline nanocomposites. The study of SEM confirms the morphology of nanowires and polyaniline nanocomposites with different diameter ranges from 50nm to 82nm, 100nm and 152nm.

The XRD study tells crystallographic information about nanowires and nanocomposites. All diffraction peaks of β -AgVO₃ nanowires matches with the indexed β -AgVO₃, having monoclinic structure space group: 12/m (No.12) matching with card No.29-1154. The calculated density of nanowires was found to be 5.45 g/cm³ and measured density is 5.50 g/cm³. The crystallite size is 43nm measured using the full width half maximum for maximum Bragg's reflection (-411) by using Scherrer formula. After addition of different weight percentage of aniline from 50%,60%and70% to as prepared nanowires(taken as standard) the monoclinic structure changed to cubic having space group Fm-3m (225).The calculated density of nanocomposites is 6.30 g/cm³ and measured density was 6.04 g/cm³.The average size of crystalline is found to be 43nm and after addition of different weight percentage of aniline its size changes to 44nm. The intensity peaks were measured between the angle 200° to 800° The cell parameters are measured as a =17.875, b = 3.58, c = 8.03 for monoclinic and a = 4.09, b = 4.09 .c = 4.09 for cubic crystal structure.

The FTIR spectra of β -AgVO₃ nanowires showed their best absorption peaks in the range between 1000cm⁻¹ to 600cm⁻¹.After the addition of aniline, nanocomposites (β -AgVO₃/ aniline) showed the four characteristic peaks at 1147cm⁻¹,1304cm⁻¹,1500cm⁻¹and1589cm⁻¹ can be assigned as C-H plane bending vibration, C-N stretching vibration, benzenoid ring starching mode and quinoid ring stretching mode. The LCR meter measurements give the dielectric properties of

nanowires and improvements after the affect of aniline. The dielectric constant, dielectric loss and AC Conductivity is measured as a function of frequency (100Hz-5MHz) at standard temperature. The dielectric constant of β -AgVO₃ nanowires is measured as 300 but after addition of aniline in different wt.percentage (50%, 60%, 70%) changed to 19, 23 and 24. The dielectric loss of β -AgVO₃ nanowires is 19, after the addition of aniline value of dielectric loss is improved to 0.36, 0.43 and 0.44. The AC conductivity of β -AgVO₃ nanowires is also improved after addition of aniline. The dielectric loss is decreased and AC conductivity increases after addition of aniline to nanowires. The dielectric properties of β -AgVO₃ nanowires are being improved after addition of aniline and would be proved for better replacement material as passive components in electronics.

In this work β -AgVO₃ nanowire is being coated with different percentages of aniline. The diameter of nanowires is 50nm and after the different weight percentage of aniline (50%, 60%, 70%) the diameter is increased to 82nm, 100nm and 152nm. The size of diameter increases then band gap decreases from 2.20eV to 1.17, 1.13 and 1.11eV. The tauc plot is used to study the band gap analysis. The absorption coefficient is being reduced when thickness of material is increased. The reduced band gap with increased diameter materials would be used in application of solar cells.

In future it would become possible to do work on different aspects.

- The dielectric properties of TMO's can also be enhanced and can be explored as high dielectric constant materials.
- The dielectric properties which are temperature dependent can be studied.
- The electrical properties of TMO's can be increased by introducing new species as metal ions, conducting materials. The novel structures can be proved to be better candidate for electronic and optoelectronic devices.
- The optical properties can be studied by increasing and decreasing the band gap of TMO's after addition of conducting polymer and metal ions.

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