Silicon nanowire/TiO_2 heterojunction acting as an efficient UV photodetector

Thesis is submitted in partial fulfilment of the requirement for the degree of

Masters of Technology in

Nanoscience and Technology

By:

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Certificate Of Recommendation

This is to certify that the thesis entitled **"Silicon nanowire/TiO_2 heterojunction acting as an efficient UV photodetector "** has been carried out under our guidance by Ms. **Dipa Bala Sarkar** during the academic session **2020–21** in partial fulfilment of requirement for the award of degree of **Master of Technology in Nano Science and Technology at School of Material Science and Nanotechnology**, Jadavpur University,Kolkata-700032.

In our opinion the work fulfils the requirement for which it is submitted. It is further certified that the materials obtained from other sources have been acknowledged in the thesis.

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I hereby declare that this thesis contains literature survey and original research work by the undersigned candidate, as part of his Master of Technology.

All information in this document have been obtained and presented accordance with academic rules and ethical conduct.

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This foregoing thesis is hereby approved as a credible study of an engineering subject carried out and presented in a manner satisfactory to warrant its acceptance as a prerequisite to the degree for which it has been submitted.

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Dedicated to my beloved

Parents for their endless love,

support and encouragement

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"Work" is a definition of a joint endeavour that requires togetherness not only in respect of spreading our hands towards it but also the knowledge and experience builds its foundation. In this section, I am overwhelmed in all humbleness and gratefulness to acknowledge my depth to all those who have helped me to put these ideas, well above the level of simplicity and into something concrete.

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ABSTRACT

The development of energy-efficient, long-term optical energy detection systems has been prompted by the significant increase in global energy consumption and population over the last decade. UV photodetectors are among the energy detection systems that have attracted potential applications in society, science, and military defence. The research community is currently focused on the development of ultraviolet (UV) photodetectors due to the wide range of applications that photodetectors have in modern society. To achieve higher photosensitivity, a variety of wide-band gap nanomaterials were used for UV detection. Wide band gap semiconductors, such as TiO_2, have unique optoelectronic properties that have led to a wide range of applications in sensors and optoelectronics. TiO_2 have become more popular in a variety of consumer products due to their unique properties resulting from the reduction of material size from the macro to the nano scale. In recent years, there has been a lot of focus on the development of various methods for synthesising TiO_2 nanomaterials as well as its application in various fields. The use of a hydrothermal process to obtain TiO_2 nanomaterials allows for the development of new synthesis methods that feature, among other things, the ability to control properties, repeatability, reproducibility, short synthesis time, low cost, purity, and compliance with the eco-friendly approach criterion.

The work is on metal assisted chemically etched at 60 °C temperature porous silicon nanowires. The etching time is optimized at 60 minutes. Important characterizations are carried out. FESEM image signifies uniform growth of silicon nanowires. Then a seeding layer is deposited on the silicon nanowire. After preparation of seeding layer porous SiNWs/TiO_2 nanowire photodiode were prepared by a combination of hydrothermal synthesis.

The goal of this thesis is to review the current state of the art in the hydrothermal synthesis of TiO_2 nanomaterials by the variation in concentration of time variation. The introduction, properties of TiO_2 nanomaterials, and new applications of TiO_2 nanomaterials are presented in the first section of the thesis. Following that, the properties of the hydrothermal process, reactants, process parameters, and the synthesis mechanism are discussed. Gradually, it moves on to the various characterization instruments that are used, defining not only the basic principles but also their benefits. The final section of the thesis discusses the morphology of products and divides the characterization results into three categories: i) Optical properties through FTIR (Fourier transform infrared spectroscopy), ii) XRD (X-RAY DIFFRACTOMETER), ii) Morphological properties through FESEM (Field emission scanning electron microscopy) and HRTEM, and iii) Electrical properties through I-V (Current-Voltage) characterization, which describes it as a perfect material for photodetection applications.

Keywords: Titanium Dioxide (TiO_2), Hydrothermal synthesis, Optical properties, Morphological properties, Electrical properties

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CHAPTER:1

INTRODUCTION

1. 1.Introduction to Nanotechnology

Tiny is beautiful is a known phrase of the past, but now it has to be replaced with tiny is not only beautiful but also powerful. It is an age of nanotechnology where everything is going smaller and smaller to create big impressions. [1,2] Nanoscience and technology is the study and application of extremely small objects and particles. Nanoscience can be used across all other science fields, such as physics, chemistry, materials science, engineering field, and biomedical field. The prefix 'nano' is derived from the Greek word dwarf. [3] One nanometer is a billionth of a meter or 10-9 of a meter. With the help of Nanoscience and technology, we can see and control individual molecules and atoms. Everything on Earth is made up of atoms—the food we eat, the clothes we wear, the buildings and houses we live in, and our own bodies. But everything cannot be seen with the naked eye. In fact, it's impossible to see with the typical microscopes which are used in colleges. The microscope through which things can be seen at the nanoscale was invented in the early 1980s. However, nanotechnology is not a new discipline. Actually, nanotechnology is the merging of multiple scientific disciplines. It is a combination of physics, chemistry, biology, and engineering. The ideas and concepts behind nanoscience and nanotechnology started with a talk entitled "There's Plenty of Room at the Bottom" by physicist Richard Feynman. Feynman Richard described a process in which scientists can manipulate and control individual atoms and molecules. [4]

Over a decade later, Professor Norio Taniguchi conceived the term nanotechnology. [5] After 1981, with the innovation of the scanning tunneling microscope scientist can "see" and manipulate individual atoms. In this new era, actual modern nanotechnology began.

The year was 1981, the development of the first scanning tunneling microscope by IBM was successful and with the help of it we could finally see the individual atoms and this is where the modern science of nanotechnology began its path. 1989 saw another breakthrough as researchers at IBM spelled out IBM with individual atoms. The distance between the atoms in the pattern was about 50 billionths of an inch. [6] In general, nanotechnology is a technology, which allows for the creation of nanomaterials and also to operate.

1. 2.What makes nanoscience special:

There are various reasons why nanoscience and nanotechnology became so popular and emerging nowadays. Actually, nanoscience and technology is not only working at smaller dimensions, it is the paradigm where the scientist works at the nanoscale.[7-8] Working in nanoscale enables researchers and scientists to look into and utilize the unique physical, mechanical, chemical, and optical properties of materials. Nanoscience and technology is the study of the properties of matter at nanoscale; basically, it focuses on the unique, size-dependent properties of solid-state materials. Researchers and chemists are very excited about nanoscience and technology—if more surface areas are visible to them then they can get more catalytic action and it will help in the research area more. The unique properties of nanomaterials are allocated to quantum effects, larger surface area, and self-assembly. The Quantum effect describes the electron properties in solids. It is done with a great and perfect reduction of particle size. Nanoscience is a mixture of physics, materials science, and biology, which deal with the manipulation of materials at atomic and molecular scales; while nanotechnology is the ability to observe measure, manipulate, assemble, control, and manufacture matter at the nanometer scale.

The same material (e.g. gold) at the nanoscale can have properties (e.g. optical, mechanical and electrical) which are very different from (and even opposite to) the properties the material has at the macroscale. Properties like electrical conductivity, optical property, and mechanical strength change when the nanoscale level is reached: the same metal can become a semiconductor or an insulator at the nanoscale level. In other words, the properties of materials can be size-dependent. Finally, when a bulk material is subdivided into an ensemble of individual nanomaterials, the total volume remains the same, but the collective surface area is greatly increased. Nanomaterials have an increased surface-to-volume ratio compared to corresponding bulk materials. This has important consequences for all those processes that occur at the surface of a material, such as catalysis and detection.

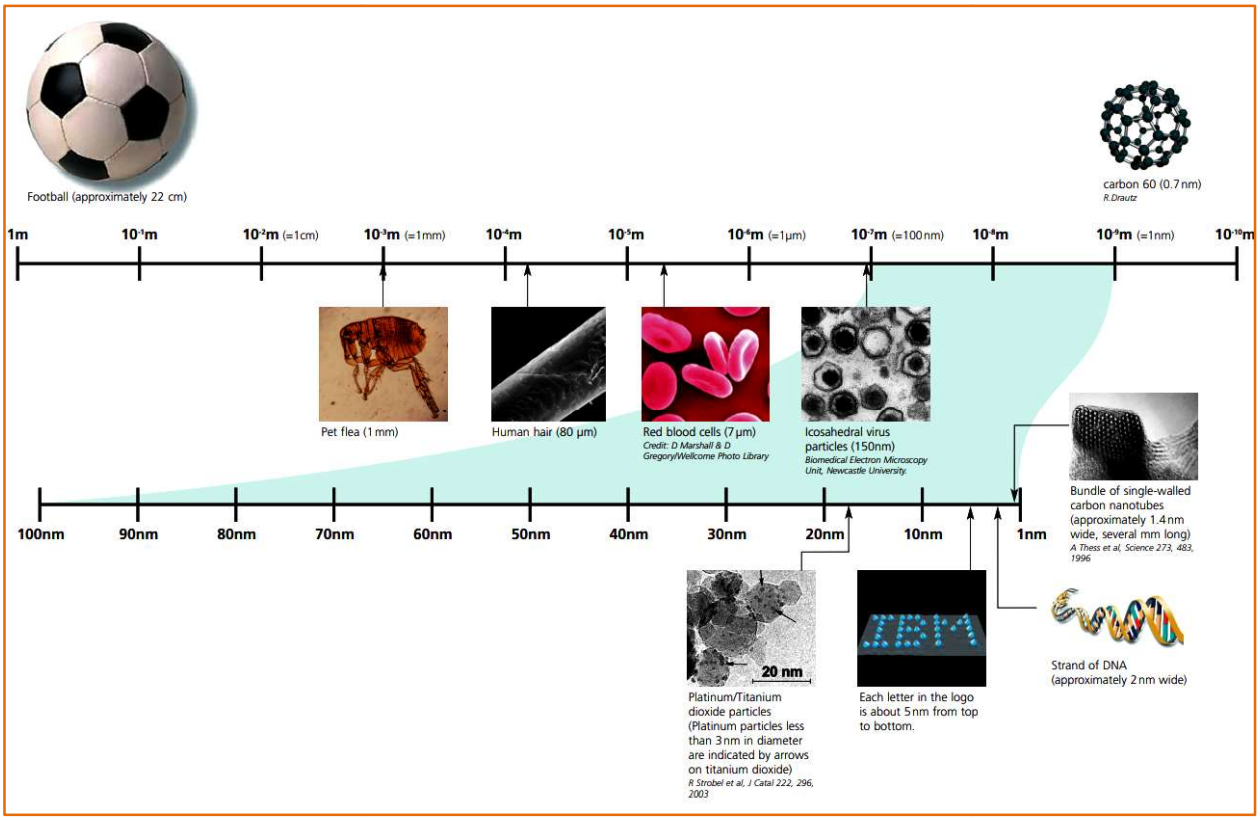


Fig1. 1: Size comparison of Nanomaterials, Schematic diagram(Length scale showing the nanometer in context) [9]

1. 3.History of Nanotechnology

The word "nanotechnology" was introduced for the first time into the scientific world by N. Taniguchi at the international conference on industrial production in Tokyo in 1974 in order to describe the superthin processing of materials with nanometer accuracy and the creation of nano-sized mechanisms.

Ideas of nanotechnological strategy, which were put forward by Feynman, were developed by E. Drexler in his book "Vehicles of creation: the arrival of the nanotechnology era" published in 1986. [10-15]

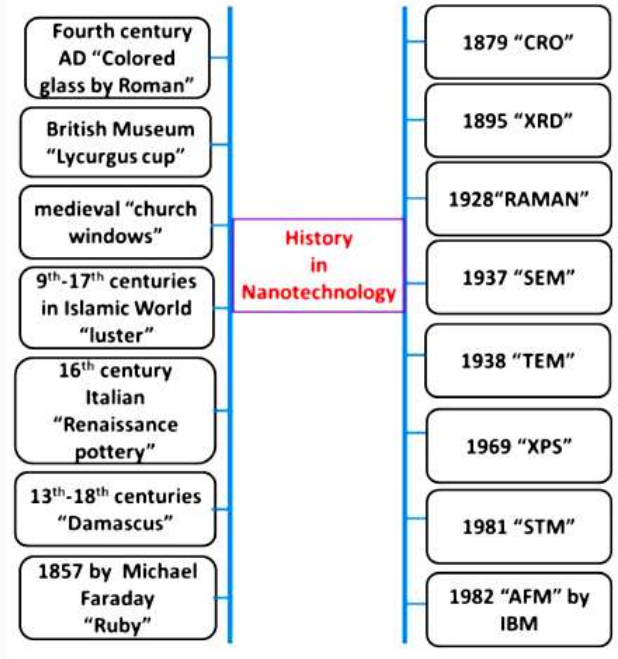


Fig1. 2: History in Nanotechnology

The first mentioned of purposely created and applied technological process, which was termed as nanotechnology. This nanotechnology is usually connected with the well-known lecture of Mr. R. Feynman, a professor at the Californian institute of technology, delivered in 1959 at the session of the American Physical Society. For the first time, the possibility to create nanosized products with the use of atoms as building particles was considered in a lecture at this session. Nowadays this lecture is referred to as the origin of the nanotechnology paradigm.

From the second half of the 1980s to the early 1990s a number of important inventions were made, which created an impact on the further development of nanotechnology. Since then, nanotechnological begins to grow, the number of publications on nanotechnological subjects increases sharply, the practical application of nanotechnology expands; project financing in nanotechnology increases significantly, and many number of organizations and countries involved in it. In 1991 the first nanotechnological program of the National Scientific Fund started to operate in the USA. In 2001 the National Nanotechnological Initiative (NNI) of the USA was approved. The principal idea of this program was formulated as follows: "National Nanotechnological Initiative defines the strategy of interaction between federal

departments of the USA for the purpose of prioritizing nanotechnology development, which should become a basis for the economy and national security of the USA in the first half of the 21st century". [16]

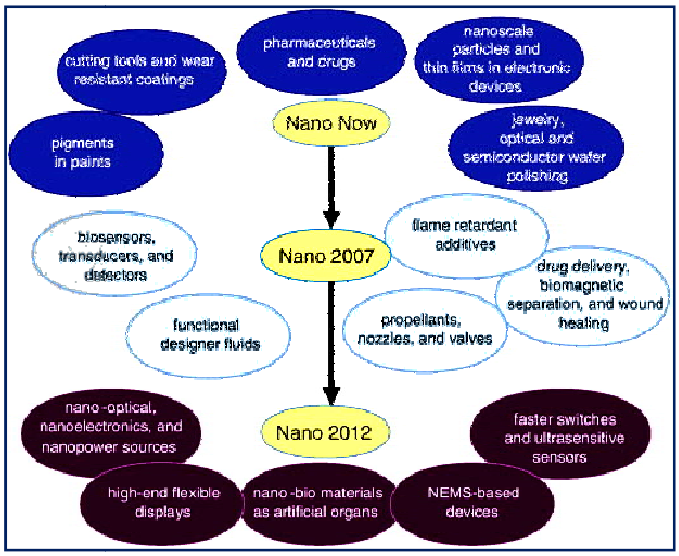


Fig1. 3: Evolution of Nanoscience and Technology.

In Germany research in nanotechnology is supported mainly by the Ministry Of Education, Science, Research, and Technology. In England, nanotechnology development is supervised by the Council of Physics and Technology Research and by the National Physical Laboratory. In France, the nanotechnology development strategy is defined by the National Center of Scientific Research. More and more attention is given to nanotechnology development in China, South Korea, and other emerging countries. Recently nanotechnology research began in the CIS countries, usually within the framework of state scientific programs. As in the USA, considerable attention to nanotechnology development is given in Japan. In 2000 the Japanese Economic Association organized a special department on nanotechnology under the auspices of the Industrial and Technical Committee, and in 2001 the Framework Plan of nanotechnology research was developed. The nanotechnology paradigm was formed at the turn of the 1960s, while the 1980s and 1990s are the start of the development of nanotechnology in its own right. Accordingly, the whole period up to the 1950s may be called as pre-history of nanotechnology. The end of this period was the appearance of conditions for managed nanotechnology development,

which was facilitated by the scientific and technical revolution, by which the second half of XIX and the beginning of XX centuries were marked. [17-20]

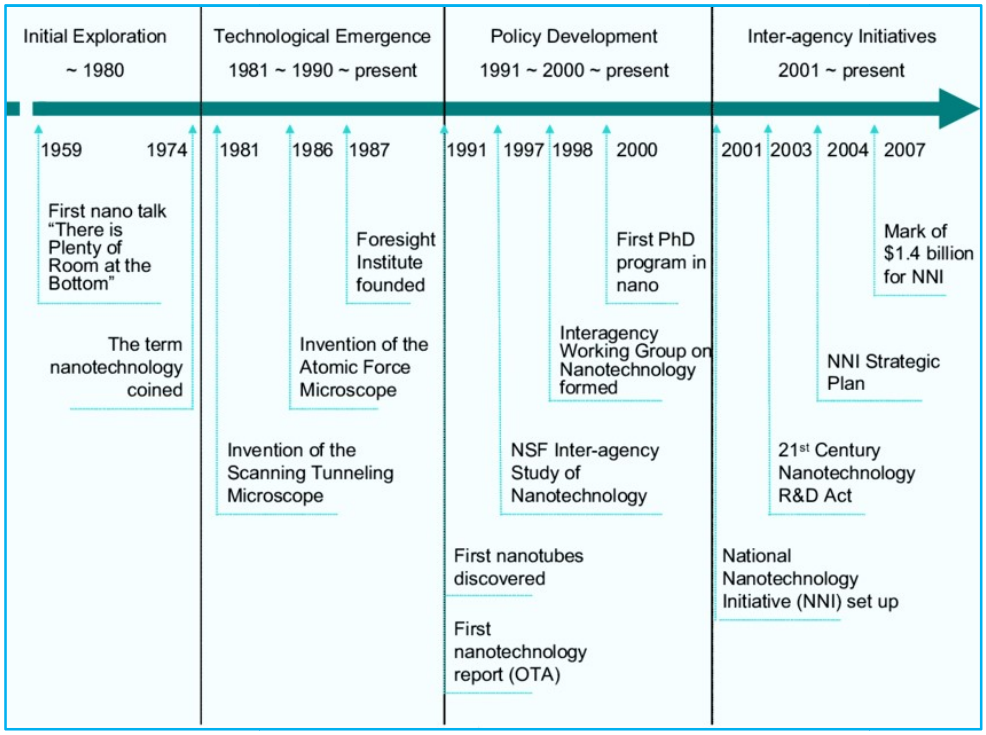


Table1.1: Milestone in the history of Nanotechnology [21]

In 1857 Michael Faraday discovered colloidal "ruby" gold, demonstrating that nanostructured gold. In 1936, Erwin Müller, working at Siemens Research Laboratory, invented the Field Emission Microscope. In 1956, Arthur von Hippel introduced the term—"molecular engineering". Jack Kilby of Texas Instruments originated the concept of, designed, and built the first integrated circuit in 1958. [22]

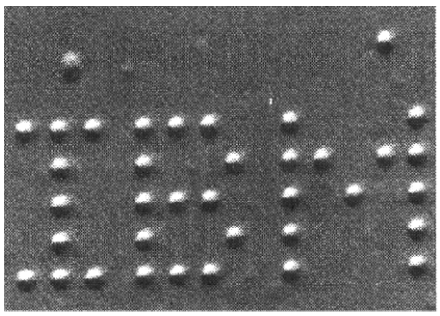


Fig1. 4: "IBM" spelled out by by individual xenon atom (Image magnifies approx. 2.9 million times) [23-24]

1. 4.Importance of Nanoscience and technology:

Nanoscale science and technology is nothing but simply science and engineering that deals with the nanometer scale, 10^{-9} meters. [25] In the last two decades, scientists and researchers started developing the power to operate and handle the matter at the level of single atoms and small groups of atoms and to characterize the properties of materials and systems at that scale. This potentiality has led to the amazing discovery that congregates of small numbers of atoms or molecules which often have properties (such as strength, optical absorption, and conductivity, electrical resistivity) that are remarkably distinctive from the properties of the same matter at either the single-molecule scale or the bulk scale. For example, carbon nanotubes are much less chemically reactive than carbon atoms and combine the characteristics of the two naturally occurring bulk forms of carbon, strength (diamond) and electrical conductivity (graphite). Additionally, carbon nanotubes conduct electricity in only one spatial dimension, along one axis, but in case of graphite, it conducts electricity in three dimensions. Nano-science and engineering also work towards to discovering, narrating, and manipulating those distinctive properties of matter at the nanoscale for the sake of developing new capabilities with potential applications across all fields of science, engineering, technology, and medicine.

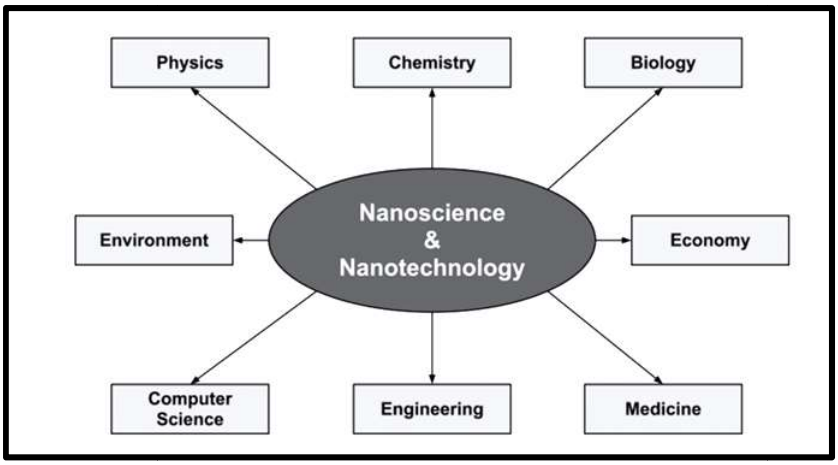


Fig1. 5: Multidisciplinarity areas of nanotechnology[26]

❖ Importance in Electronics and IT areas:

Information technology is a rapidly growing industrial sector. It is an important sector with a high rate of innovation. Expansive progress has been made by adapting nano-based electronics. Nanoscience and technology have created an enormous change in information technology. [27]

❖ Developments

Evolution is taking place on ultra-integrated (Opto) electronics combined with powerful wireless technology as ultra miniaturization. The design of innovative sensors, production of cheap and powerful circuits, novel system architectures using nanotechnology for future DNA computing which is an interface to biochemical processes, and quantum computing which can solve problems for which there are no efficient classical algorithms. Due to the development of nanoelectronic components, quantum cryptography for military and intelligence applications is emerging.

❖ Memory storage

Before the emergence of nanotechnology memory storage was dependent on transistors but now reconfigured arrays are developed where a large amount of data can be stored in a small space. Each and every single nano bit of a memory storage device is used for preserving information.

❖ Semiconductors

For fabrication of semiconductor devices chip embedding and sometimes nano amplification can be utilized. This nano amplification and chip building smoothen the flow of electric charge. To reduce the size of the processor integrated nanocircuits can be used in silicon chips.

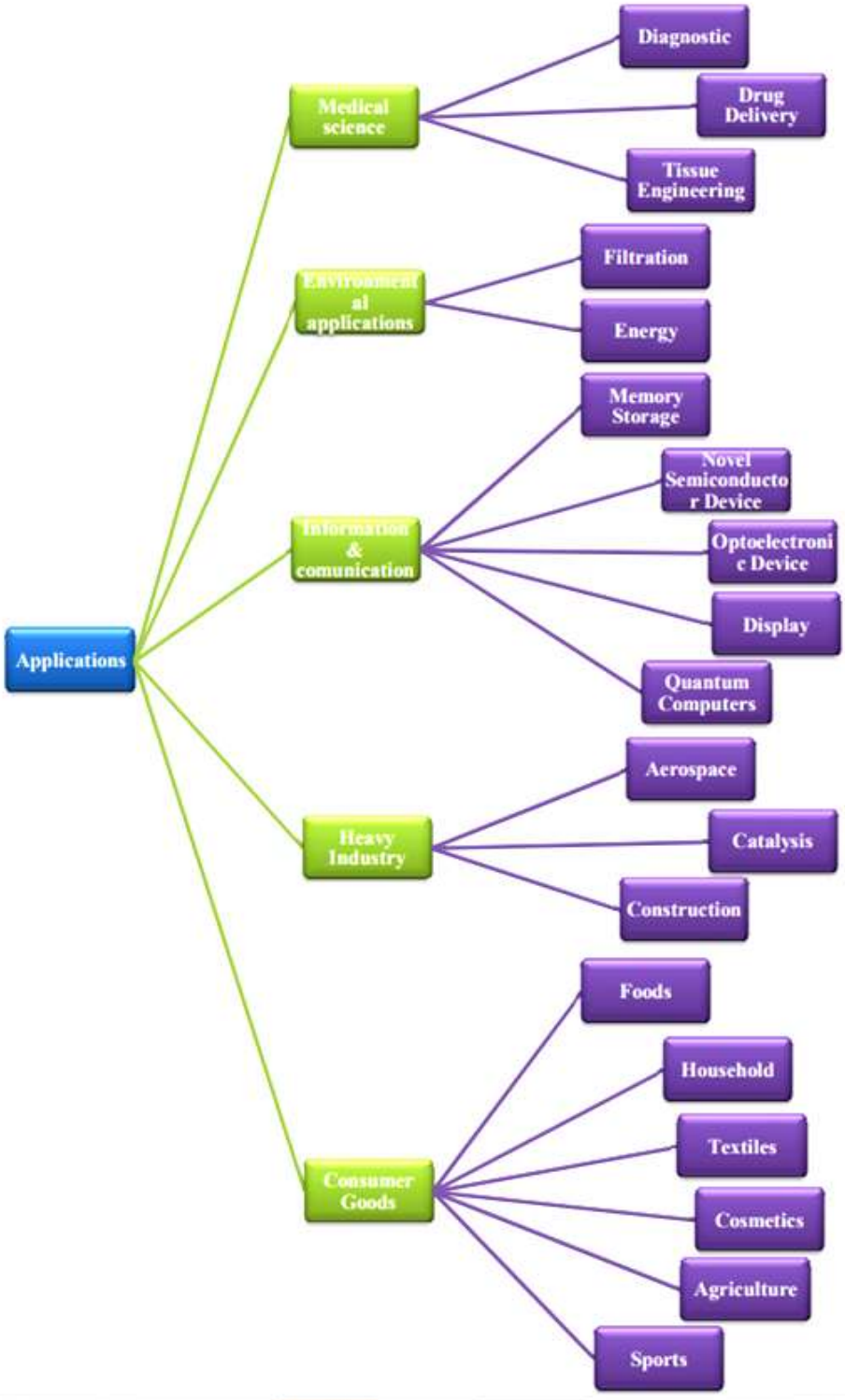


Fig1. 6: Application of Nanoscience and Technology

- **Display and audio devices**

  As a result of the enhancement of nanotechnology resolution of picture and picture quality has improved.Nanopixelation of devices makes pictures actual and non-fictional. Likewise, frequency modulation in audio devices has been computerized and digitized to a billionth bit of signals.

- **Transmission and Data processing:**

  Optoelectronic and optical components are expected to lead to lower cost or more precise processes in the field of manufacturing technology and in the field of data processing and transmission development of electronics. Using carbon nanotubes, quantum dots development of nanoscale logical and storage components are made for the currently dominant CMOS technology. Photonic crystals possess the potential for use in entirely optical circuits. It is the basis for future information processing based solely on light (photonics). Nanotechnology can be used to fabricate electronic components adding new properties and characteristics at the atomic level in molecular electronics with potentially high packing density. Faster, better and smaller components based on quantum mechanical effects, new architectures, and a new biochemical computing concept called DNA computing are possible with nanotechnology. The new phenomenon is called the "quantum mirage" effect which enables data transfer within future nanoscale electronic circuits.

1. 5.Properties of Nanoparticles:

- The percentage of [28] atoms at the surface of bulk materials larger than one micrometre (or micron) is insignificant in comparison to the number of atoms in the bulk of the material. The large surface area of the material, which dominates the contributions made by the small bulk of the material, is thus largely responsible for the interesting and sometimes unexpected properties of nanoparticles. Because nanoparticles are small enough to confine their electrons and produce quantum effects, they often have unexpected optical properties. Quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles, and super para-magnetism in magnetic materials are examples of size-dependent property changes in nanoparticles.

- A bulk material should have constant physical properties regardless of size, but size-dependent properties are frequently observed at the nanoscale. As a result, as a material's size approaches the nanoscale and the percentage of atoms on its surface becomes significant, its properties change.
- The percentage of atoms at the surface of bulk materials larger than one micrometre (or micron) is insignificant in comparison to the number of atoms in the bulk of the material. The large surface area of the material, which dominates the contributions made by the small bulk of the material, is thus largely responsible for the interesting and sometimes unexpected properties of nanoparticles.

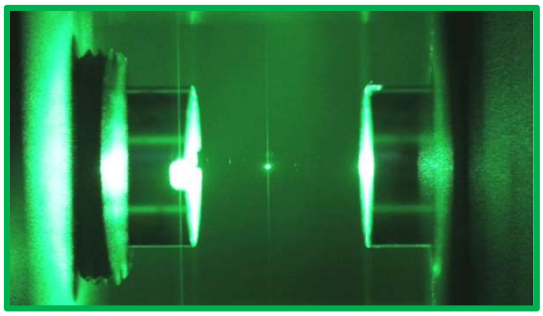


Fig1. 7: Glass nanoparticle suspended in optical cavity[29]

- Nanoparticles of yellow gold and grey silicon are red in colour; gold nanoparticles melt at much lower temperatures (nearly 300°C for 2.5 nm size) than gold slabs (1064°C), and solar absorption in photovoltaic cells is much higher in nanoparticle-based materials than in thin films of continuous sheets of material; the smaller the particles, the greater the solar absorption.
- Nanoparticle suspensions are possible because the particle surface's interaction with the solvent is strong enough to overcome density differences, which would otherwise result in a material sinking or floating in a liquid.
- Nanoparticles have a large surface area to volume ratio, which provides a powerful driving force for diffusion, especially at high temperatures.
- Nanoparticles often have unexpected optical properties because they are small enough to confine their electrons and produce quantum effects. In solution, gold nanoparticles, for example, appear deep red to black.

- Furthermore, nanoparticles have been discovered to impart additional properties to a variety of everyday products.

1. 6. Synthesis of Nanomaterials:

The synthesis mechanism of nanomaterials can be categorized into two types [30-31]

- Bottom-up: Smaller components arranged to bulk assemblies such as the formation of carbon nanotubes.
- Top Down: Creation of smaller materials from larger ones

The synthesis of these nanomaterials is classified into 3 methods:

- Physical
- Chemical
- Biological.

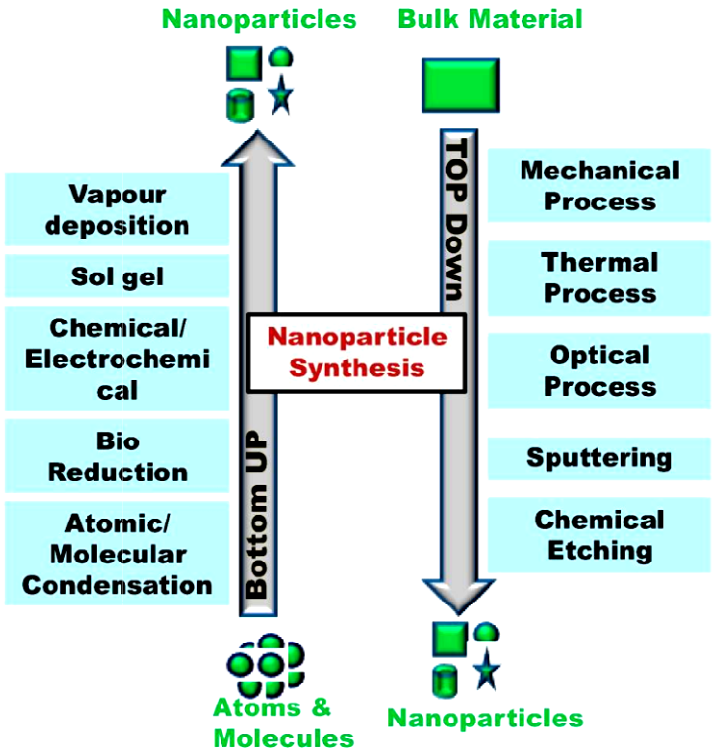
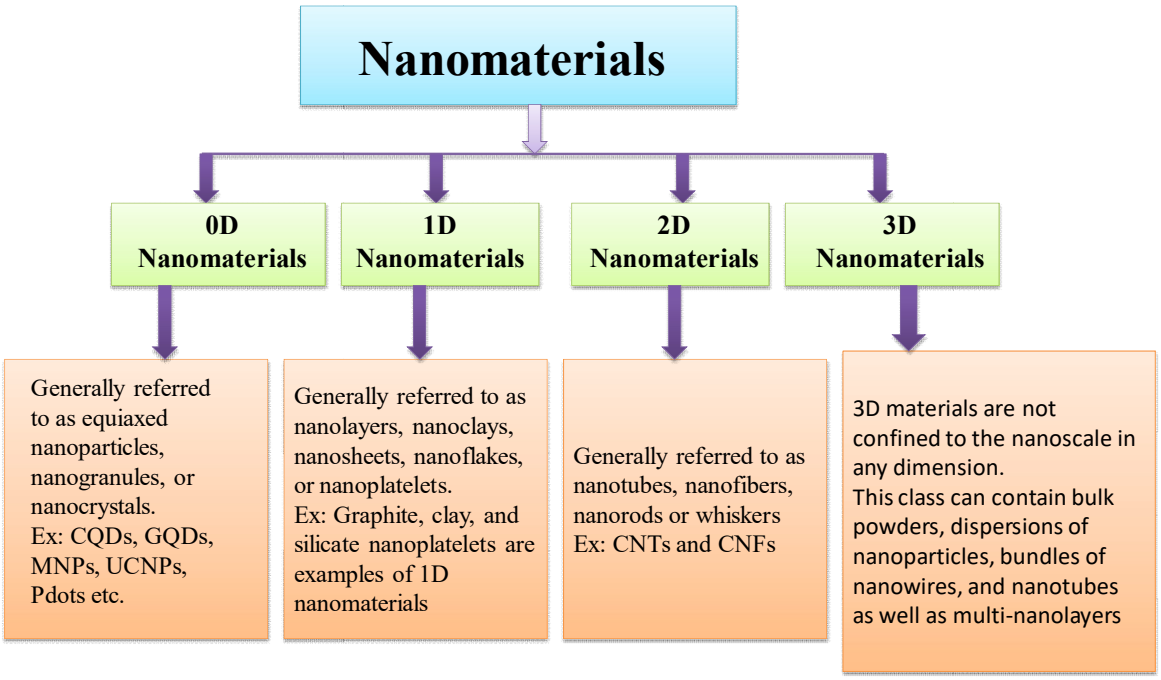


Fig1. 8: Synthesis of Nanomaterials through bottom up and top down technique

Based on nanoparticle geometry, nanomaterials are classified as 0D,1D, 2D, or 3D. [32-34]



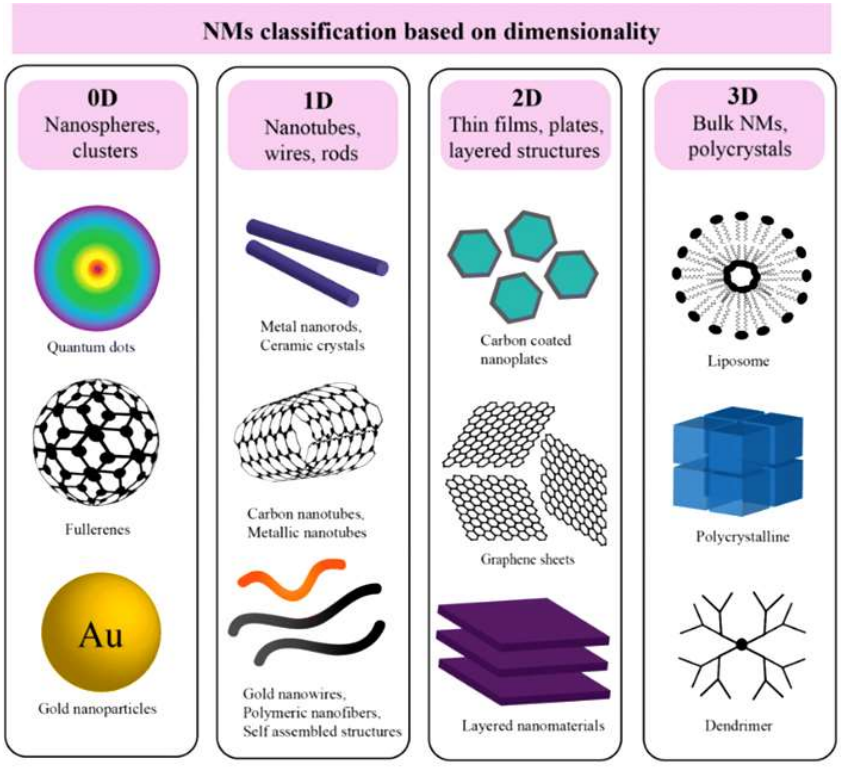


Fig1. 9: Schematic illustration of the relative dimensions of the nanoparticles with examples of each category

1. 7. Application of Nanotechnology:

Nanotechnology has a greater impact on our lives. The applications of nanotechnology are extensive and have a worldwide impact. Nanotechnology eventually furnish with the capability to design custom-made materials and products with new boosting properties, new nanoelectronics components, new types of ―smart medicines and sensors, and even interfaces between electronics and biological systems. Nanotechnology provides a novel and better approach to cancer diagnosis and treatment. Nanotechnology presents a number of biological processes and tools and also provides faster, smaller and more powerful computers. It presents carbon nanotubes which plays an important role in maintaining the development of computer power.

A lot of daily commercial products rely on nanotechnology in market. The transparent nanoparticles or membranes on computer screens, glasses, windows, cameras and other surfaces can help make them resistant to UV or IR radiation, anti-reflective, conductive to electricity waterproof, or scratch-resistant.

Nanotechnology topped the list of scientific and research interests in many countries of the world. Nanotechnology is being used in a variety of fields of research, with a variety of unique applications. When a particle is shrunk to the nanoscale, the material's properties change in proportion to its size. As a result, it opens up new possibilities in a variety of fields. Because the surface to volume ratio increases as the size increases, there is more surface area to react. The diameter or size of particles has an impact on a number of optical and mechanical properties.

It covers a wide range of topics, from traditional device physics to completely new approaches based on molecular self-assembly, from nanoscale materials to determining whether we can control matter at the atomic level. It can make a variety of new materials with a wide range of applications, including medicine, biomaterials, electronics, and energy production. However, nanotechnology raises numerous concerns about the toxicity of nanomaterials, their impact on the environment, and their implications for global economics.

Nanotechnology in Medical Science: Near infrared-laser-heated gold-silica nanosheets are being used to destroy tumours in prostate cancer patients. Different types of nanoparticles are also being developed for targeted drug delivery in cancer therapy. This technology has helped to detect some diseases through a "Nanobiotix" sensor. In addition, it has been used in the treatment of cancer, where gold-plated nanoparticles are used to destroy cancer cells. [35,36]

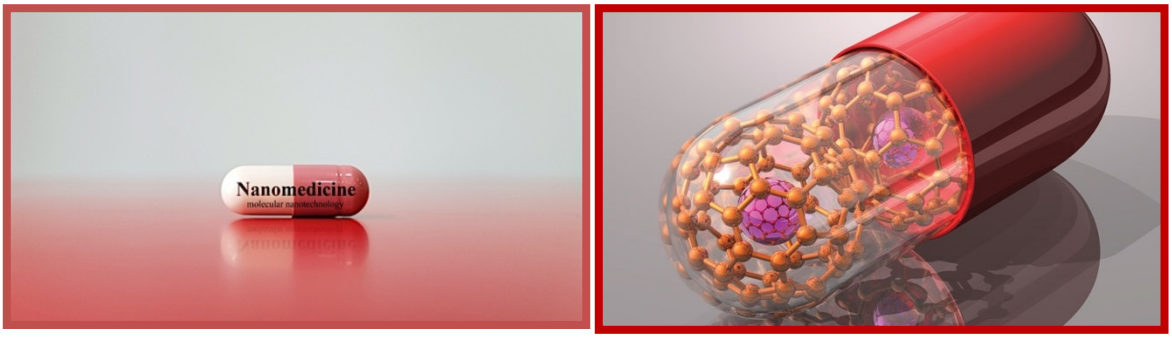


Fig1. 10: Nanotechnology is used in manufacturing medicine

At the University of Bari Italian researcher, Silvano Dragonieri invented an electronic nose using carbon nanotubes. It helps to diagnose cancer tablets by analyzing the air coming out of the lungs during the exhalation process. [37-40]

Nanotechnology in Industry: Lithium-ion batteries have a higher capacity and a faster rate of discharge than traditional batteries. As an energy storage device, PV solar cells, photo capacitors, and supercapacitors are used [41].

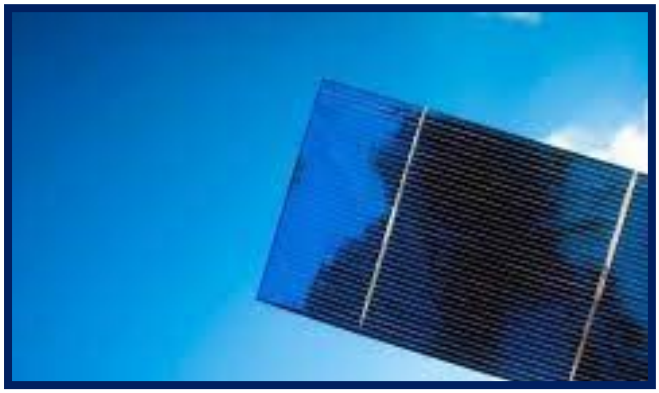


Fig1. 11: Graphene-based solar system

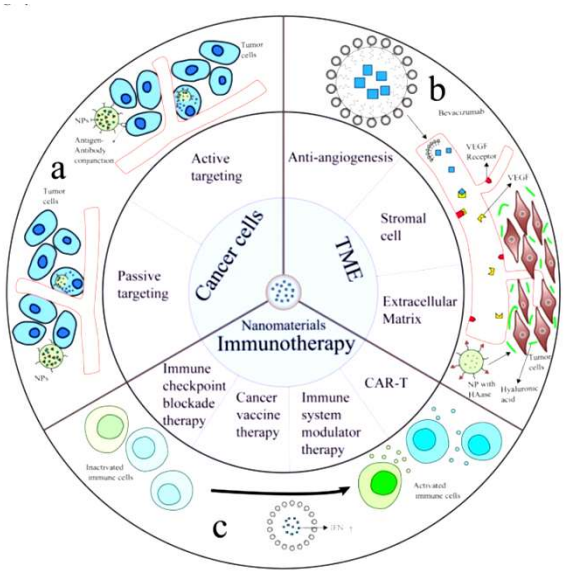


Fig1. 12:Cancer treatment approaches based on nanomaterials. a Targeting cancer cells by passive targeting or active targeting. b Targeting TME including anti-angiogenesis, stromal cell and extracellular matrix. Bevacizumab was loaded in liposomes and conjugated with VEGF to inhibit angiogenesis. HAase was modified onto the NP surface and enhanced NP penetration ability. c IFN-γ as an immune modulator delivered by liposomes activated immune cells in cancer immunotherapy. HAase: hyaluronidase; IFN-γ: Cytokine Interferon gamma; NP: nanoparticle; TME: tumor microenvironment; VEGF: vascular endothelial growth factor [42]

Nanotechnology in Agriculture: Nanotechnology introduced innovative methods and techniques in agricultural sector.In many developed countries, nanotechnology is trying to improve accurate and errorless farming techniques, resist environmental pressures and intensify plant capacity to absorb nutrients.

Nanotechnology for sustainable energy: Through the use of less fuel-efficient nanostructures nanotechnology has helped to improve the aircraft and automobile industry. Nano-sensors based on silver, copper and a variety of other nanowires are used in space, automobiles, and robotics applications. [45]

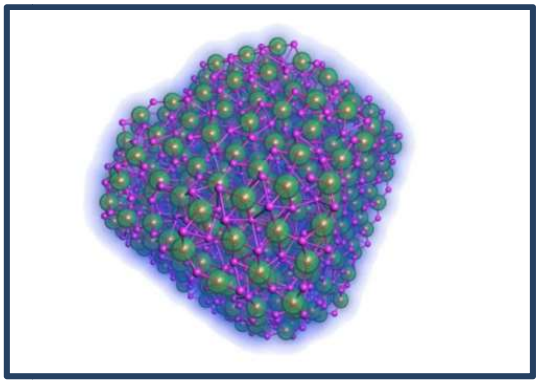


Figure1. 13: Nanoparticle matrices in battery electrodes can drastically increase their ability to store lithium ions, increasing the storage density of the battery [43]

Nanotechnology in Aeronautics: The National Aeronautics and Space Administration (NASA) manufactured ultra-precision nanotechnology machines for injection into astronaut bodies to monitor health conditions.

Nanotechnology in Defence and Security: Nanotechnology will improve future combat soldiers' protection, lethality, endurance, and self-supporting capabilities. Threat detection, novel electronic display, and interface systems, as well as a key role in the development of miniaturized unmanned combat vehicles and robotics, are all expected to be significant benefits.

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CHAPTER:2

Literature Review Of Silicon Nanowire and TiO_2

2.1. Review of Past Work of Silicon nanowires:

Nanotechnology is a current emerging branch of technology, which bears high-level expectations of its prospective to change the world radically. Nanotechnology development is in its early phase. There is some uncertainty on its potentiality, benefits, and risks. Some technology developers speak about "the Next Industrial Revolution". Although, the evolution of nanotechnology is in an early state. Nanomaterials and silicon nanowires are extensively using in worldwide. Nanomaterials (NMs) have acquired eminence in technological improvements due to their tunable chemical, biological and physical properties with better performance. Nanomaterials are classified based on their shape, size, composition, and origin. Due to expanding the growth of production of Nanomaterials and their commercial and industrial applications toxicity related to nanomaterials are inevitable. Silicon nanowire also abbreviated as SiNWs, have an unique quasi one-dimensional electronic structure. It has a high surface-to-volume silicon ratio.As a consequence, silicon nanowire-based devices can conquer their conventional counterparts in various ways. SiNWs are playing a key role in many applications exp. solar cells, sensors, catalysts, and lithium batteries.

Some technology developers assert that nanotechnology is a particular and separate domain of research. Nanotechnology is said as a general purpose technology (GPT). Basically, GPT has three features or characteristics.

These three features are:

a)Pervasiveness

The quality to functioning of a large segment of products and production systems,

b) Scope for improvement

Breakthrough technology which is used for advancement,

c) Innovation spawning

Develop new technologies that directly or indirectly taken from the past major invention

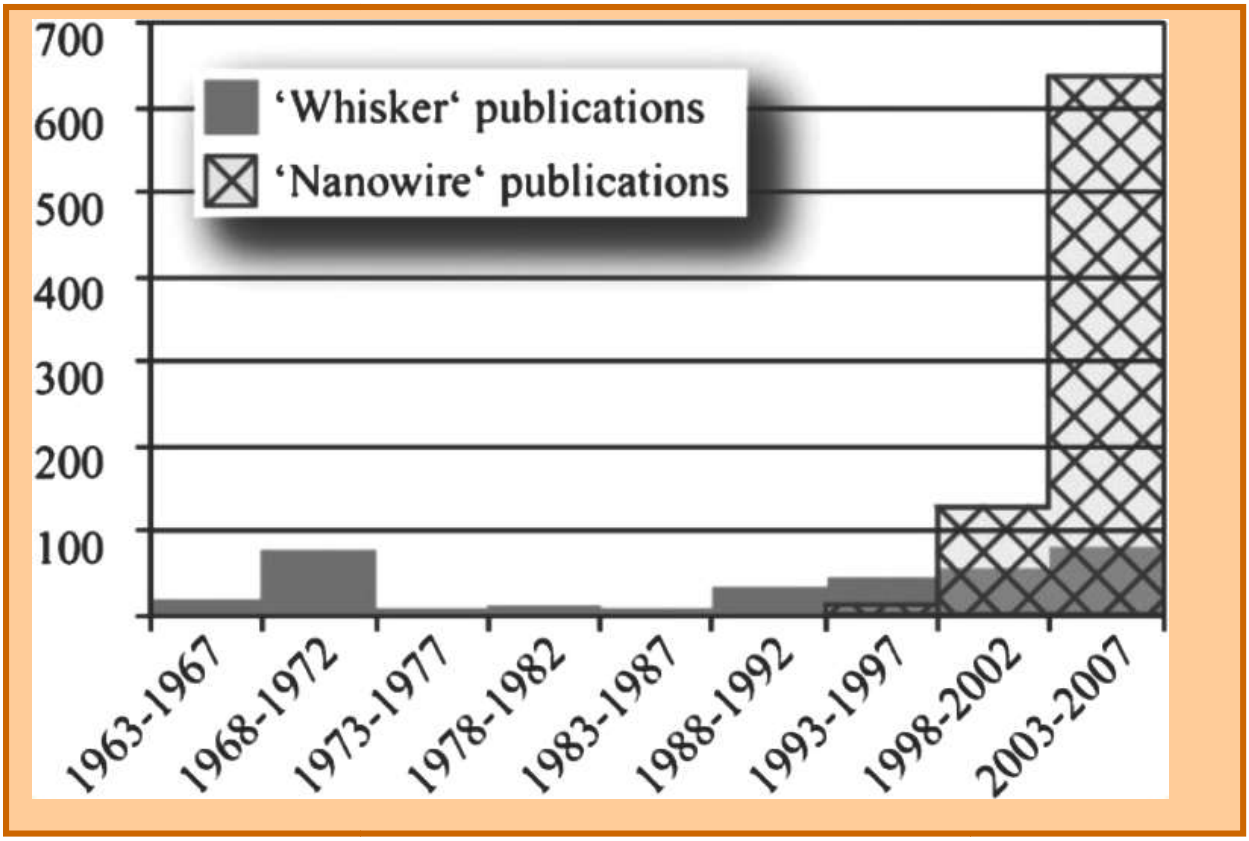

Fig2. 1: Histogram of Silicon "whisker" and "nanowire" publications

Many researchers gave opinion that nanotechnology is just a new dimension that put on research projects in related fields of science – such as physics, electrical engineering,biomedical engineering, chemistry, and materials science.

- R.S.Wagner and W.C.Ellis reported the synthesis of silicon nanowires (SiNWs) for the very first time via (VLS) vapor– liquid–solid growth. They used gaseous silane (SiH4) as a precursor and gold (Au) nanoparticles as catalysts [1].
- Dimova-Malinovska et al. reported fine silicon layers were fabricated. The fabrication was done by the etching of aluminum (Al) covered Silicon substrate in a solution that is a combination of HNO_3, HF, and H2O. He did this for both p-type Si and n–p Si junctions. [2]
- Li and Bohn first explored the extensively and universally used metal-assisted chemical etching method(MACE) [3]. Depending on the classification and category of metal deposited and Si doping type and doping quantity and amount, porous Si with individual morphologies were constructed.

Metal-Assisted Chemical Etching (MACE) is a simple and cost-effective process through which semiconductors (mainly silicon) are chemically etched in several steps.

By Metal-Assisted Chemical Etching (MACE) different Si nanostructures can be fabricated with the suitability to control numerous parameters.[4]

- Lu et.al. investigated their interesting and fruitful field emission properties.Lu et.al. explored arrays of silicon nanowire (SiNWs) in 2003. This array was produced by a new technique named Chemical Vapor Deposition (CVD process) without catalyst. This method is exemplified as an efficient approach to the production of highly ordered and isolated nanowires arrays. [5]
- A taper-like SiNWs was synthesized by Chueh et al. The SiNWs was annealed by high-density FeSi2 nanodots on (001)Silicon. It was annealed at 1200 °C in N2 ambient. The taperlike Si nanowires exhibit a turn-on field of 6.3–7.3 V/μm generating a current density of 0.01 mA/cm^2 and the threshold field of 9–10 V/mm for current density is 10 mA/cm^2.
- Kulkarni et al. demonstrated the report of electron field-emission characteristics of SiNWs grown by the vapor-liquid-solid(VLS) technique. vapor-liquid-solid(VLS) technique, a type of bottom-up technique has been used to produce semiconducting Nanowires (NWs) biosensors. [8]
- McClain et al. devoted attention to the field emission performance of silicon nanowires. These silicon nanowires were basically synthesized by the chemical vapor deposition(CVD) technique. The turn-on was the applied fields required to obtain current densities of 10 A/cm^{2t} and the threshold fields were 10 mA/cm^2. The resulting field enhancement factors were calculated to be 540, 270, and 265 for 5, 10, and 20 min growthtimes, respectively.The radius of curvature of the emitting tip decreases is directly related to the radius of SiNWs and emitter surface density also effected on the field emission performance of the SiNW specimens.[10]

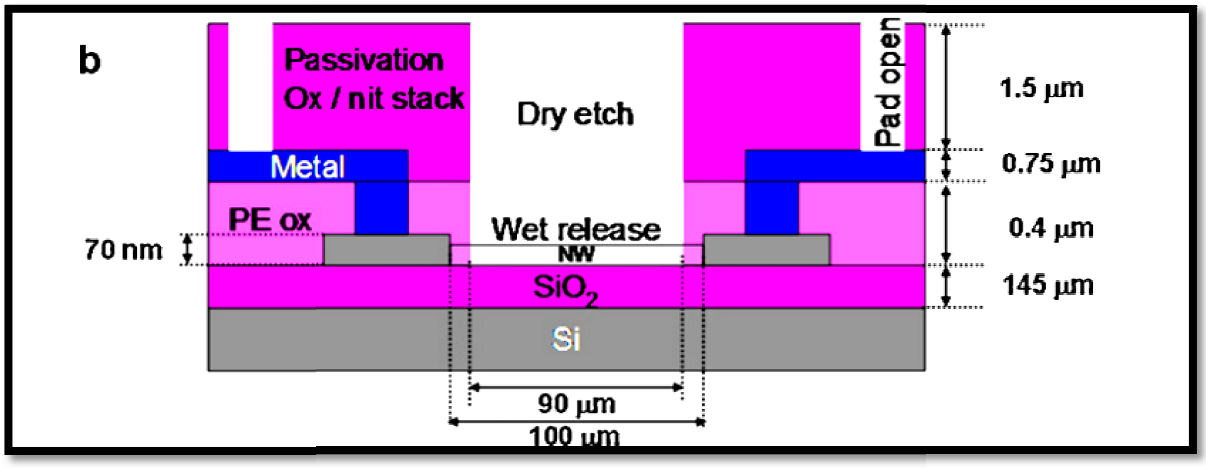

Fig2. 2: Schematic diagram of a cross-sectional view of a SiNW sensor

- Hsin-Luen Tsai fabricated SiNWs in the low-pressure chemical vapor deposition chamber by the vapor-liquid-solid (VLS) mechanism. Au was used as a catalyst and silane (SiH4) was used as a precursor at three various Au sputtering times. The Au sputtering time was 10, 30, and 60 sec. The growth time was 60 minutes for this experiment.

YEAR	AUTHOR	OBJECTIVE	CONTRIBUTION	CONCLUSION
1964	R.S.Wagner and W.C.Ellis	The consideration used as a basis is a semi-empirical model of stationary growth.	They reported the synthesis of silicon nanowires (SiNWs) for the very first time via (VLS) vapour–liquid–solid growth.	The synthesis of silicon nanowires (SiNWs) was confirmed for the very first time.
1997	Dimova-Malinovska et al.	The researchers wanted to fabricate silicon nanowire.	He reported that thin porous silicon layers (1000Å) were fabricated.	Dimova-Malinovska et al. endeavored fabrication of thin porous silicon layers (1000Å).

2000	Li and Bohn	Li and Bohn tried some extraordinary experiments. They were successful in making an advanced etching process for semiconductors.	A thin layer of noble metal (e.g., Au, Au/Pd alloy, orPt) sputtered on the external surface of a Si substrate(100) yielded the etching of Silicon in a heterogeneous solution resulting in straight pores or columnar structures was established.	This is the first demonstration of metal assisted chemical etching of silicon. Metal-Assisted Chemical Etching (MACE) is particularly promising among all other methods. Though before this report some researchers showed about MACE process but it was not in limelight at that time.
2003	Lu et.al.	Lu et.al. tried out a process ofsynthesizing well-equipped arrays of silicon nanowires (SiNWs) by a new procedure termed as chemical vapor deposition (CVD) method.	The turn-on field for electron emission produces a current density of 0.01 mA/cm^2 is ~14V/m. By their experiment, it can be said that the superior field emission behavior originates from the sharp tips and oriented growth of SiNWs.[6]	Researchers got success in manufacturing arrays of SiNWs by CVD technique.
2005	Chueh et.al.	Chueh et.al. reported field emission characteristics of taperlike geometry of the Silicon nanowires.	As Si is the most important semiconductor for the development of modern microelectronic technology, attempts have been made to develop excellent field emission properties in Si	Chueh et.al. reported field emission characteristics of taper-like geometry of the crystalline Silicon nanowires.[7]

			nanostructures.	
2005	Kulkarni et al.	The electron field-emission characteristics of SiNWs grown by the vapor-liquid-solid(VLS) technique was reported by Kulkarni et al. in 2005.	The average threshold field for emission current density of 10mA/cm2 was found to be 11.58 V/μm. The threshold field was further reduced via post-growth processing steps such as in situ annealing and in situ cessation.	This is the first demonstration of field-emission characteristics of SiNWs grown by the vapor-liquid-solid(VLS) technique.
2006	She et al.	She et al. reported a technique involving a combination of using a self-assembled nano mask and anisotropic plasma etching developed for fabricating vertically aligned single-crystalline SiNWs.	The typical J-E curve of the as-fabricated SiNWs gave a turn-on field of 0.8 MV/m and the threshold field of 5.0 MV/m(defined as the electric field required to extract a current density of 10 μA/cm2 and 10mA/cm2, respectively). [9]	She et al. endeavored plasma etching was developed for fabricating vertically aligned single-crystalline SiNWs.
2006	McClain et al.	McClain et al. studied the effects of growth parameters on the morphology and field emission performance of silicon nanowires which were synthesized by chemical vapor deposition using indium tin oxide-coated glass as a substrate.	Silicon Nanowires having growth- times of 5, 10, and 20 mins, the turn-on fields were determined to be 7.4, 7.9, and 11.5 V/ μm respectively.	The effects of growth parameters on the morphology and field emission performance of silicon nanowires were studied for the very first time.
2007	Zeng et al.	Zeng et al. investigated field emission of single	It came to an end thatwith decreasing	The well-built field emission of single

		crystal SiNWs of 100 nm in diameter by chemical vapor deposition growth procedure. This process was done at 480 °C from silane using Au as catalyst. [11]	radius of curvature of the emitting tipincreased with field enhancement factor.	crystal Silicon nanowire of 100 nm in diameter was attributed.This silicon nanowire were prepared by chemical vapor deposition growth procedure.
2007	Fang et al.	Fang et al. synthesized well-aligned and evenly distributed Silicon nanowires assembled in micro-sized semisphere ensembles through simple thermal evaporation. It was done without using any templates and metal particle catalysts. [12]	A typical nanowire array density was of 109×~4 cm^{-2}. The turn-on field for field-emission of the arrays was found out to be 7.3 V/ mμ.	Well-aligned and evenly distributed Silicon nanowires were assembled in micro-sized semisphere.
2013	Hsin-Luen Tsai	SiNWs device was developed based on an electroless etching method. Silicon nanowire arrays of various lengths were investigated at different etching times. [13]	Silicon nanowire thermoelectric device has been arrived by Hsin-Luen Tsai.	With longer sputtering time higher number of silicon nanowire were obtained in this experiment.

2.1.1. History of Metal Assisted Chemical Etching:

Metal Assisted Chemical Etching of Silicon was first revealed in the year of 1997. By etching of aluminum substrate covered with silicon actual porous silicon was achieved. This aluminum substrate covered with silicon was immersed in a combined solution of HF, HNO_3, and H_2O. Due to the existence of aluminum on the silicon wafer, the evolution time period for the development of porous silicon was decreased. [15] The extensively used Metal Assisted Chemical Etching process was developed by Li and Bohn in 2000. This

process of etching got more notability and numerous view point derived from this MACE process. In a prototypical approach, silicon underneath the noble metal is etched more quickly than silicon without noble metal coverage.

2.1.2. Influence of Temperature on the Etching:

The length of silicon nanowires fabricated by Metal Assisted Chemical Etching in $HF/AgNO_3$ or HF/H_2O_2 solution increases approximately with etching time. Cheng et al. comprehensively studied the relationship between the length of silicon nanowires at different temperatures (temperatures were in the range of 0^o to 50^o C) and the etching time.

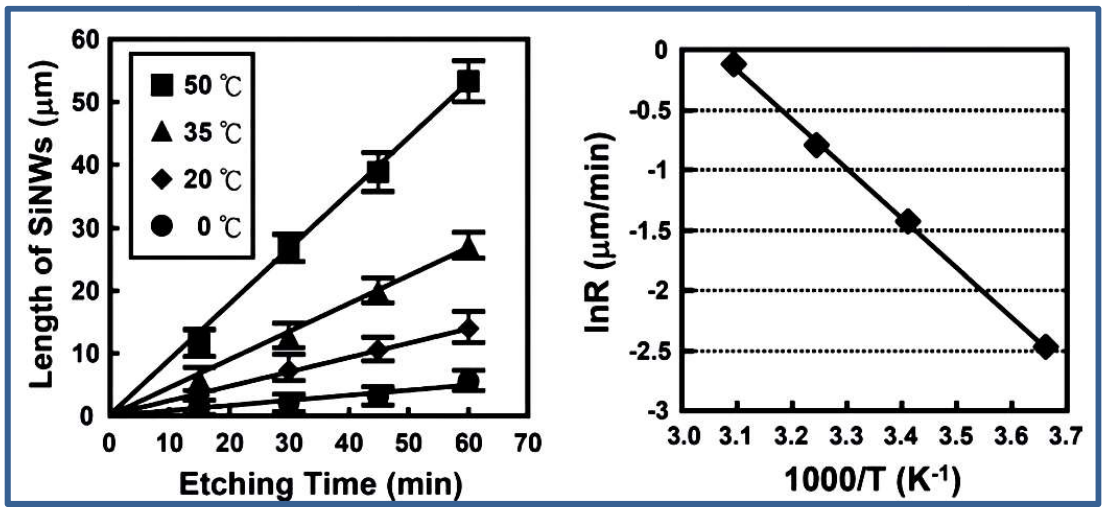

Fig2. 3(a) Relationship of length of Si nanowires and the etching time at different temperatures and (b) Arrhenius plot of the development rate versus reciprocal absolute temperature. Adapted with permission. [93] Copyright 2008, ECS.

A linear relationship was achieved at all temperatures. With increasing temperature, the observed rate was also increased. Cheng et al. also acquired apparent activation energy of 0.36 eV for the development of silicon nanowires on a Si (100) substrate via Arrhenius Plot.

Literature Review Of TiO_2

2.2. Review of Past Work of Titanium Dioxide:

TiO_2 powders have generally been used since the prehistoric period. TiO_2 powders are chemically stable, harmless, and inexpensive. They are white in colour. Scientific studies on the photoactivity of TiO_2 were promulgated in the 20^{th} century. Mashio et.al disclosed a series of reports on TiO_2, entitled "Autooxidation by TiO_2 as a photocatalyst". Researchers from Japan disseminated TiO_2 powders into numerous organic solvents.

Titanium dioxide is extensively used in many industries such as paints, energy storage, photocatalysis,cosmetics and the food industry from the late eighteenth century and early twentieth century. Here the history of the production and increasing use of TiO_2 is presented since the end of the Second World War. The evolution of TiO_2 regulation, within the regulation of chemical products, is described here, particularly in Europe. The certain role played by the stakeholders: regulatory agencies, scientists, and associations is highlighted here. With the increasing demand for chemical products, and food additives in industry, the regulation of chemical products progressed with the double aim to master and adapt to risks marked in the first period (1945–2000).The regulation of TiO_2 as a food preservative in Europe has developed in the second period, beginning in the 2000s, in the context of the regulation of nanotechnology.TiO_2 plays a significant role in academic work, and food safety governance while civil society groups give promotion to mediatization and they are imposing the preventive and precautional concept as a basis for this kind of regulation.

2.3. History Of Titanium Dioxide Whites:

Titanium dioxide was discovered in 1821 but in 1916 modern technology had advanced to the point where titanium dioxide could be mass produced.There are many industrial classifications of titanium white pigment but none of these are used for artists' oil color.In1921 American manufacturers introduced a titanium white oil color suitable for artistic purposes.

- Mashio et.al showed a comparison among numerous TiO_2 powders. They used twelve types of commercial and three types of rutile phase. The experiment was

based on the comparison of photocatalytic effects of TiO_2 powders. They concluded with that report that anatase activity of autooxidation is much better than the rutile phase. [14]

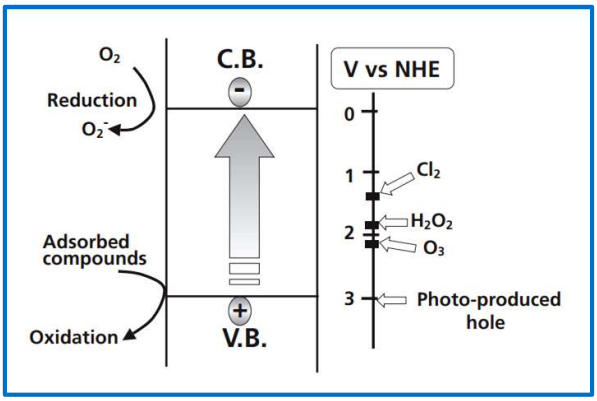

Fig2. 4: Schematic diagram of energy band for TiO_2

- In late 1960, researchers started experiments on photoelectrolysis of water using n-type TiO_2 (rutile) semiconductor electrodes. TiO_2 is extremely stable even in the presence of an aqueous solution(electrolyte solution). In 1969, the probability and hope of solar photoelectrolysis was first exemplified by researchers. One of the perspectives ofutilizing wavelength (mainly longer wavelength) light can involve the dye sensitization of TiO_2. In 1990s the conversation efficiency of TiO_2 electrodes as sensitizers reached 10-11%. [15]
- The first report on systematic and well-planned hydrogen production of organic compounds and water took attention at the time of the second oil crisis. TiO_2 photocatalysis became one of the most popular methods for hydrogen production. TiO_2 showed higher efficiency and stability compared to CdS and CdSe. CdS and CdSe materials were also investigated as their band gap is small compared to TiO_2. But TiO_2 gave more prominent results than those materials.
- In 1977, researchers demonstrated the decomposition of cyanide. Frank and Bard reported these in the presence of aqueous TiO_2 suspensions. The holes generated in TiO_2 were extremely oxidized. Each constitution element was oxidized to its final oxidation state. [16]

- In 1990, it is observed and experimented that TiO_2 photocatalysis could not be an effective practical and laboratory technology. TiO_2 can only deploy a little amount of UV light contained in solar energy.
- In 1992, photocatalytic cleaning material with a ceramic tile has been reported. Heller et.al came up with the homogeneous separately. One of the most materialistic and profit-oriented products using this effect self cleaning cover glass for tunnel light.
- In 1992 Heller et al. came up with an idea of photocatalytic cleaning material. There exist various types of hundreds of $\mu W/cm^2$ of UV light even outside of daytime. Let's consider , fig4. Shows the atomic force micrograph (AFM) images of monolayer stearic acid are prepared on TiO_2 rutile (110) single crystal. TiO_2 rutile (110) single crystal was invented by the Langmuir-Blodgett method. The number of stearic molecules was 10^{16}-$10^{17}/cm^2$. The thickness of the organic substance was around 2nm. When this substance was exposed to Ultraviolet light (UV light intensity is about 2.5 $\mu W/cm^2$), the most distinctly observed characteristic was the surface morphology. This experiment recommends the possibility of employment of photocatalysis of TiO_2-coated materials. [17]

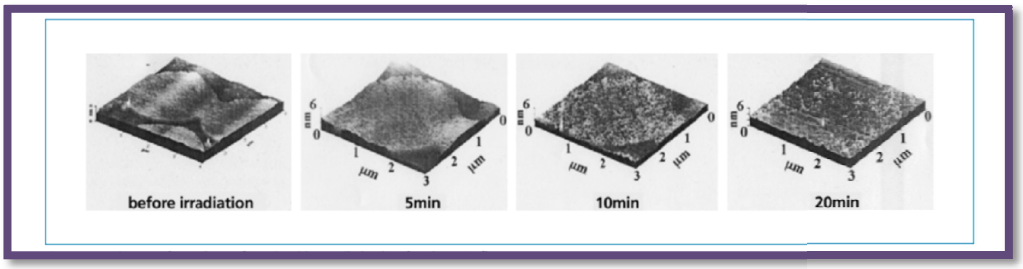

Fig2. 5: Atomic Force Micrograph (AFM) images of a monolayer of stearic acid on a rutile(100) surface(1 mW/cm^2)

- In 1995, TOTO ltd. Started manufacturing the antibacterial ceramic tile with coated TiO_2. This photocatalytic TiO_2 contains Ag or Cu. This technology was introduced in other country (mainly in western countries). **Escherichia coli** (abbreviated as E. coli) which can be found in the intestines of people and animals, and the environment can completely be lost on the surface of TiO_2. This **Escherichia coli** (E. coli) on the surface of TiO_2 is kept under the ultraviolet rays(intensity of 1

mW/ cm^2).The survival rate of microorganisms started to decrease when the Cu/TiO_2 is treated with radiation of weak ultraviolet rays. The survival decay curve of **Escherichia coli** (E. coli) is shown in the following figure. The survival process of **Escherichia coli** (E. coli) undergoes through three steps. [18-19]

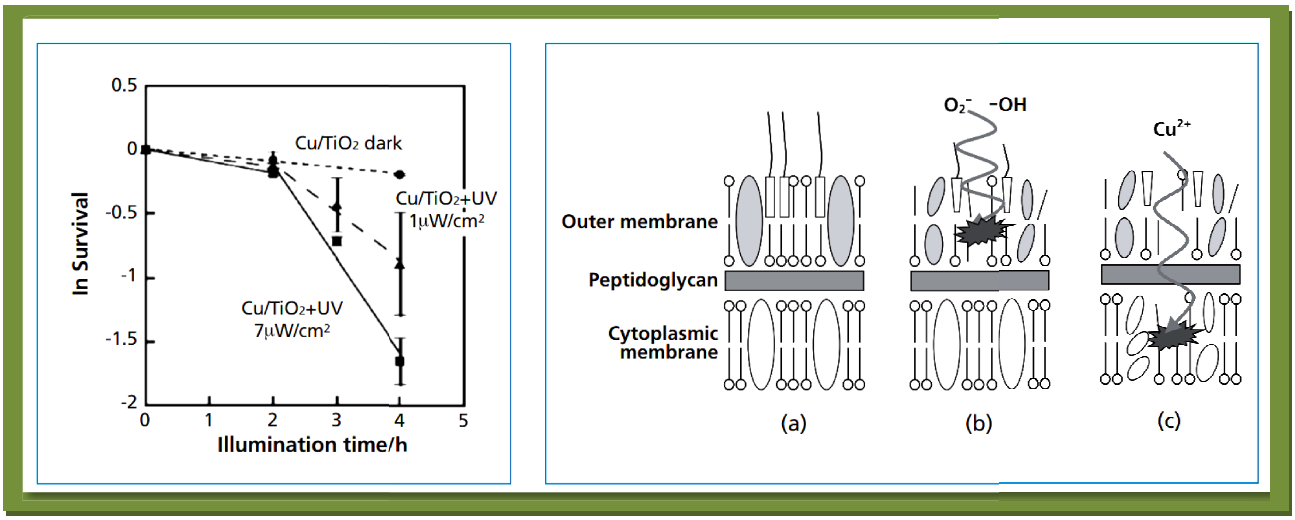

Fig2. 6: Changes in survival rate of copper-resistant E. coli cells on Cu/TiO_2 thin film. Error bars: standard deviations of three replicate experiments.

Fig2. 7: (a) Schematic illustrations of bactericidal process for copper-

- In 1995, the water wettability of TiO_2 was noticed before ultraviolet radiation and after ultraviolet radiation. The surface wettability is estimated by the water contact angle. When a TiO_2 thin film is irradiated in UV rays, the contact angle (CA) starts to decrease (High surface energy) and it nearly reaches to 0^o and the surface becomes highly hydrophilic. Under a normal atmosphere and without UV radiation the contact angle starts to increase and the surface becomes less hydrophilic and slowly it returns to its initial states. [20]

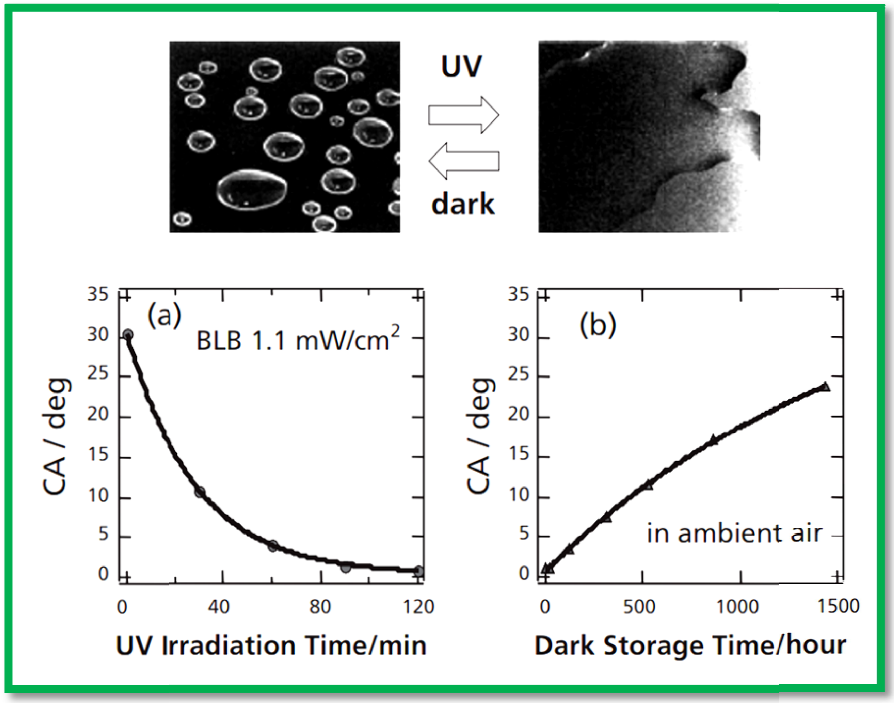

Fig2. 8: Changes in CA of TiO_2 surface (a) under UV irradiation & (b) in the dark

- Recently, distinctive behavior before and after UV rays irradiation by SFG spectroscopy has been reported by Uosaki et al. Sum frequency spectroscopy commonly abbreviated as SFG is a laser spectrographic analysis used to examine the interfaces and surfaces subsequently.

Literature Review Of SiNWs/TiO_2 Photodetector

- In 2018, Porous Si/TiO_2 nanowire photoanode for photoelectric catalysis under simulated solar light irradiation was developed. The photoelectric catalysis (PEC) activities of porous Si/TiO_2 nanowire photoanodes were evaluated in degradation experiments of methylene blue under simulated solar light irradiation. Diffuse reflection spectra show that the porous Si/TiO_2 nanowire photoanodes have a strong absorption. PEC is the optimal catalysis process for the porous Si/TiO_2 nanowire photoanode relative to DP and EC.

- The photovoltaic impact of atomic layer deposited TiO2 interfacial layer on Si-based photodiodes was showed in a paper in 2018. The diode and photodiode performances of atomic layer deposited as Al/TiO2/p-type Si structure were investigated using I-V and C-V-f measurements. In that study, the ALD technique was used due to its advantageous features such as surface stability and controlled surface reaction. Some parameters such as fill factor and power efficiency for photovoltaic properties of the device were calculated from I-V measurements under different illumination conditions.

- A study proposes a diferent technique known as the thermionic vacuum arc to produce a TiO_2/Si heterojunction photodiode with better electrical properties than literature like the ideality factor indicating that the method is very suitable to form an outstanding quality heterojunction interface. The heterojunction is highly sensitive to diferent light intensities and has stable photocurrent characteristics as a photodiode. Structural and morphological properties of the produced TiO_2/Si heterostructure surfaces were investigated via XRD and AFM, respectively. According to XRD analysis, it was observed that the TiO_2 thin flm was in a polycrystalline structure with the Anatase and Brookite phases in 2021.

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CHAPTER:3

Introduction to SiNW, TiO_2 And Photodetectors & its Properties

3. 1.SiNWs Properties:

3.1.1. Physical Properties of SiNWs:

Molecular Weight	28.08
Appearance	Black to grey
Density	~1 g/cm^3
Thermal Expansion	(25^o C) 2.6 µm-m^{-1}.K^{-1}
Young's Modulus	51-80 GPa

Table3. 1: Physical Properties of SiNW

3.1.2. Optical Properties of SiNWs:

The fabrication of silicon nanowire strive to reduce the reflection of incident light and expand utmostabsorption. The antireflective property of silicon nanowires is mostly highlighted feature as the major disadvantage of solar cell is optical reflection. The uses of these silicon nanowire in photosensitive device (convert light into an electric current) can terminate the requirements for antireflective coatings.

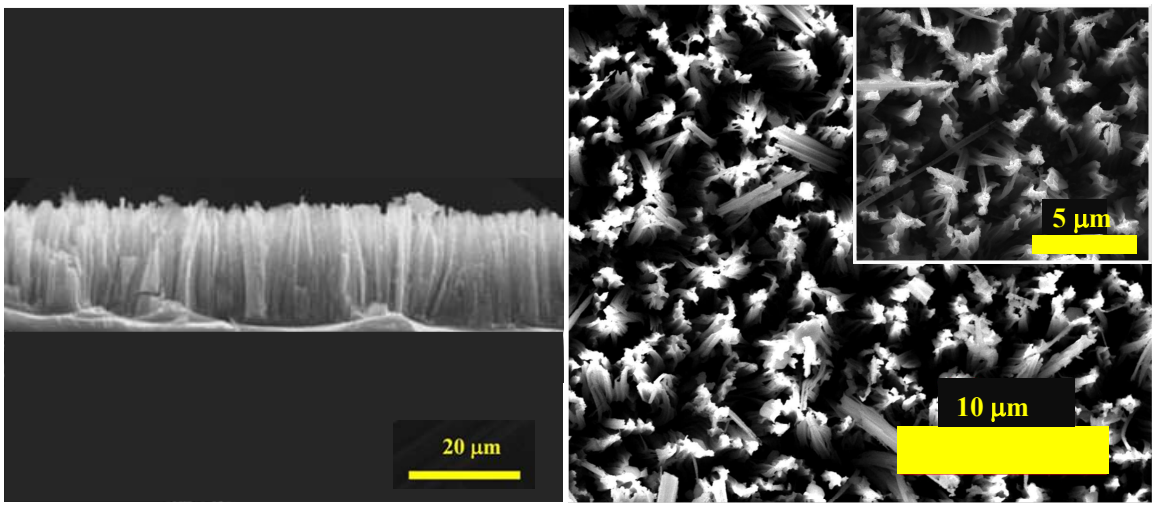

Fig3. 1(a).Cross-sectional view of SiNW, (b)FESEM images of silicon nanowire

3.1.3. Electrical Properties of SiNWs:

The electrical properties are dependent on size, morphology, growth direction etc. The diameter of the SiNW is inversely proportional to the width of the band gap. Silicon nanowire has a high electrical conductivity. As the diameter decreases, the band gap of the wire widens and deviates from the bulk silicon gradually. It is important to understand the electrical properties of semiconducting nanowires because they determine the suitability of silicon nanowires to be used in electronics and sensor applications. SiNWs are considered as one of the most important one-dimensional materials because of their formation of building blocks for nanoscale electronics.

3.1.4. Chemical Properties of SiNWs:

An important chemical reaction, which makes silicon nanowires very useful in sensor and transistor applications, is the natural oxidation.

3.1.5. Mechanical Properties of SiNWs:

Mechanical properties of nanowires are of great importance in device processing since changes in temperature, induced strain and external stress can change the electrical conductivity of the nanowire due to internal dislocations.

3.1.6. Thermal Properties of SiNWs:

Silicon nanowires, when used within applications or experiments, may have a curved like shape and not be straight.

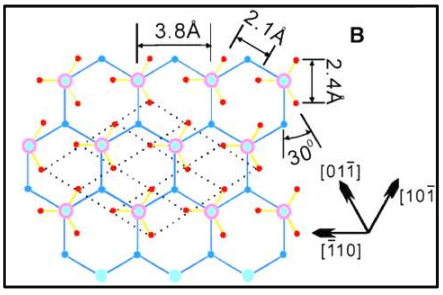

Fig3. 2:Crystal Structure of SiNW(Plane 011, 110 and 101)

3. 2.TiO_2 Structure:

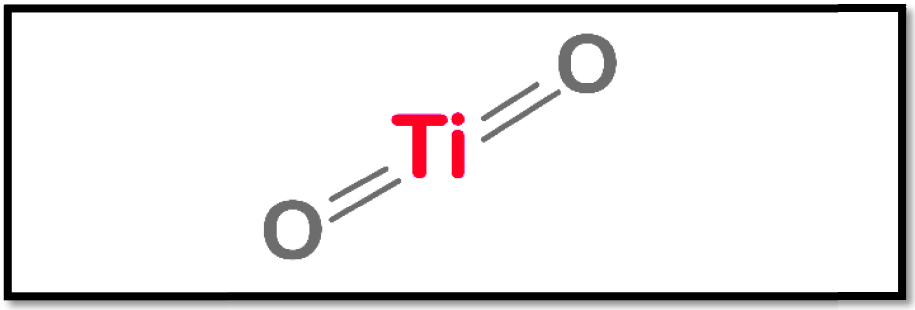

Fig3. 2: Structure of Titanium Dioxide

Chemical Symbol	TiO_2
Chemical Abstracts Service No	13463-67-7
Group	Titanium 4 Oxygen 16
Electronic Configuration	Titanium[Ar]$3d^2 4s^2$ Oxygen[He] $2s^2$ $2p^4$

Table3. 2.1. Chemical Properties of TiO_2

Properties	Metric	Imperial
Density	4.23 g/cm^3	0.152 lb/in^3
Molar Mass	79.9378 g/mol	

Table3. 2.2. Physical Properties of TiO_2

Properties	Metric	Imperial
Melting Point	1,843° C	3,349° F
Boiler Point	2,972° C	5,382° F

Table3. 2.3. Thermal Properties of TiO_2

Element	Content (%)
Titanium	59.93
Oxygen	40.55

Table3. 2.4.Chemical Composition

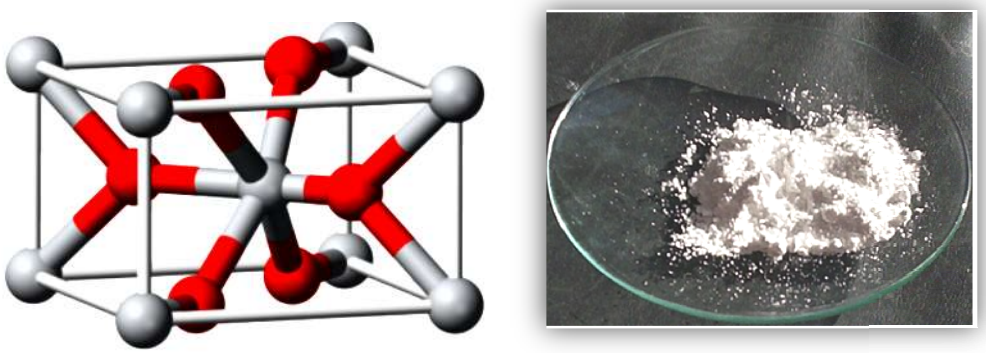

Fig 3. 3: Titanium Dioxide Or Titanium(IV) oxide(Chemical Structure and Powder form)

Titanium Dioxide (TiO_2) has been known as a useful photocatalytic material. It shows high photocatalytic activity compared with other metal oxide photocatalysts. It is compatible with traditional construction materials without changing any original performance. Actually physical and rheological properties remain same in case of TiO_2 (Rheology is the branch of science which deals with the deformation and flow of matter). TiO2 nanoparticles have been widely studied because of their low production costs, bio- and chemical inertness, hydrophilicity, mechanical and chemical stabilities, high light conversion efficiency, thin film transparency and corrosion resistance.

High light-conversion efficiencies of TiO_2 have been utilized for the production of energy devices. Theirthin film transparency, chemical stability, and low production costs are accountable for their usefulness as photocatalysts for numerous sustainable remediation strategies etc. wastewater treatment, soil viability improvement. A short time ago, TiO2 nanoparticles were utilized for cancer photothermal therapy (PTT), using their non-radiative recombination ability.

3. 2.1.Crystal Properties of TiO_2:

Based on fabrication technique and post fabrication heat treatment, three major polymorphic (occurring several distinct forms) forms can be created. Such as: Rutile (tetragonal, space

group I41/amd), Anatase (tetragonal, space group P42/mnm) and Brookite (orthorhombic, space group Pbca).

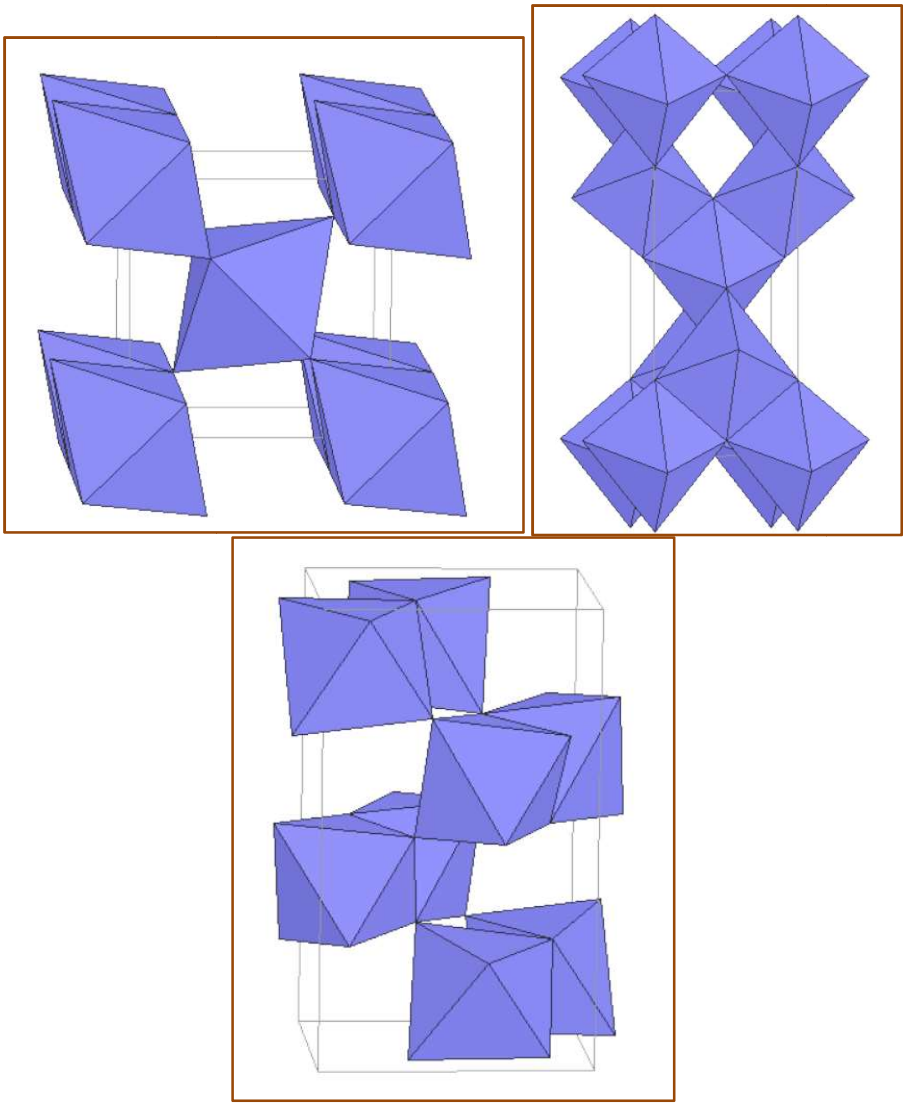

Fig 3. 4: (a) Rutile phase, 4(b) Anatase, 4(c) Brookite

The third polymorphic form Brookite (TiO_2(B)) is relatively uncommon. Both the anatase and rutile phases acquire tetragonal crystal structures while brookite has an orthorhombic structure. Anatase phase has low density, at high temperature(~450-1200^{o}C) it easily experience transformation to the rutile phase. It has also noticed that both the Brookite and Anatase phases go through transition to the rutile phase. At particle size greater than 14 nm rutile phase gain higher stability than the anatase phase. Researchers reported that, the

formation time of rutile phase is lower than the anatase phase. Anatase forms starts at comparatively lower temperature than rutile forms(formation starts above 600° C).

Properties	Anatase	Rutile	Brookite
Crystal Structure	Tetragonal	Tetragonal	Orthorombic
Density(gm/cm^2)	3.894	4.250	4.120
Space Group	$I4_1/amd$	$P4_2/mnm$	Pbca
Molecule(cell)	2	2	4
Lattice Constant(Å)	a = 3.784 b = 9.515	a =4.594 b = 2.959	a = 9.184 b = 5.447 c = 5.154
Ti—O bond length (Å)	1.937(4) 1.965(2)	1.949(4) 1.980(2)	1.87–2.04
O—Ti—O bond angle	77.7° 92.6°	81.2° 90.0°	77.0°–105.0°
Volume/molecule (Å3)	34.061	31.216	32.172

Table3. 2.5: The crystal properties of TiO_2

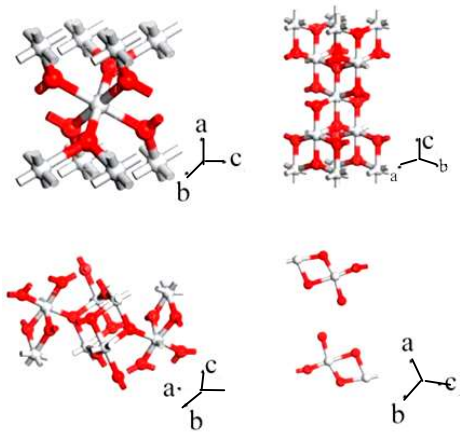

Fig 3. 4.1:Crystal Structure of TiO_2 (a) Rutile; (b) Anatase; (c) Brookite; and (d) TiO2(B)

[5]

3. 3.Introduction to Photodetectors:

The interest in light sensitive devices has been increasing at an almost exponential rate in recent years. The resulting field of optoelectronics will be receiving a great deal of research interest as efforts are made to improve efficiency levels. Though the advertising media, the layperson has become quite aware that light sources offer a unique source of energy. This energy, transmitted as discrete packages called photons, has a level directly related to the frequency of the travelling light wave as determined by the following equation:

$$W=kf$$

Where $W$is in joules, k is called Planck's constant and is equal to 6.624×10^{-34} joule-second. It clearly states that since k is a constant, the energy associated with incident light waves is directly related to the frequency of the travelling wave.

The frequency is, in turn, directly related to the wavelength (distance between successive peaks) of the travelling wave by the following equation:

$$\lambda = \frac{v}{f}$$

Where $\lambda =$ wavelength, meters,

v = velocity of light, 3×10^8 m/s,

f = frequency of the travelling wave, hertz

The wavelength is important because it will determine the material to be used in the optoelectronic device.

The photodiode is a semiconductor p-n junction device whose region of operation is limited to the reverse-bias region.

Photodetector is an important element in Optical Fiber Communications which generally converts optical signal to electrical form (Hence referred as O/E converter).

A photodetector should have the following properties:

- **Quantum Efficiency:** The number of electron or holes (carriers) generated per photon. Basically it is the ratio between the number of charge carriers collected to

the number of photons hitting on the photo reactive surface. It is dimensionless and closely related to responsivity.

- **Responsivity:** Responsivity measures the input output gain of a photodetector. It measures the electrical output per electrical input. It is a measure of optical-electrical conversion efficiency of a photodetector.

$$\textbf{Responsivity} = \frac{\textbf{The output current}}{\textbf{Total light power falling upon the photodetector}}$$

- **Noise Equivalent Power:** The Noise Equivalent Power (NEP) is the familiar measure that evalutes a photodetector's sensitivity or the power generated by a noise source. It's a measure of the weakest optical signal can be detected.

$$NEP_{\lambda} = NEP_{min} \times (R_{max}/R_{\lambda})$$

Here, NEP $_{\lambda}$ at a different wavelength λ, NEP_{min} is the NEP as given in the specifications, R_{max} is the maximum responsivity of the detector, and R_{λ} is the responsivity of the detector at wavelength λ.

- **Detectivity:**Detectivity is basically inverse of noise equivalent power. The square root of the detector area divided by the noise equivalent power.
- **Spectral Response:** The response of photodetector as a function of photon frequency.
- **Response Time:** Response time is the time required to reach 90% from 10% of final output.
- **Dark Current:** Even when outside radiation is not entering into the device or no photons entering into the device the current flowing through the photodetector.

  The ratio of maximum withstandable reverse voltage to the dark current of a photodiode is called dark resistance of that diode.

$$R_d = \frac{\textbf{Maximum Reverse Voltage}}{\textbf{Dark Current}}$$

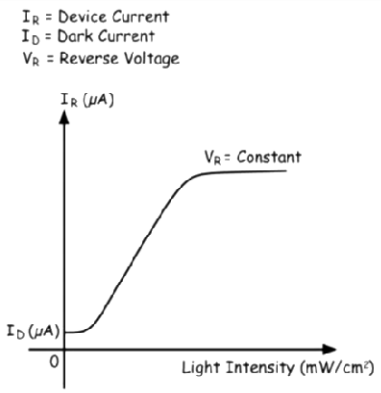

Fig 3. 5: Light intensity of dark current vs device current graph

A photodetector should have the following characteristics:

- High sensitivity at operating wavelength
- High fidelity
- Short response time to obtain a suitable bandwidth
- Stability of performance characteristics
- The linearity should be good with respect to the incident light
- Noise should be minimum
- Rugged mechanically
- Long life
- Small size
- Low cost

It is operated in reverse biased mode only. Forward biased, resistance offered is zero. When diode is reverse biased, resistance offered is infinity. It acts as a perfect switch. When diode is Photodiode is a two terminal electronic device when it is exposed to light the current starts flowing in the diode. When the typical diode is reverse biased the reverse current starts increasing with reverse voltage. This same strategy can be applied to the photodiode. But in case of Photodiode this reverse applied voltage is not needed despite the photodiode is illuminated by light energy. Here the current can flow without application of reverse voltage. Photodetector is also known as photodiode or photosensor. The figure below shows the symbolic representation of a photodiode.

3. 3.1.Construction:

The photodiode consists of two semiconductors, P-type & N-type. The development of P-type material feasiblydone from the diffusion of the P-type substrate. The front area of the diode is divided into two types that are active surface and non-active surface. The non-active surface is made up of SiO2 (Silicon di Oxide) and the active surface is coated with anti-reflection material. The active surface is called so because the light rays are incident on it.

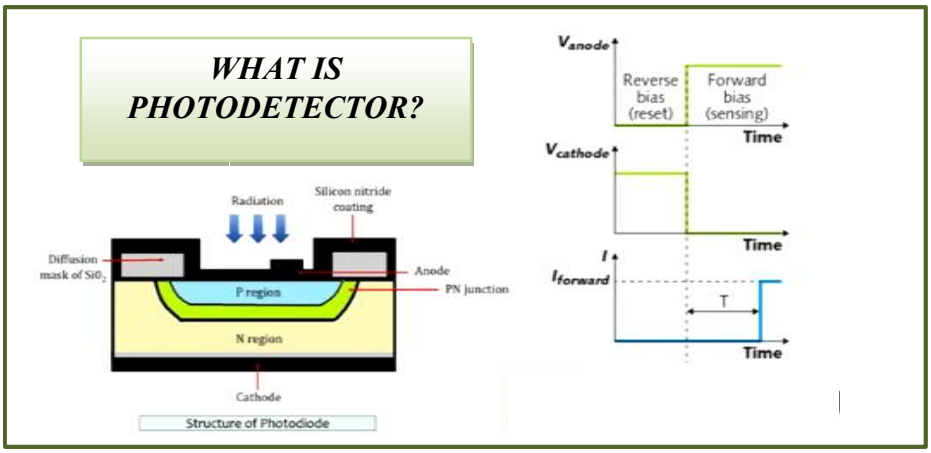

Fig 3. 6: Structure of photodetector and forward and reverse biased voltage with respect to time

3. 3.2.Principle of Photodiode:

It works on the principle of the photoelectric effect. The operating principle of the photodiode is such that when the junction of this two terminal semiconductor device is illuminated then the electric current starts flowing through it. Only majority current flows through the device when the certain reverse potential is applied to it. The photons (strike)afflict on the junction surface of diode. The photons transmit their energy in the form of light to the junction. Due to which electrons from valence band acquire the energy to jump into the conduction band and contribute to current. In such manner, the photodiode converts light energy into electrical energy.

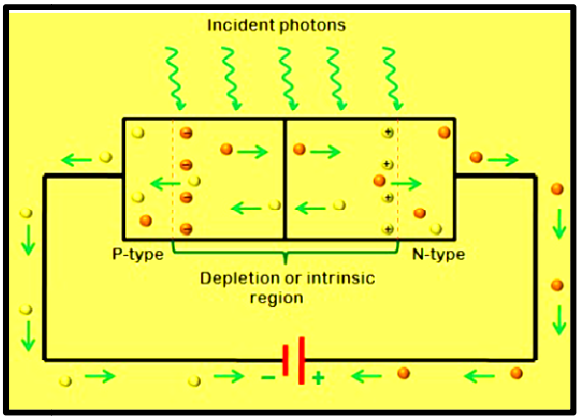

Fig 3. 7: Schematic of Photodiode

Generally, electrons are negatively charged and holes are positively charged. Normally, when a light is elucidated on the PN junction, covalent bonds get broken and generates hole and electron pairs. Photocurrents are produced due to generation of electron-hole pairs. When the photon enters the depletion region of diode, it hits the atom with high energy. Only the pn junction portion of the diode must be exposed in light as electron-hole pairs created in the junction or very nearby to the junction which can disseminate easily towards opposite polarity. It is due to the influence of electric field across the junction. Thus the current through the photodiode is created. This results in release of electron from atom structure. After the electron release, free electrons and hole are produced.The depletion energy creates an electric field. Due to that electric field, electron-hole pairs move away from the junction. Hence, holes move to anode and electrons move to the cathode to produce photocurrent.Photon excitation happens in two ways such as Intrinsic Excitations and Extrinsic Excitations.

3. 3.3.Connecting a Photodiode in an External Circuit:

A Photodiode works in reverse bias. Anode is connected to circuit ground and cathode to positive supply voltage of the circuit.

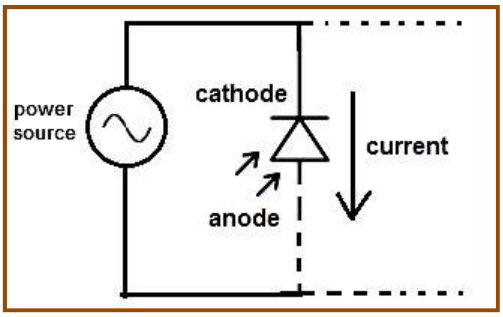

Fig 3. 8:Connecting a Photodiode in an External Circuit

When photodiodes are used with external circuits, they are connected to a power source in the circuit. The current flows from cathode to anode when light fall on the p-n junction.The amount of current produced by a photodiode will be very small. As this value of current is not enough to operate an electronic device, they are affixed to an external power source, it delivers more current to the circuit. So, battery is used as a power source.

3. 3.4.Modes of Operation of Photodiode:

Photodiode operates in two modes that are **Photo-conductive** and **Photo-voltaic.**

Photo-Conductive: When the Photodiode operates in reverse biased mode it is called Photoconductive mode. The terminal resistance of photoconductive cell will vary (linearly) with the intensity of the incident light. In order to turn-off the diode, it should be provided with forward voltage. For obvious reasons, the photoconductive cell is sometimes called the photoresistive device. The photoconductive materials most frequently used include cadmium sulfide (CdS) and cadmium selenide (CdSe).

Photo-Voltaic: When the diode is operated without reverse biased it is said to be operated in photovoltaic mode. When the reverse biased is removed, actually it is zero biased. The flow of current is restricted and voltage builds up. This principle is used in solar cell. When light shines on the cell it creates an electric field across the layers causing electricity to flow. In photovoltaic mode, the amount of dark current is kept at minimum.

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CHAPTER:4

Aims & Objective

The present study aims to synthesize and stabilize the SiNW/TiO_2 photodetector. The synthesis procedure was metal assisted chemical etching technique. The particles which were synthesized were tested for environmentally friendly applications. The detailed descriptions of aims and objectives are listed below

- *Synthesis of Silicon Nanowires by a single step, room temperature, a cost-effective procedure using metal-assisted chemical etching (MACE) technique.*
- *Preparation of TiO_2 layer on uniform Silicon Nanowires (SiNW) by hydrothermal Process.*
- *A brief study of its various property using different mechanisms like X-ray Diffraction, FTIR, Morphological analysis, FESEM, TEM.*
- *A brief study on I-V Characterization, Switching Characteristics of SiNWs/TiO_2 structure is done.*
- *A stable and fast photodiode is developed which can be used as UV photodetector.*

CHAPTER:5

Instruments and Apparatus Used in the Experiment

In this chapter, major apparatus and instruments, which were used while characterization of the samples has been discussed. A brief description of their working principle has also been given.

5. 1.Crystal Structure Analysis:

5. 1.1.X-RAY DIFFRACTOMETER (XRD):

X-Ray Diffraction is commonly abbreviated as XRD. It is a popular analytical technique that is used to characterize the phase of the synthesized nanoparticle as a powder form and its molecular and crystal structure, qualitative identification of various compounds, degree of crystallinity and particle size, etc. X-rays are a form of electromagnetic radiation that has high energies and short wavelengths on the order of the atomic spacing for solids. When a beam of x-rays impinges on a solid material, a portion of this beam will be scattered in all directions by the electrons associated with each atom or ion that lies within the beam's path. Furthermore, diffraction is a consequence of specific phase relationships established between two or more waves that have been scattered by the obstacles. The phase relationship between the scattered waves, which will depend upon the difference in path length, is important.

X-Ray is electromagnetic radiation. X-ray is usually produced by bombarding high-energy electrons on any heavy metal. Visible light has a longer wavelength so it can't go inside a crystal. But X-rays have a wavelength that can go inside the crystal and we can get crystallographic information using X-Ray. Half of its wavelength is less than the interatomic distance (D).

$$\lambda/2 \leq D$$

Diffraction is the main technique used to identify crystal structure.

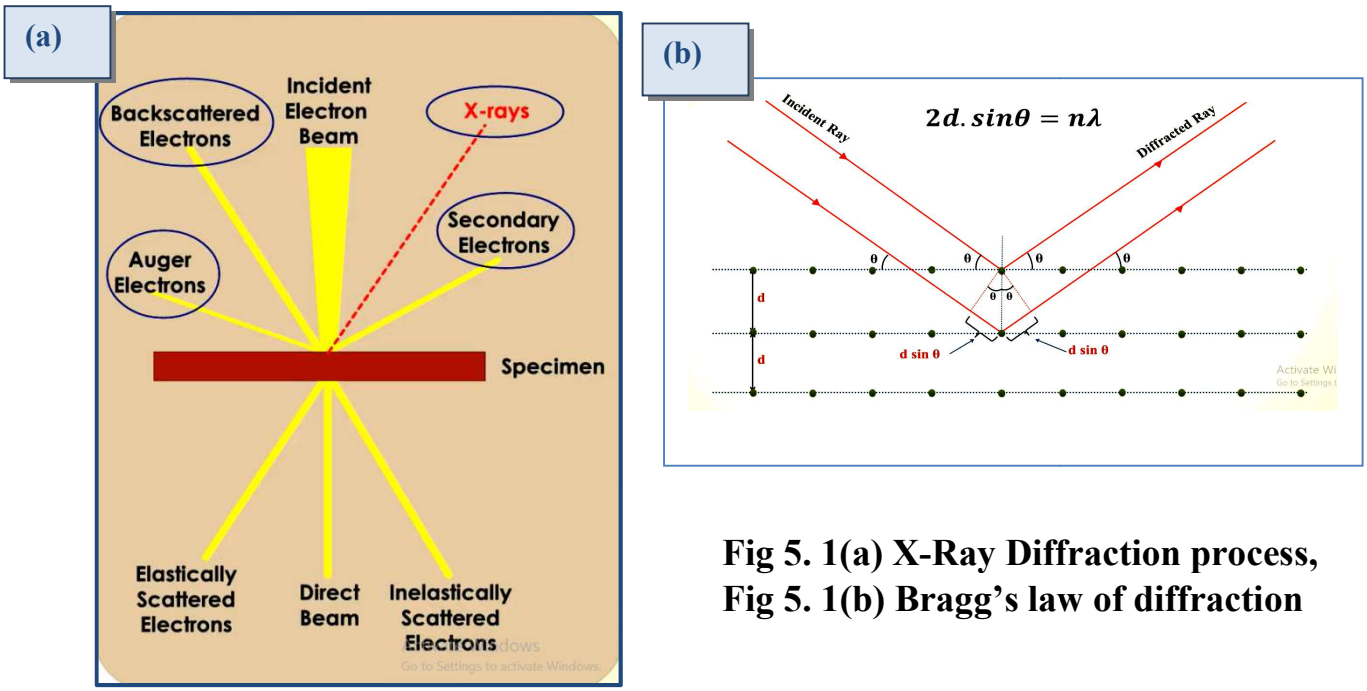


Fig 5. 1(a) X-Ray Diffraction process,
Fig 5. 1(b) Bragg's law of diffraction

Normally, the polychromatic X-rays are produced by a Cu-k cathode ray tube,these polychromatic rays are filtered by a monochromator which produces the monochromatic radiation, that hits the powder sample's atomic planes and some of the rays are absorbed and some are transmitted or scattered, this basically follows the brag's law of diffraction. The condition for this law is –

$$\mathbf{2dsin\theta = n\,\lambda}$$

Here λ is the wavelength of the incident x-ray

The inter atomic distance (d) and

Theta (θ) is the angle of the diffracted x-ray beams.

Different Method of XRD Measurement:

Method	Wavelength(λ)	Incident Angle(θ)
Powder Method	**Fixed**	**Variable**
Rotating-Crystal	**Fixed**	**Variable**
Laue Method	**Variable**	**Fixed**

Table5. 1: Table for Method of XRD Measurement

By using the analysis we plot a graph between angle of incident x-ray vs intensity of x-ray beam, to analyze whether the phase of the nanomaterial is pure or not. Here the sample are placed in a sample holder, which is rotating and when the x-ray beams are bombarded onto the sample it excites the electrons of the sample and we obtained diffracted pattern, this is usually done by the Bragg-Brentano geometry (θ - 2θ). The diffraction patterns were detected by the scintillation detector. Here in this literature, the XRD measurements were done by Ultima III x-ray diffractometer at room temperature (Cu kα radiation, λ = 1.5404 Å, Rigaku, Japan).

Fig 5. 2: X-RAY DIFFRACTOMETER in lab

5. 1.2.Scanning Electron Microscope (SEM) and Field Emission Scanning Electron Microscope (FESEM):

Scanning electron microscope is the technique to visualize topographic details on the surface. It is a device that generates a largely magnified image by using electrons instead of light. A beam of electrons is generated at the top of the microscope. An electron gun basically produces this beam of electrons. The electron beam follows the upright path (vertical path) through the microscope. The SEM is operated under high vacuum. The electron beam travels through the vertical path, through the magnetic path and reaches to the length and ultimately focuses on the downward sample. When the electron beam strike on the sample electrons, X-rays are ejected from the sample. Secondary electrons and backscattered electrons are commonly used for imaging samples. As the SEM is operated in high vacuum the liquids and the materials containing water cannot be studied directly. Secondary electrons are most important for showing morphology and topography on samples and backscattered electrons are important for illustrating contrasts in composition of samples.

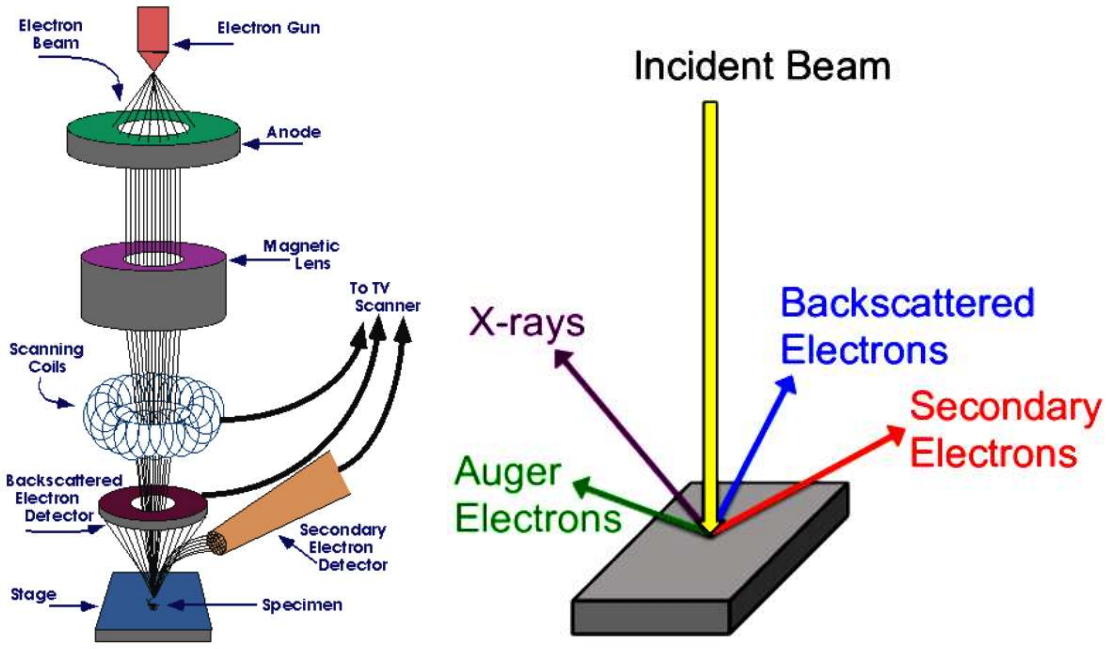


Fig 5. 3: Schematic diagram of Scanning Electron Microscope (SEM)

WHAT DOES THE WORD FESEM MEAN?

FESEM is the abbreviation of Field Emission Scanning Electron Microscope. A FESEM is microscope that works with electrons (particles with a negative charge) instead of light. These electrons are liberated by a field emission source. The object is scanned by electrons according to a zig-zag pattern.

WHAT CAN BE DONE WITH A FESEM?

A FESEM is used to visualize very small topographic details on the surface or entire or fractioned objects. Researchers in biology, chemistry and physics apply this technique to observe structures that may be as small as 1 nanometre (= billion of a millimetre). The FESEM may be employed for example to study organelles and DNA material in cells, synthetical polymers, and coatings on microchips. The microscope that has served as an example for the virtual FESEM is a Jeol 6330 that is coupled to a special freeze-fracturing device (Oxford Ato).

The main components of a typical SEM are:

a) **Electron column:** The electron column of the SEM consists of an (i) Electron Source ("gun") (ii) Electromagnetic lenses (two) operating in vacuum (SEM),3-stage electromagnetic lens, reduction type (FESEM). Modern SEM systems require a steady electron beam from the electron gun with a high current, small spot size, tunable energy, and low energy dispersion. Several types of electron guns are used in a SEM system, and the quality of the electron beam produced by each differs significantly. Tungsten "hairpin" or lanthanum hexaboride (LaB6) cathodes were used in the first SEM systems, but field emission sources, which provide more current and reduce energy dispersion, are now the standard. Another important factor to consider when selecting electron sources is the emitter's lifespan.

b) **Scanning system:**In an analog scanning system, the beam is moved continuously; with a rapid scan along the X-axis. The scan coils deflect the electron beam in a zigzag pattern as it passes over the item. The movement of the scanner is timed to coincide with the creation of the image on the display. The scan velocity determines the screen refresh rate and the

amount of noise in the image. In scan coils, upper and lower coils are commonly used to prevent the formation of a circular shadow at low magnification.

c) **Detectors:**When the beam is focused on the specimen, analog signal intensity is measured by the detector,

d) **Display / Data Input Devices:** The numerical value of magnification is determined by the ratio of the length of the monitor versus the length of the scan on the M = Lmon/Lspec.

Lspec= Length of the scan on the specimen

Lmon= constant length of scan on the monitor ,

e) **Vacuum system**,

f) **Electronics controls**,

g) **Electron Lenses:**Electron beams can be concentrated by electrostatic or magnetic fields. The SEM system, on the other hand, only uses a magnetic field because an electron beam controlled by a magnetic field has less aberration. Electromagnets can change the paths of electrons.

h) **Condenser Lens:**The electron beam will diverge after passing through the anode plate from the emission source. The electron beam is converged and collimated by the condenser lens into a nearly parallel stream. A magnetic lens is made up of two rotationally symmetric iron pole pieces that are connected by a copper winding to create a magnetic field. The electron beam can pass through a hole in the middle of the pole pieces. Through a lens-gap that separates the two pole components, the magnetic field influences (focuses) the electron beam. The condenser lens current can be changed to change the focus point location.

i) **The Objective Lens:**The electron beam will diverge below the condenser aperture. The electron beam is focused into a probe point on the specimen surface using objective lenses, which also provide additional demagnification. The diameter of the electron beam on the specimen surface (spot size) is reduced as the aperture and Fundamentals of Scanning Electron Microscopy 15 are increased, which improves picture resolution.

j)**The Stigmator Coil:**The stigmator coils are used to correct x and y deflection inconsistencies in the beam, resulting in a perfectly round beam.The image appears fuzzy and stretched when the beam is ellipsoidal rather than circular.

k)**Object Chamber:**After being coated with a conductive coating, the item is placed on a specific holder. Through an exchange chamber, the item is introduced into the microscope's high vacuum section and anchored on a movable stage. The secondary electron emission detector (scintillator) is located at the back of the object holder in the chamber.

l)**Image Formation:** Complex interactions occur when an electron beam in a SEM impinges on a specimen surface and excites different signals for SEM inspection. Secondary electrons, back scattered electrons (BSEs), transmitted electrons, and specimen current can all be collected and displayed on a computer monitor. The composition of the specimen is determined by examining the excited x-ray or Auger electrons. The interactions of the electron beam with the specimen surface, as well as the principle of picture creation using various signals, will be covered in this section.

m) **Infrastructure Requirements**:

- Power Supply
- Vibration-free floor
- Room free of ambient magnetic and electric fields
- Cooling system

Energy Dispersive X-ray analysis (EDX): Consequently, X-rays are emitted with the interaction of the incident electron beam with the sample. Their energies are characteristic for the atoms present in the volume that is examined.

Energy Dispersive X-Ray analysis: The detection and analysis of these X-rays is called Energy Dispersive X-Ray analysis. The combination of EDX and STEM permit for mapping of the lateral distribution of elements.The EDS data present as a graph. The peak intensity is on the Y-axis and the KeV on the X-axis. As shown in the above figure, we can see that EDX basically used to analyze and detection of elemental composition of the given sample.

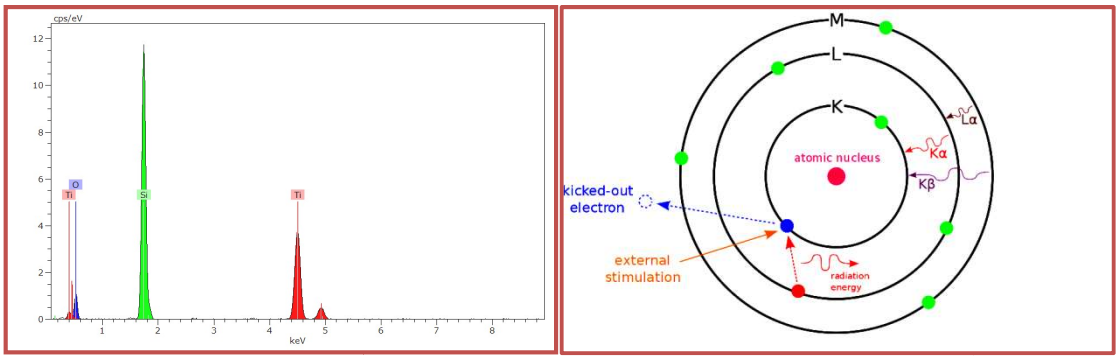


Fig 5. 4(a) EDS Data representation through graph, 5. 4(b) Working principle diagram of EDX

Fig 5. 5: FESEM (Hitachi S-4800) set up

5. 2.Bond Structure Analysis

5. 2.1.FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR):

For studying the vibrational properties of synthesised materials, FTIR spectroscopy is a very useful tool. The band positions and absorption peak of thin films are influenced not only by their chemical composition and structure, but also by their morphology [1].

The preferred method of infrared spectroscopy is known as Fourier Transform InfraRed (FT-IR). Infrared spectroscopy involves passing IR radiation through a sample. The sample absorbs some of the infrared radiation and passes some of it through (transmitted). The resulting spectrum depicts the sample's molecular absorption and transmission, resulting in a molecular fingerprint. No two unique molecular structures produce the same infrared spectrum, just like a fingerprint. As a result, infrared spectroscopy can be used for a variety of purposes.

So, what kind of information can FT-IR give you?

- It can determine the quality or consistency of a sample
- It can determine the number of components in a mixture
- It can identify unknown materials

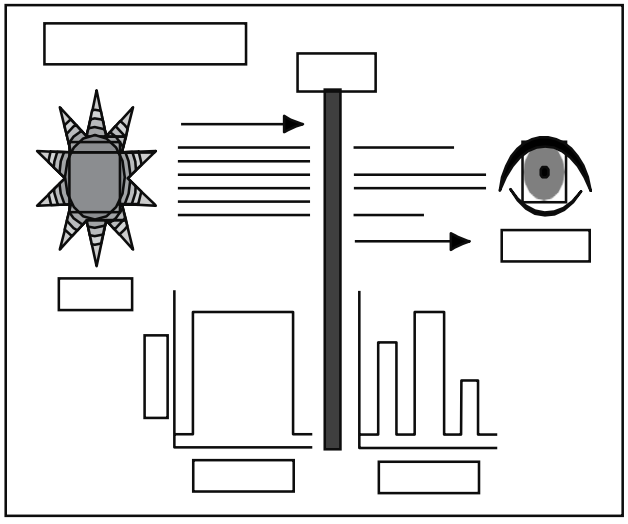


Figure 5. 6: FTIR spectrometer experimental set up

WHY FT-IR?

In order to overcome the limitations of dispersive instruments, Fourier Transform Infrared (FT-IR) spectrometry was developed. The slow scanning process was the main issue. It was necessary to develop a method for measuring all infrared frequencies simultaneously rather than individually. An interferometer, a very simple optical device, was used to develop a solution. The interferometer generates a unique signal that contains all of the infrared frequencies "encoded." The signal can be measured very quickly, usually in a fraction of a second. As a result, the time element per sample is reduced from several minutes to a few seconds.

Fig 5. 7: Interferogram

A beam splitter is used in most interferometers to divide the incoming infrared beam into two optical beams.

A flat mirror, which is fixed in place, reflects one beam. The other beam reflects off a flat mirror that moves a very short distance (typically a few millimetres) away from the beam splitter thanks to a mechanism. When the two beams meet again at the beam splitter, they reflect off their respective mirrors and are recombined. The signal that exits the interferometer is the result of these two beams "interfering" with each other because one beam's path is fixed and the other's is constantly changing as its mirror moves.

The resulting signal is known as an interferogram, and it has the unique property of having information about each infrared frequency that comes from the source in every data point (a function of the moving mirror position) that makes up the signal. This means that all frequencies are measured simultaneously as the interferogram is measured.

(a)

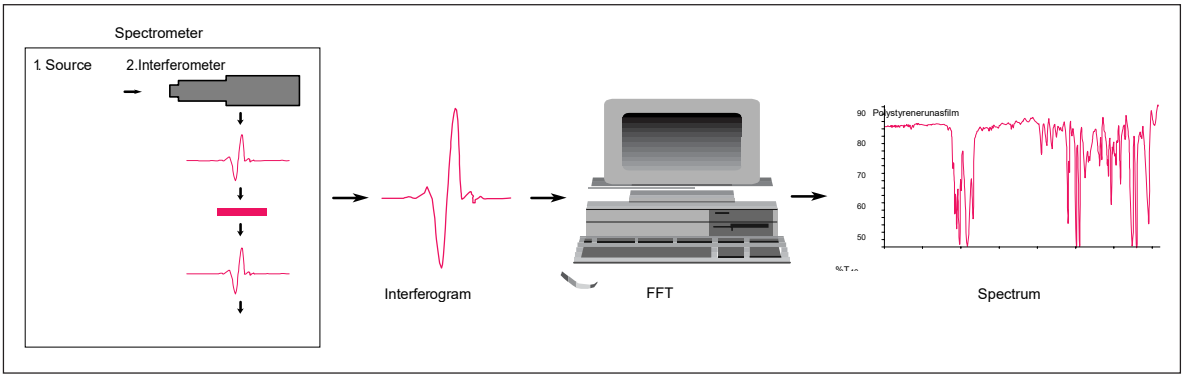


Figure 5. 8(a), (b) & (c) Schematic of spectrometer experimental setup

It's necessary to have a way of "decoding" the individual frequencies. The Fourier transformation, a well-known mathematical technique, can be used to accomplish this. The computer performs this transformation and then presents the user with the desired spectral information for analysis.

As a result of the interferometer's use, measurements are extremely quick.The measured interferogram signal cannot be interpreted directly because the analyst requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to identify.

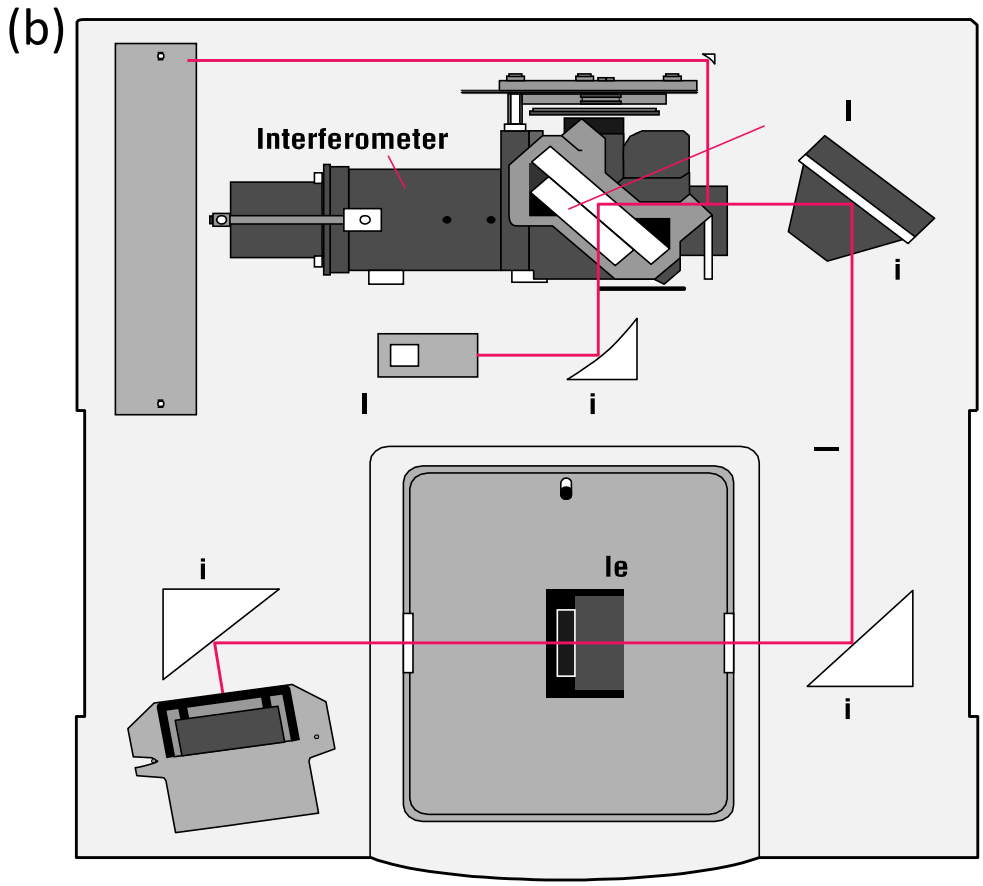


Figure 5. 9: Schematic setup of spectrometer

WHY INFRARED SPECTROSCOPY?

For over seventy years, infrared spectroscopy has been a workhorse technique in the laboratory for materials analysis. An infrared spectrum is a sample's fingerprint, with absorption peaks corresponding to the frequencies of vibrations between the bonds of the material's atoms. Because each material is made up of a different set of atoms, no two compounds have the same infrared spectrum. As a result, infrared spectroscopy can be used to positively identify (qualitatively analyze) any type of material. Furthermore, the size of the peaks in the spectrum indicates the amount of material present. Infrared is an excellent tool for quantitative analysis thanks to modern software algorithms.

(c)

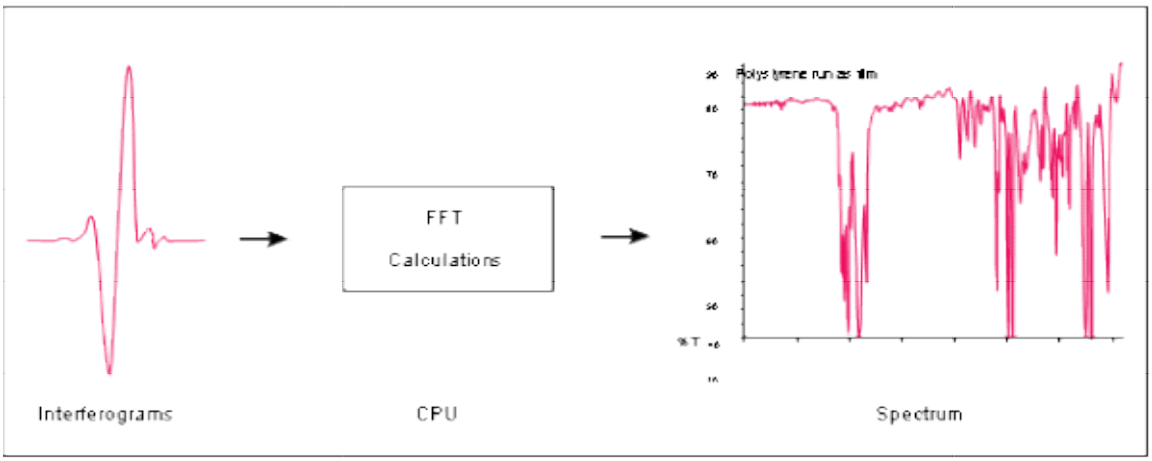


Figure 5. 10: Outline of spectrometer experimental setup

Because the absorption intensity must be measured on a relative scale, a background spectrum must also be measured. Normally, this is a measurement without a sample in the beam. This can be compared to the "percent transmittance" measurement taken with the sample in the beam. This method yields a spectrum that is devoid of all instrumental characteristics. As a result, all spectral features present are solely due to the sample. Because the instrument's spectrum is characteristic, a single background measurement can be used for multiple sample measurements.

OLDER TECHNOLOGY

The first infrared instruments were dispersive in nature. Individual frequencies of energy emitted from the infrared source were separated using these instruments. A prism or grating was used to accomplish this. A visible prism separates visible light into its colours, and an infrared prism does the same (frequencies). A grating is a more modern dispersive element that separates infrared energy frequencies better. The detector counts the amount of energy that has passed through the sample at each frequency. As a result, a spectrum is created, which is a plot of intensity against frequency.

For several reasons, Fourier transform infrared spectroscopy is preferred to dispersive or filter methods of infrared spectral analysis:

• It is a non-destructive technique

• It provides a precise measurement method that does not require external calibration

• It can increase speed, collecting a scan every second

• It can increase sensitivity – one second scans can be co-added together to ratio out random noise

• It has greater optical throughput.

THE SAMPLE ANALYSIS PROCESS OF NEW INNOVATIVE FTIR:

The standard instrumental procedure goes like this [2]:

1. **The Source**: A glowing black-body source emits infrared energy. This beam passes through an aperture that regulates how much energy is delivered to the sample (and, ultimately, to the detector).

2. **The Interferometer**: The beam passes through the interferometer, which performs "spectral encoding." The interferogram signal is then output from the interferometer.

3. **The Sample**: Depending on the type of analysis being performed, the beam enters the sample compartment and is transmitted through or reflected off the surface of the sample. This is where the sample's specific frequencies of energy, which are unique to it, are absorbed.

4. **The Detector**: The beam finally reaches the detector, where it is measured. The detectors used were created specifically to measure the interferogram signal.

5.**The Computer**: The measured signal is digitized and sent to the computer, which performs the Fourier transformation. The user is then presented with the final infrared spectrum for interpretation and any further manipulation.

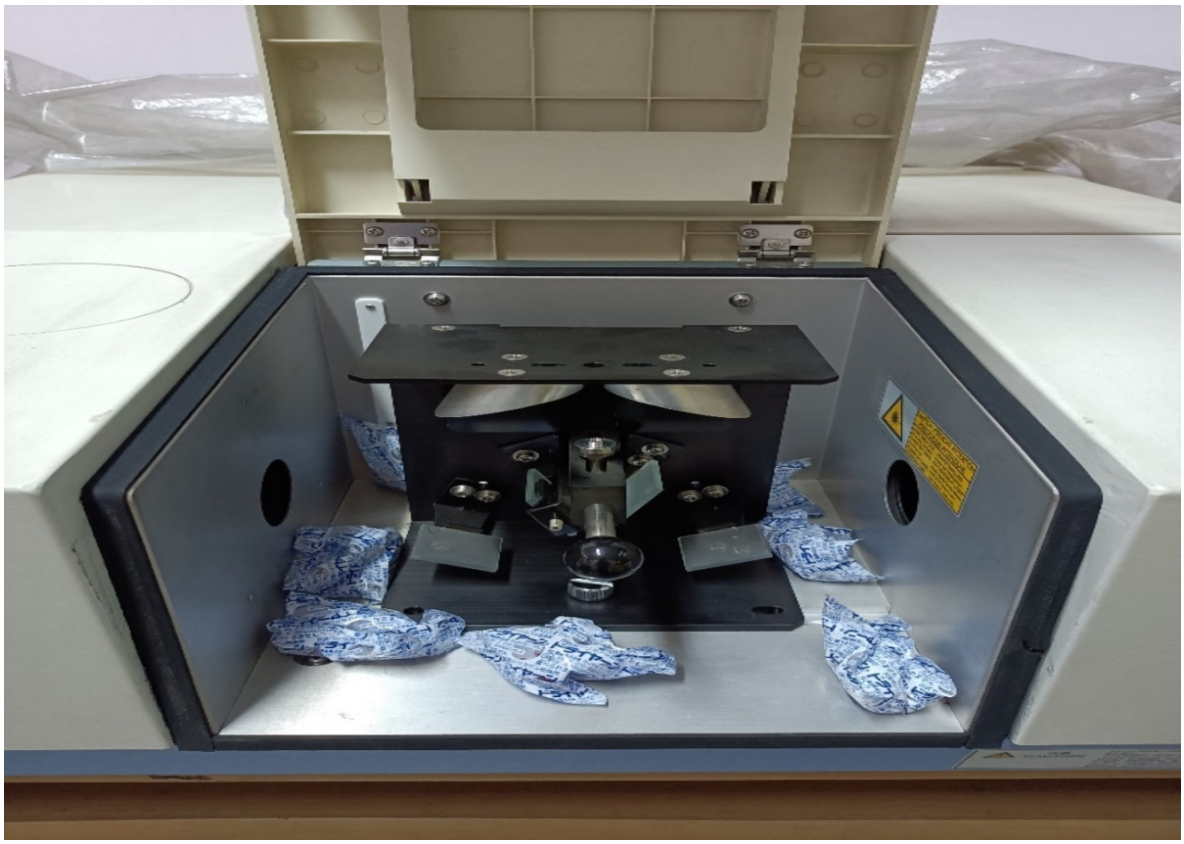


Figure 5. 11: Internal components of FTIR instrument.

ADVANTAGES OF FT-IR

The following are some of the major advantages of FT-IR over the dispersive technique:

• **Speed**: Because all of the frequencies are measured at the same time, most FT-IR measurements are completed in seconds rather than minutes.

• **Sensitivity**: FT-IR dramatically improves sensitivity for a variety of reasons. The detectors used are much more sensitive, the optical throughput is much higher resulting in much lower noise levels, and the fast scans allow the co-addition of multiple scans to reduce random measurement noise to any desired level.

• **Mechanical Simplicity**: The interferometer's moving mirror is the instrument's only continuously moving part. As a result, mechanical failure is extremely unlikely.

• **Internally calibrated**: A HeNe laser is used as an internal wavelength calibration standard in these instruments (referred to as the Connes Advantage). These instruments are self-

calibrating and do not require user calibration. These advantages, along with a number of others, make FT-IR measurements extremely precise and repeatable. As a result, it's a very reliable technique for positively identifying almost any sample. The sensitivity benefits allow even the tiniest contaminants to be detected. As a result, whether it's batch-to-batch comparisons to quality standards or analysis of an unknown contaminant, FT-IR is an invaluable tool for quality control and quality assurance applications.

Figure 5. 12: FTIR spectra of different samples by using- Shimadzu IR Prestige, (Japan)

5.2.2. HIGH RESOLUTION TRANSMISSION ELECTRO MICROSCOPE (HRTEM):

Transmission electron microscope (TEM) is an analytical tool allowing visualization. A beam of electrons is transmitted through an ultrathin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused on to an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected

by a sensor such as a CCD camera. TEMs are capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons.

Working Principle:

- The "Virtual Source" at the top represents the electron gun, producing a stream of monochromatic electrons. The first lens (usually controlled by the "spot size knob") largely determines the "spot size"; the general size range of the final spot that strikes the sample. The second lens (usually controlled by the "intensity or brightness knob" actually changes the size of the spot on the sample; changing it from a wide dispersed spot to a pinpoint beam.
- The beam is restricted by the condenser aperture (usually user selectable), knocking out high angle electrons (those far from the optic axis, the dotted line down the centre).
- The beam strikes the specimen and parts of it are transmitted.
- This transmitted portion is focused by the objective lens into an image.
- Optional Objective and Selected Area metal apertures can restrict the beam; the Objective aperture enhancing contrast by blocking out high-angle diffracted electrons, the Selected Area aperture enabling the user to examine the periodic diffraction of electrons by ordered arrangements of atoms in the sample.
- The image is passed down the column through the intermediate and projector lenses, being enlarged all the way.
- The image strikes on the phosphor image screen and light is generated, allowing the user to see the image.

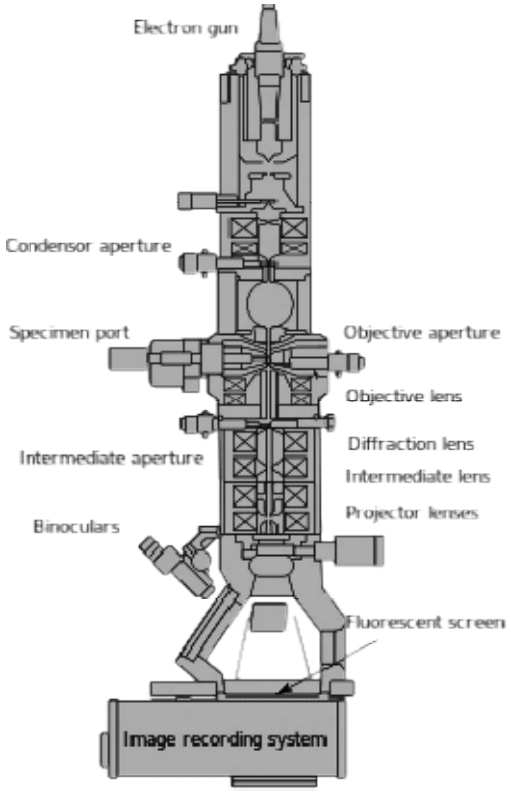


Fig5. 13. Schematic of HRTEM

Sample preparation for TEM generally requires more time and experience than for most other characterization techniques. A TEM specimen must be approximately 1000 A^o or less in thickness in the area of interest. The entire specimen must fit into a 3 mm diameter up and be less than about 100 microns in thickness. A thin, disc shaped sample with a hole in the middle, the edges of the hole being thin enough for TEM viewing, is typical. The initial disk is usually formed by cutting and grinding from bulk or thin film/substrate material, and the final thinning done by ion milling. Other specimen preparation possibilities include direct deposition onto a TEM-thin substrate (Si_3N_4, carbon); direct dispersion of powders on such a substrate; grinding and polishing using special devices like tripod; chemical etching and electro-polishing; and lithographic patterning of walls and pillars for cross-section viewing.

Figure5. 14. HRTEM (JEOL-200 kV)

5. 3.INSTRUMENTS USED FOR I-V CHARACTERIZATION:

The two-probe method is based on the definition of resistance when two electrodes are used to measure the electrical resistance. Figure 1 schematically shows a specimen, on which a pair of contacts (probe 1 and probe 2) with conductive wires is attached.

Two probes are used for the electrical current input, as well as for the voltage measure. The resistance of the segment between the voltage contacts can be calculated through Ohm's law:

$$V = I * R$$

Where, V and I are the voltage and current from the voltage and current contacts, respectively.

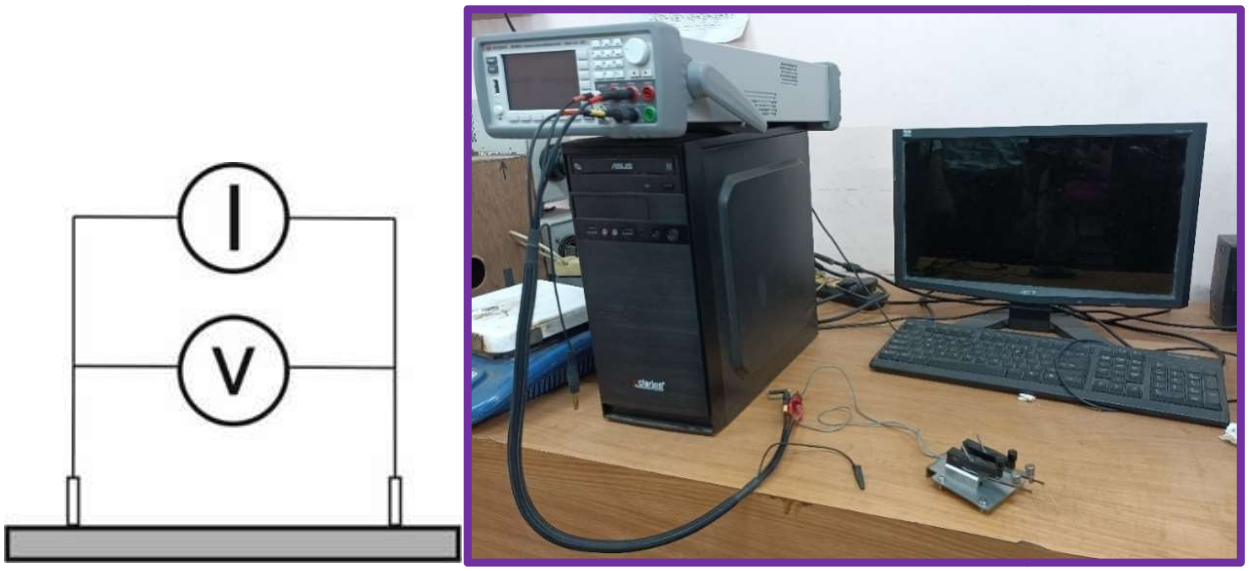
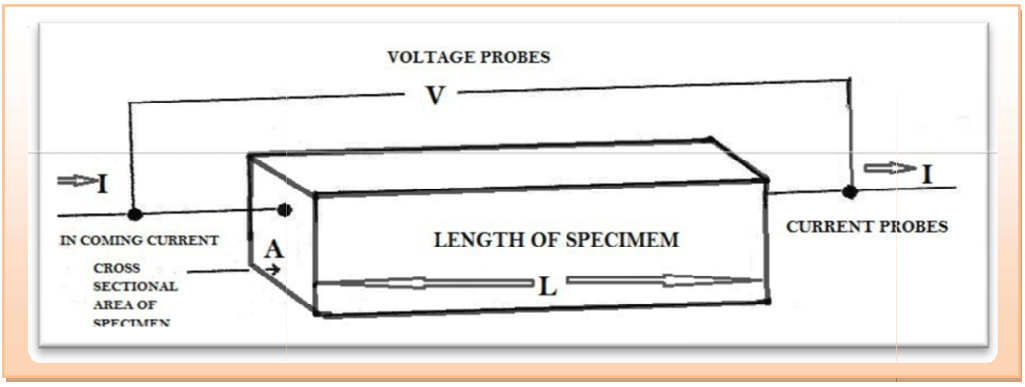


Figure5. 15. Two probe device used in the Thesis



5. 3.1.KEYSIGHT SOURCE METER:

Keysight B2902A source meter used to measure all current-voltage measurements including resistive switching and synaptic properties during my project work. This SMU is very much portable and advanced, cost effective, easy to use compare to other competitors in market. A 2-channel, small, and reasonably priced bench-top SMU, the Keysight B2902A Precision Source/ Measure Unit (SMU) has the ability to source and measure both voltage and current.

It can easily and accurately monitor current vs. voltage because of its versatility. I/V measurement is made simple and straightforward without the need to configure different instruments than to the integration of 4 quadrant source and measurements capabilities. The minimal expenditure is made possible by the single instrument's extensive coverage of 210 V, 3 A DC and 10.5 A pulse. Accurate characterization of the DUT is supported by a minimum measurement resolution of 100 fA/100 nV. The Keysight B2902A precision Source/Measure Unit (SMU) is a benchtop SMU SMU with two channels that can source and measure current as well as voltage.

Tungsten (W) probes also used with the system. Probes are connected to the top and bottom electrodes of the system.

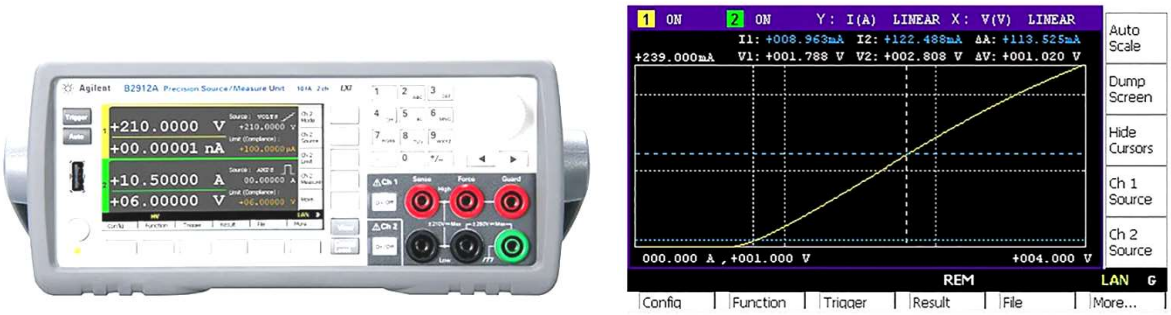


Fig5. 16. Keysight B2902A source meter

The room temperature current voltage (I-V) measurements under DARK and U-V light were performed to determine the diode characteristics of the produced Si/TiO_2 heterojunction device.

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CHAPTER:6

Synthesis of SiNWs/TiO_2 nanoheterojunction

6. 1. Introduction:

A large number of studies have been done to synthesize silicon because of its interesting physical, and chemical properties. Silicon nanowires have been synthesized by various methods which have been reported before like laser ablation, vapour-liquid-solid (VLS) process, chemical vapour deposition, oxide-assisted growth, plasma etching, physical evaporation or metal-assisted chemical etching. Out of these techniques, metal-assisted chemical etching is the most cost-effective and easy process as the other methods require high temperature, high vacuum, and ignitable silicon precursors which give rise to a high cost of synthesis [1-5].

Metal-Assisted Chemical Etching (MACE) results in Si nanowire arrays with idiosyncratic quality as compared to other fabrication techniques:

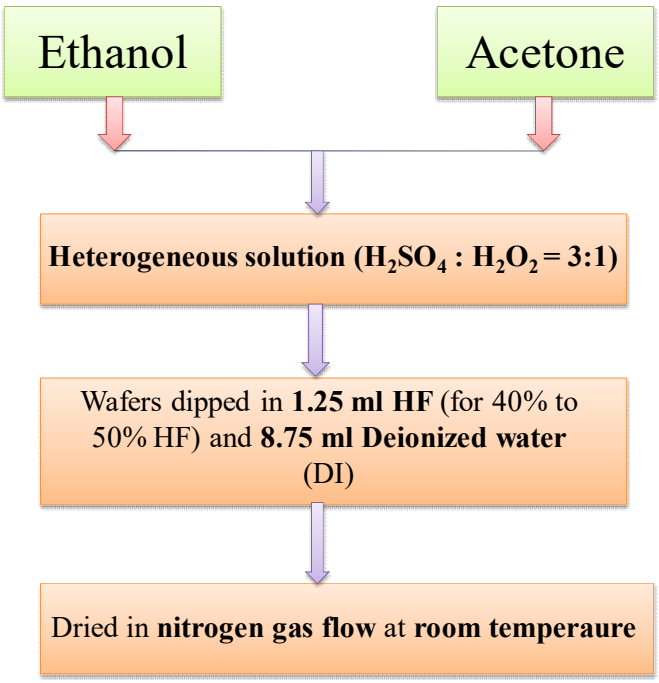
- Single crystalline
- Uniform diameter and lengths
- High aspect ratio, vertically aligned
- Uniform doping throughout the nanowires
- Large surface area to volume ratio
- Variable density

So here we have used the metal-assisted chemical etching(MACE) technique for the synthesis of the silicon nanowires and the parameters during synthesis are varied to obtain changes in the morphological structure. In this study, silicon nanowires are synthesized by metal assisted chemical etching (MaCE) at 60 ºC temperature with different etching times. SiNW 40, SiNW 60, and SiNW 80 are obtained at 40, 60, and 80 min of etching time respectively. XRD, FESEM, TEM, UV-VIS, and FTIR are studied to characterize all nanowires. In this study, porous silicon nanowires (SiNW) are synthesized through MaCE (Metal Assisted Chemical Etching) varying the etching time under a constant temperature. Different characterizations are performed to confirm its formation and properties.

6. 2. Synthesis of Silicon Nanowire:

Here p-type Si (100) B-doped wafer is used. Firstly, suitable-sized wafers were cut into small pieces. The cleaning process of silicon wafer comprises some steps. The steps are discussed here in detail.

- At first, silicon wafers were immersed in a solution of ethanol for cleansing purposes with an ultrasonic bath. Then silicon wafers were cleansed using acetone with an ultrasonic bath. Silicon wafers were immersed for atleast 5 minutes.
- Secondly, silicon wafers were immersed in a heterogeneous solution (H_2SO_4: H_2O_2 = 3:1). This was done at room temperature for 20 minutes. This process is done to remove organic deposits on silicon wafer.
- After this step, 1.25 ml HF (for 40% to 50% HF) and 8.75 ml of Deionized water (DI) are poured into a plastic beaker to make the solution 10 mL. The silicon wafers were dipped in that plastic beaker for 5 minutes again.
- Lastly, the Silicon wafers were dried in nitrogen gas flow. This was done at room temperature.



6. 2.1.Preparation of Piranha Solution: The solution is atypical mixture of 3 parts of concentrated sulfuric acid (H_2SO_4) and 1 part of 30% hydrogen peroxide (H_2O_2) solution. Sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) were taken in the ratio of 3:1. The exact process for preparing Piranha solution is to add hydrogen peroxide (H_2O_2) of 3ml to Sulfuric acid (H_2SO_4) of 9ml slowly, not in reverse. The mixture is such a strong oxidizing agent it removes organic matter. It will also hydroxylate most surfaces (-OH groups), making them highly hydrophilic (water-compatible). Mixing the solution is highly exothermic. Piranha solution is mostly used to clean organic residues off substrates.

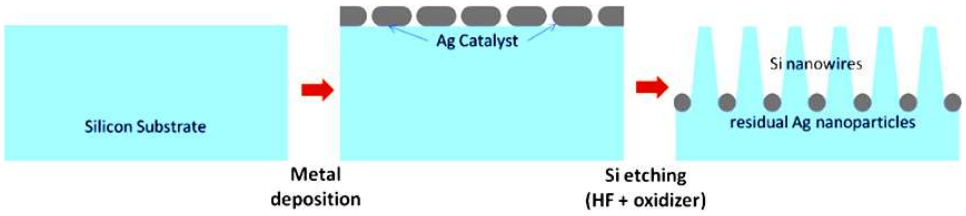


Fig6. 1. Overview of MACE process

6. 2.2.MACE process:

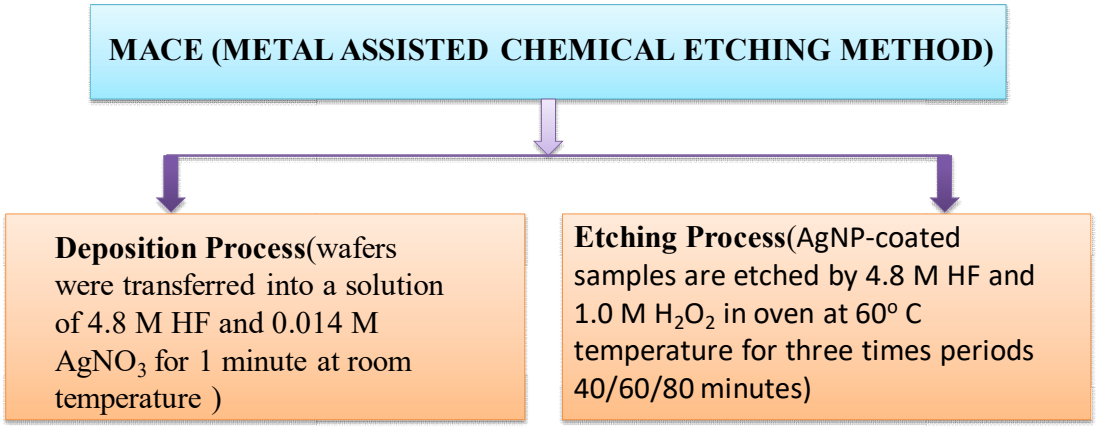
Silicon nanowires were prepared by a very familiar and conventional two-step method of **metal assisted chemical etching method**. [6-7]

a) Deposition process and **b) Etching Process.**

- In the first step of the MACE process, the treated wafers were transferred for Silver(Ag) nanoparticle deposition into a solution containing 4.8 M HF and 0.014 M $AgNO_3$ for a few seconds (nearly 60 seconds/1 minute) at room temperature for Ag nanoparticle deposition. In this step, AgNPs were deposited on the surface of silicon wafers. After that, the samples are rinsed with deionized water. The agglomeration of Silver Nitrate ($AgNO_3$) has a deep well-built impact on the morphologic structure of AgNPs deposited on silicon nanowire.

- In the second step, the AgNP-coated samples are etched by 4.8 M HF and 1.0 M H_2O_2 in oven at 60^o C temperature for three times periods. The etching times are 40, 60, and 80

minutes respectively. After the completion of the etching process, the Ag nanoparticles are eliminated by HNO_3 solution.



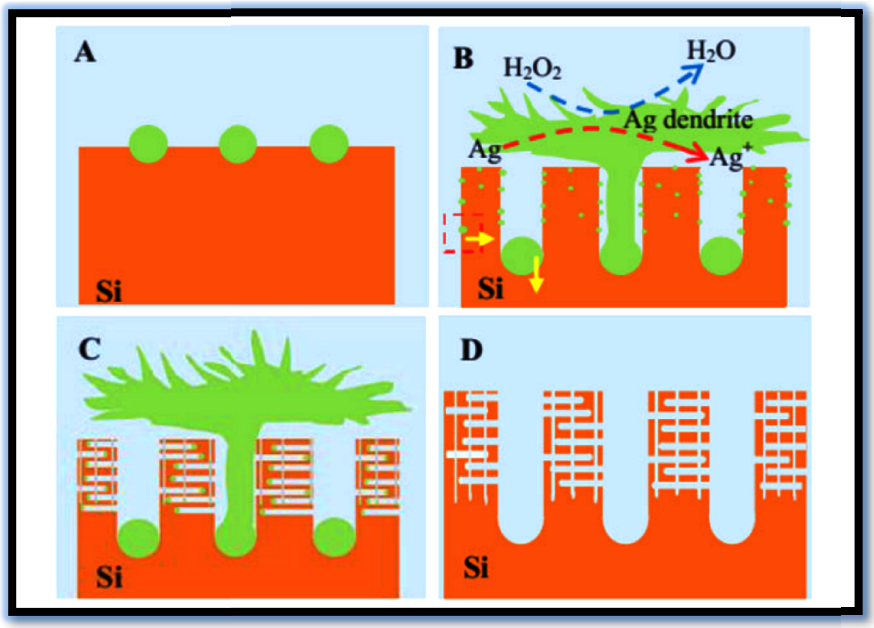


Fig6. 2. Schematic illustration of the development of SiNW through MACE method. (A) Ag nanoparticles are deposited on the silicon surface at the beginning, (B) Silicon nanowires grow with the migration of Ag particles, (C) Various perpendicular pore channels are formed with the migration of Ag nanoparticles, and (D) Porous structure can be found with the removal of Ag nanoparticle with the help of HNO_3 [8]

HNO_3 solution dissolves the silver nanoparticles (AgNPs). During the cleansing of the Ag-coated samples with HNO_3 solution, the oxide layer is generated. For removing this oxide layer the sample is immersed in HF (5%) solution for 5 minutes at room temperature. The wafer is

rinsed with deionized water several times. After that, samples are dried in a vacuum oven at 60° C for 3-4 hours.

The etch rate of silicon increases with the presence of H_2O_2. As we know, the redox potential of H_2O_2 (1.77 V vs. Standard Hydrogen Electrode (SHE)) is greater than Ag^+ (0.78 V vs. SHE). By the use of H_2O_2, the holes are injected into the silicon valence band more easily through the Ag particle surface.

$$H_2O_2 + 2H^+ = 2H_2O + 2h^+$$

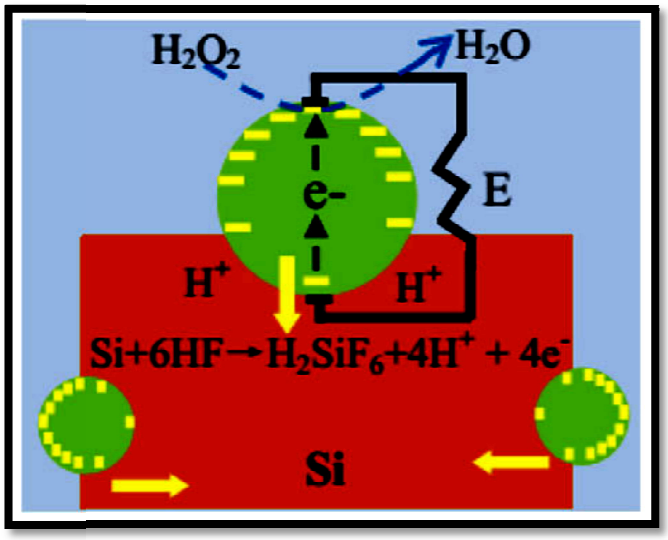


Fig6. 3. Ag nanoparticle migration in bulk silicon driven by self-electrophoresis mode [9]

At Cathode

The generated Ag particle worked as microcathodes on the surface of the silicon wafer. The Ag microcathodes catalyze H_2O_2 reduction. This was on the side of etchant, consuming proton (H^+) and electrons.

$$H_2O_2 + 2H^+ \longrightarrow 2H_2O + 2h^+$$

E^o=1.77 V (vs. SHE)

$$2H^+ + 2e^- \longrightarrow H_2 \uparrow$$

At Anode

Facing the silicon, on the other side of Silver (Ag) behave as a catalyst and oxidize Silicon and generate electron. It generates H^+ and electrons.

$$Si + 4h^+ + 6HF \longrightarrow H_2SiF_6 + 4H^+$$

E^o=1.2 V (vs. SHE)

Overall Reaction:

$$Si + H_2O_2 + 6HF \longrightarrow 2H_2O + H_2SiF_6 + H_2 \uparrow$$

6. 2.3.HF (Hydrofluoric acid) Solution Safety:

For preparing silicon nanowire Hydrofluoric acid is needed and it is known that hydrofluoric acid has a highly corrosive nature. Exposure to Hydrofluoric acid in the air can be catastrophic even if it is in a small amount. So, it must be handled very carefully and cared in the guidance of trained people. HF is extremely reactive to metal so only plastic materials are used.

6. 2.4.Piranha Solution Safety:

Piranha solution is erosive and it causes irritation to the eyes. During the formation of piranha solution, one should be very careful and preferably one should wear personal protective equipment. It must be handled with extreme safety. It is very dangerous to the skin and it can easily meet the plastic container. So, the container which is used during this piranha experiment must be labelled and keep it at enough distance.

6. 3.Some basic concepts about solutions :

- Molarity is the number of moles of solute present in 1 liter of solution.
- The mass percentage of a component in the solution is 100 times the mass of the component in the solution divided by the total mass of the solution.

- Molarity is also the number of millimoles of solute presents in 1 milliliters of solution.
- Number of moles = Mass in grams / Molar mass
- Normality equation : $V_1S_1=V_2S_2$
- Molarity equation : $M_1V_1 = M_2V_2$
- Molarity = $\frac{moles\ of\ solute}{litres\ of\ solution} = \frac{mmoles\ of\ solute}{milliliters\ of\ solution}$
- Molarity formula : M=(%x density/Molecular weight)×1000

Preparation of 4.8M HF (Hydrofluoric acid) Solution:

Density of 40% HF acid (d) = 1.13 gm/mlMolecular

weight of HF = 20.01 gm/mol

Molarity of 40% HF acid = (40% x 1130)/20.01= 452/20.01=22.6M

Now using,

$M_1V_1= M_2V_2$

$22.6\times V_1 = 4.8\times10$

$V_1 =2.125$ ml

So, add 2.125 ml HF to 2.5 ml DI and make the final volume 10 ml.

Preparation of 1 M H_2O_2 (Hydrogen Peroxide) Solution:

Hydrogen Peroxide (H_2O_2)

Density of 30% H_2O_2 (d) =1.11 gm/ml Molecular weight

of H_2O_2= 34.01gm/mol

Molarity of 30% H_2O_2 = (30% x 1110)/34.01= 333/34.01= 9.8M

Now using,

$M_1V_1=M_2V_2$

$9.8\times V_1 = 1.0\times10$

V_1=1.020 ml

So, add 1.020 ml of 30%H_2O_2 to DI and make the final volume10 ml.

Preparation of 0.014 M $AgNO_3$ (Silver Nitrate) Solution:

Density of Silver Nitrate ($AgNO_3$) is (d) = 4.35gm/cm^3

Molecular weight of $AgNO_3$ is = 169.874 gram/mole

The molar mass of silver is 107.87 gram/mole

The molar mass of nitrogen is 14.007 gram/mole

The molar mass of oxygen is 15.999 gram/mole

On adding up, we can get the value of $AgNO_3$:

(107.87+14.007+(3×15.999)) = 169.874 gram/mole

So, 1 liter of solution contains 169.874 gram/mole.

$AgNO_3$ (Silver Nitrate)

This implies, 10mL solution contains 1.69874 gm/M Of $AgNO_3$.

To prepare 10mL of 0.014 M of $AgNO_3$ solution, (1.69874 gm/M)×0.014 M =0.0234 gm of $AgNO_3$ is added to the 10mL of DI.

6. 4.Experimental Section

6. 4.1.Seeding Layer preparation after synthesis of silicon nanowire:

A seed layer for deposition of titanium dioxide (TiO_2) was prepared on silicon nanowires. This process comprises three steps which are described as follows. The porous silicon was submerged in a solution at a room temperature for about 2 minutes. The solution is a mixture of isopropanol and 0.075 M tetrabutyltitanate or titanium butoxide. The samples were immersed in ethanol for 1 minute. Then, the samples were dehydrated in nitrogen gas flow. This procedure was repeated five times. At the end of the seeding layer process, the samples were annealed at 500^{o} C. The time was 2 hours.

6. 4.2.Hydrothermal Synthesis after Seeding Layer Preparation on silicon nanowire:

The hydrothermal process was accomplished in stainless steel autoclaves. The 40 mL hydrochloric acid (HCl) was mixed in 40mL deionized water (DI) drop by drop. This mixed solution was kept on a magnetic stirrer until tetrabutyltitanate was added to it. 2 mL tetrabutyltitanate or titanium butoxide was added to the mix solution. Now, the TiO_2 nanowires were immersed in it. The solution was then moved in the autoclave limited up to 15 mL. The sample was poured in it and the autoclave was tightened with polytetrafluoro ethylene liners (25 ml). The autoclaved was then set down in an oven at 150^{o}C. The reaction time was scheduled at 2, 4, 6, and 8 hours respectively. After that, the samples were rinsed with deionized water. Next, the samples were dehydrated through nitrogen gas flow. In the end, the samples were annealed for 30 minutes. The annealing temperature was 450^{o} C. Finally, porous Si/TiO_2 nanowires were obtained at 2, 4, 6, and 8 hours respectively.

6. 4.3.Hydrothermal Synthesis:

The hydrothermal process is the most frequently used process in nanotechnology for preparing nanomaterials. “Hydros” means water and thermal related to temperature. The establishment of the latest nanomaterial can happen through this hydrothermal method. It is mainly a chemical reaction in a clinched pressure vessel. The temperature in it varies widely. It varies from room

temperature to extreme temperature. Byrappa and Yoshimura proposed a definition of the "hydrothermal reaction" as any heterogeneous chemical reaction in the presence of a solvent (whether aqueous or non-aqueous) above room temperature and at a pressure greater than 1 atm in a closed system. For the purposes of this review, we assume that the "hydrothermal synthesis" is a process occurring in an aqueous environment (where $mH_2O > 50\%$), with the pressure equal to or higher than atmospheric pressure. In hydrothermal processes, reaction products are mainly oxides and salts due to the properties of water as a solvent.

ADVANTAGES OF THE HYDROTHERMAL METHOD:

I. Possible to precipitate powders directly from the solution
II. Ability to synthesize crystals of substances that are unstable near the melting point
III. Suitable when it is difficult to dissolve precursors at room or lower temperatures
IV. Can be hybridized with other processes like microwave, electrochemistry, ultrasound, etc.

DISADVANTAGES OF THE HYDROTHERMAL METHOD:

I. High cost of equipment e.g., the need for expensive autoclaves.

II. Inability to observe the crystals in the process of their growth.

Fig6. 4. Stirring machine

Fig6. 5. Ultra sonicate machine

I have investigated and evaluated the basic synthesis procedures of nanoparticles of SiNW. After completing my first laboratory experiment, I concentrated on the basic synthesis process for synthesizing Titanium dioxide nanoparticles i.e., hydrothermal synthesis. Before that, I have done the seeding layer preparation and then various characterizations were also carried out in order to know the optical properties and surface morphologies as well as ohmic characteristics of the samples.

6. 4.4.Preparation of 0.075 M tetrabutyltitanate:

Deionized water (DI) was taken= 40 mL.

Hydrochloric acid (HCl) was taken = 40 mL

Tetrabutyltitanate was taken = 2mL

2 mL titanium butoxide or tetrabutyltitanate was added to the combined solution of DI and HCl.

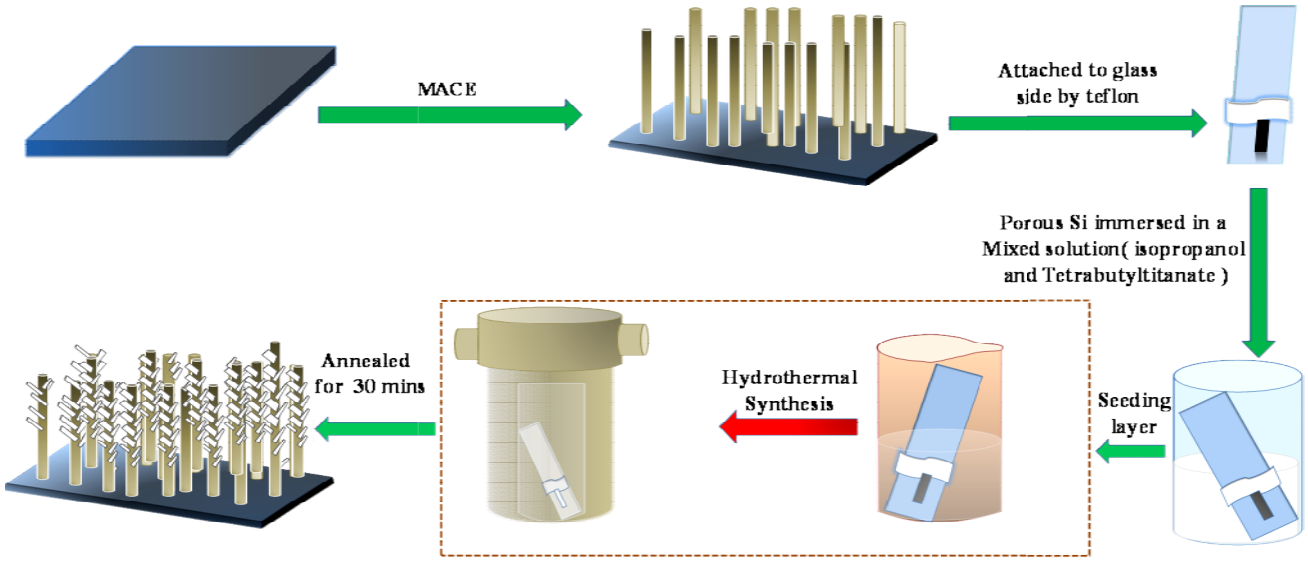


Fig6. 6. Schematic representation of the synthesis technique of SiNW/TiO_2 nanojunctions

The whole synthesis process and characterization process are described in the following figure 6.7.

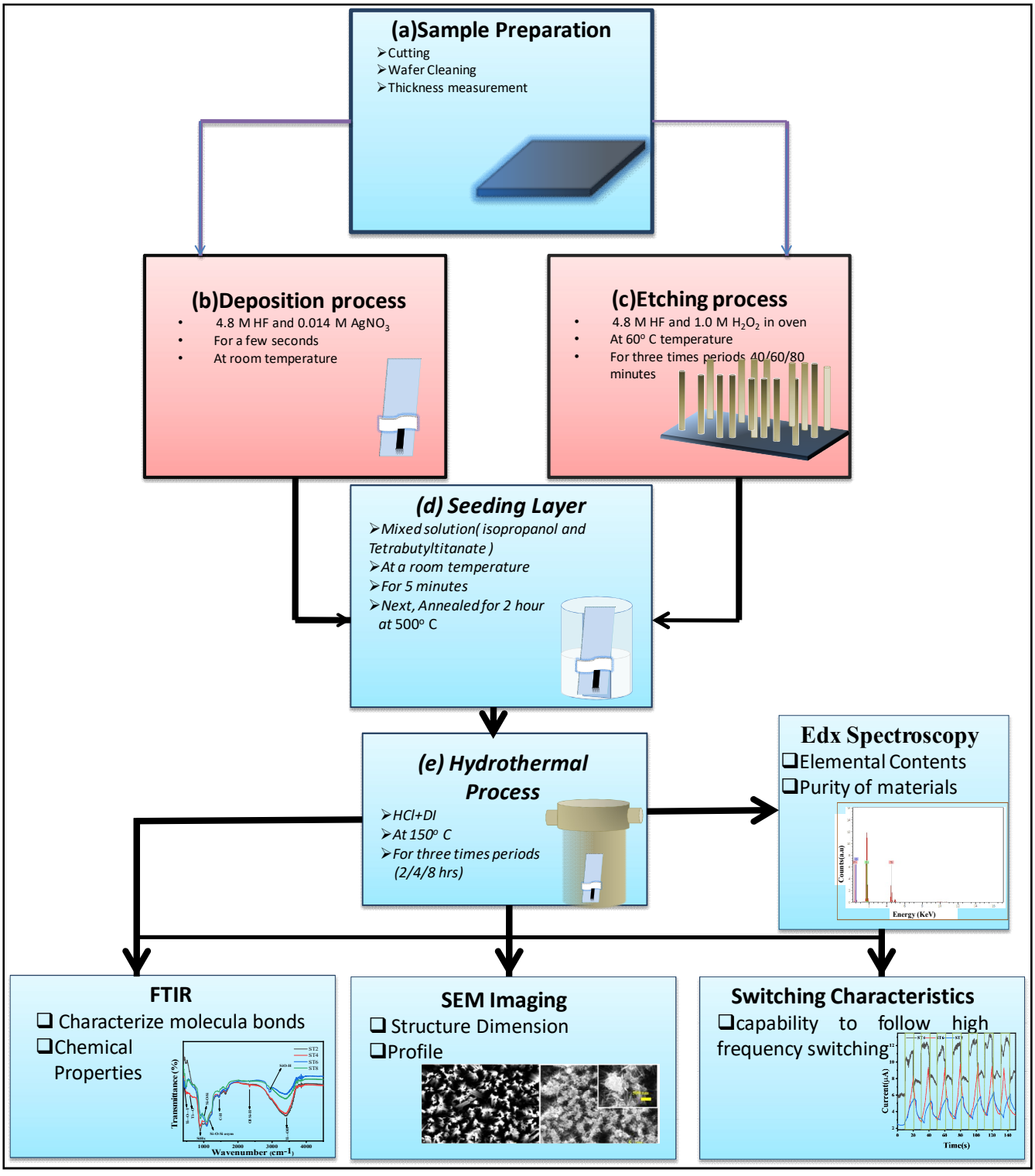


Fig6. 7. Overall Schematic technique of SiNW/TiO_2 nanojunctions (Preparation & Characterization)

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CHAPTER: 7

RESULT AND DISCUSSION

CHARACTERIZATION TECHNIQUES:

There are different characterization techniques used to characterize the phase, morphology, band gap, interplanar distance, crystal plane, crystal structure, and many properties of Si/TiO_2.

They are:

- **XRD**
- **FTIR**
- **FESEM**

How the characterization technique work and from that how can we characterize the phase, crystal structure, and morphology are explained below –

RESULTS AND DISCUSSIONS:

7.1. Crystal Structure Analysis

X-RAY DIFFRACTION:

Besides the phase identification, the XRD analysis is also important for the determination of particle size which can be formulated by the Scherrer formula –

$$\mathbf{D = k\lambda / \beta\cos\theta}$$

$$\mathbf{D = 0.9\lambda / \beta\cos\theta}$$

(K = 0.9 used to perform the crystalline size estimations)

Where D is the average crystallite size, β is the width of the X-ray peak, λ is the X-ray wavelength, β is normally measured as the full width at half maximum (FWHM), θ is the Bragg angle, and K is the so-called Scherrer constant. K depends on the indices of the diffraction line, size distribution, and crystallite shape. Usually, XRD is done first to determine its phase from the reference of JCPDS. It is important to realize that the Scherrer formula provides a lower bound on the particle size. The reason for this is that a variety of factors can contribute to the width of a diffraction peak; besides particle size, the most important of these are usually dependent on the factors like inhomogeneous strain and instrumental effects. If all of these other contributions to

the peak width were zero, then the peak width would be determined solely by the particle size and Scherrer's formula would apply. If the other contributions to the width are non-zero, then the particle size can be larger than that predicted by Scherrer's formula, with the "extra" peak width coming from the other factors. Basically, TiO_2 has three crystalline phases. Such that: Rutile phase (tetragonal), anatase phase (tetragonal), and brookite (orthorhombic). Diffraction patterns of rutile TiO2 powders were compared with reference to JCPDS database. In Fig7. 1, XRD patterns showed strong diffraction peaks at 27°, 36°, and 55°. It indicates the presence of TiO2 in the rutile phase. All peaks are in good accordance with the standard spectrum (JCPDS no.: 88-1175).The peaks denote crystal plane (110), (101), (111), and (211) for all compositions (x).To determine, the Si/TiO_2 ratio in the solid solution and its stoichiometries for different compositions, Energy Dispersive X-Ray (EDX) analysis was performed. From the EDX analysis, all the ratios and distributions of atom % and weight % are near to actual stoichiometries of the compounds.

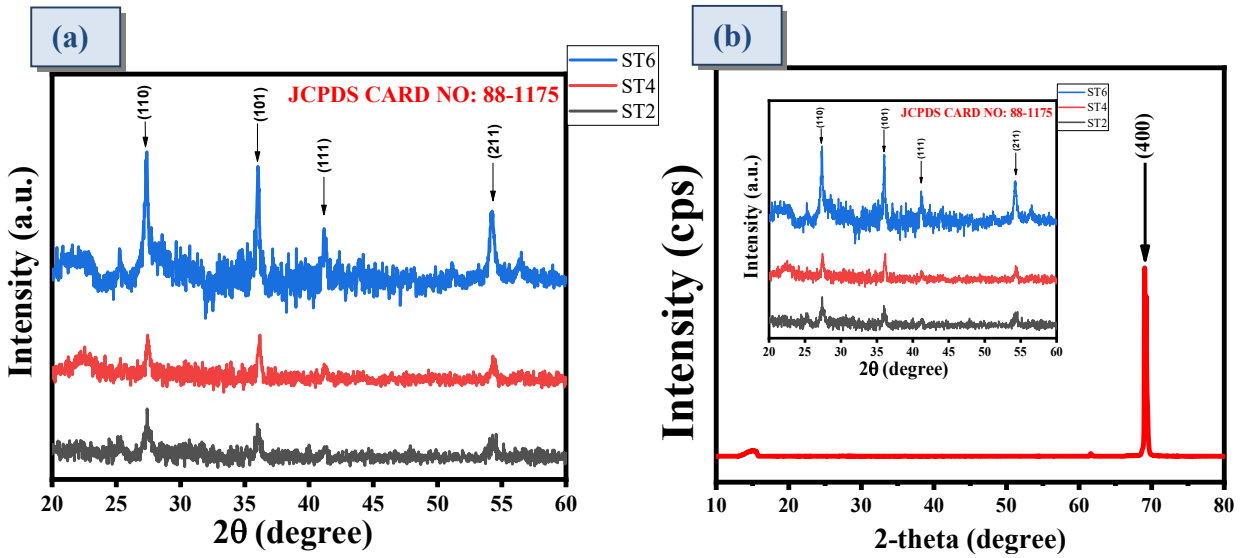

Fig7. 1(a) X-Ray Diffraction of Rutile TiO_2, (b) XRD Spectrum of SiNWs/TiO_2 Nanostructures

The elemental conformation analysis in the above figure (Fig7. 1(a) & (b)) reveals the presence of Si and TiO_2. Changes in crystallinity during the synthesis process are analyzed using X-Ray Diffraction. The results established the phase purity of the prepared SiNWs/ TiO_2 nanostructures with the acquired preparation strategy.The elemental mapping in Fig7. 2(a), (b), (c) and (d) validated the homogenous distribution of TiO_2 nanoparticles throughout the SiNWs arrays

(vertically aligned). XRD results revealed the most intense sharp peak at around 69° (2θ) which corresponds to the (400) plane.

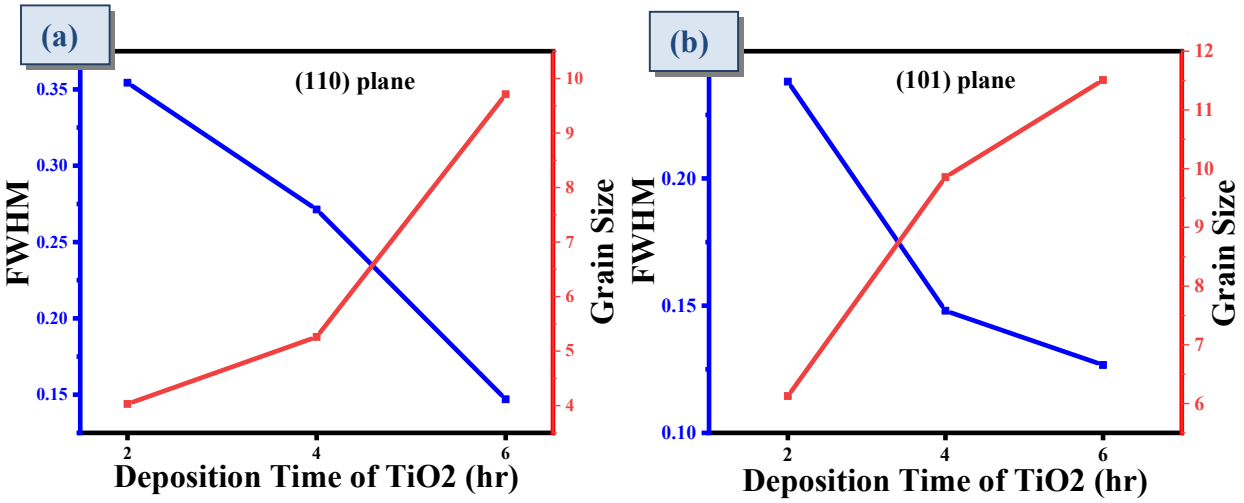

Fig7. 2(a) Grain Size and FWHM Variation in 110 plane, 7. 2(b) Grain Size and FWHM Variation in 101 plane

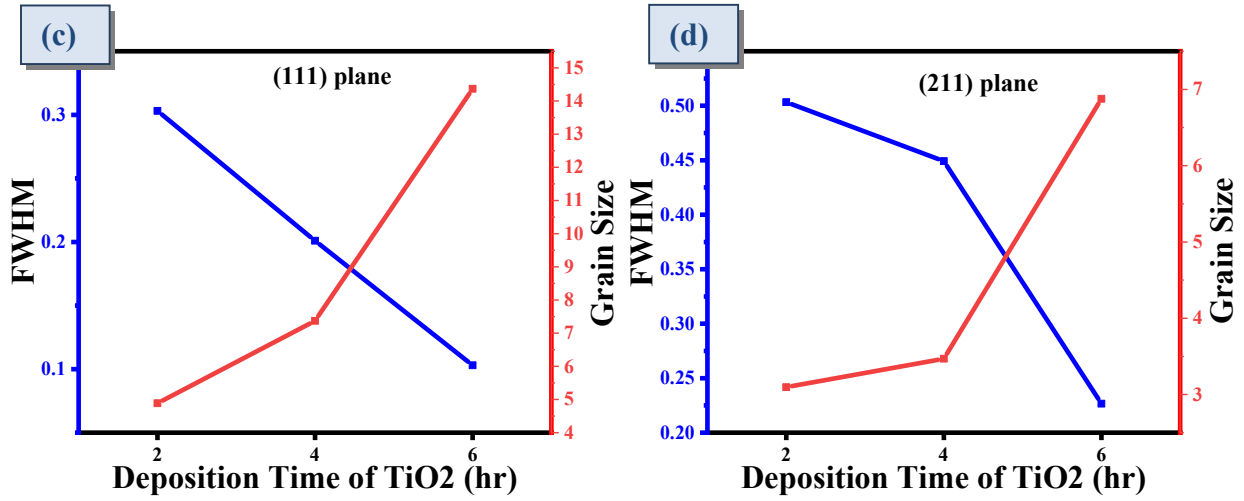

Fig7. 2(c) Grain Size and FWHM Variation in 111 plane, 7. 2(d) Grain Size and FWHM Variation in 211 plane

From the Grain Size and FWHM Variation graph, it can be concluded that the width of the X-ray peak (β) decreases with deposition time of TiO_2 whereas the grain size increases constantly for 101,110,111, and 211 planes with deposition time of TiO_2.

FWHM values of SiNWs/TiO_2 decreased with increasing deposition time which indicates that the crystallinity of the films has been improved with deposition time. The larger D and smaller

FWHM indicate better crystallization of the film. Mostly, an increase in deposition time can affect the crystallinity (crystalline quality) of polycrystalline semiconductor and change electrical properties. As we know from Scherrer's formula,

$$D = k\lambda / \beta\cos\theta$$

$$D \propto 1/\beta$$

Where D is the average crystallite size,β is the full width at half maximum (FWHM).

It is observed from Fig7. 2. that, the crystalline size values increases with deposition time, which clearly reveals the improved crystallinity. The amount of defects in a film can be determined from the formula,

$$\delta \propto 1/D^2$$

Where, Where D is the average crystallite size and δ is the dislocation density. So, with the increasing average crystallite size the dislocation density decreases and the defects in the film minimized.

Fig7. 3. EDAX Composition Table of ST4

Element Line	Atom (%)	Atom (%) Error
Si	29.86	+/- 0.49
Titanium	23.38	+/- 0.52
Oxygen	46.76	+/- 1.04
Total	100	

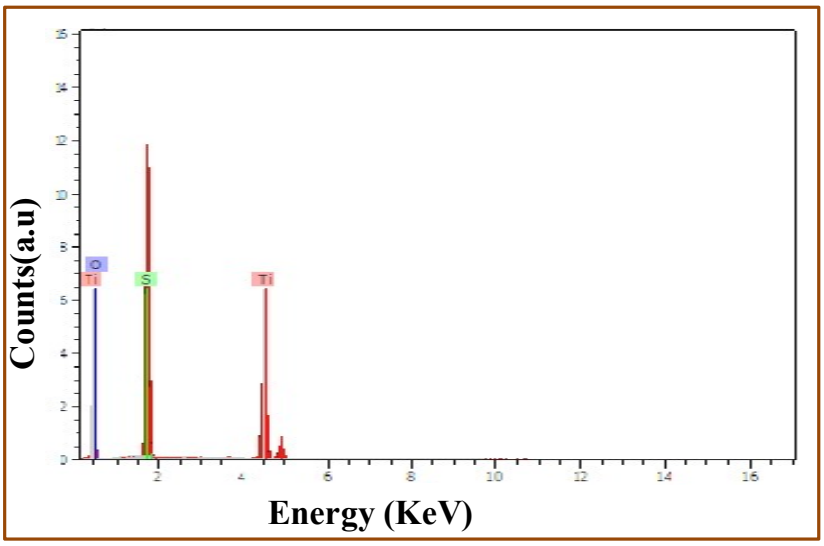

Fig7. 3. EDAX Spectra of ST4

7.2. Morphological Analysis:

FESEM IMAGES:

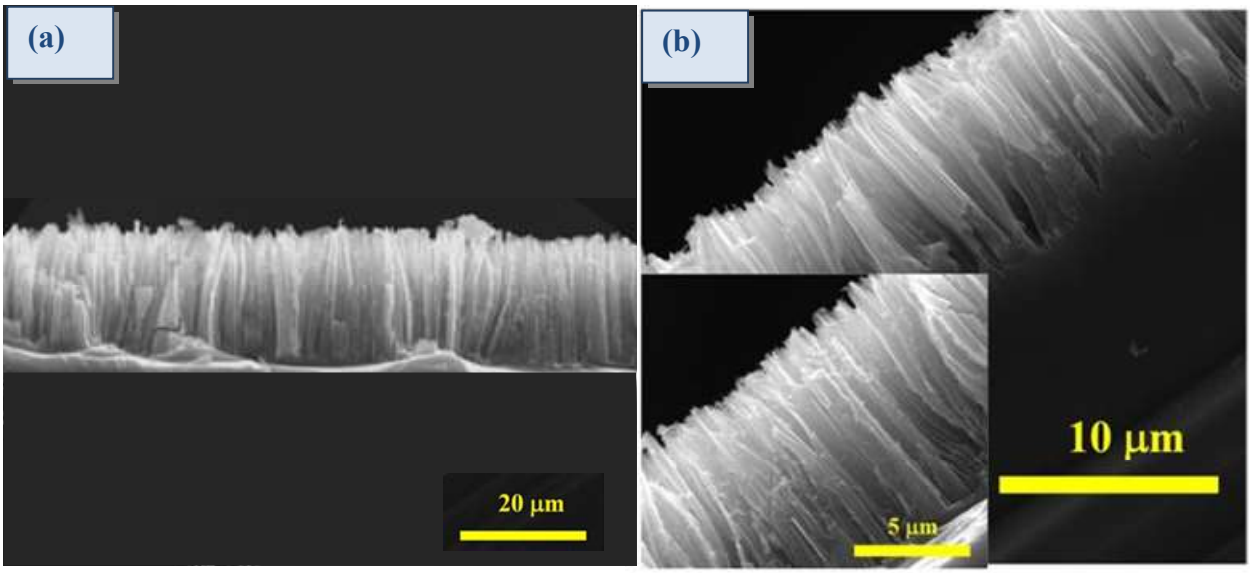

Figure7. 4(a)& 7. 4(b) Cross-sectional view of SiNW of high magnification

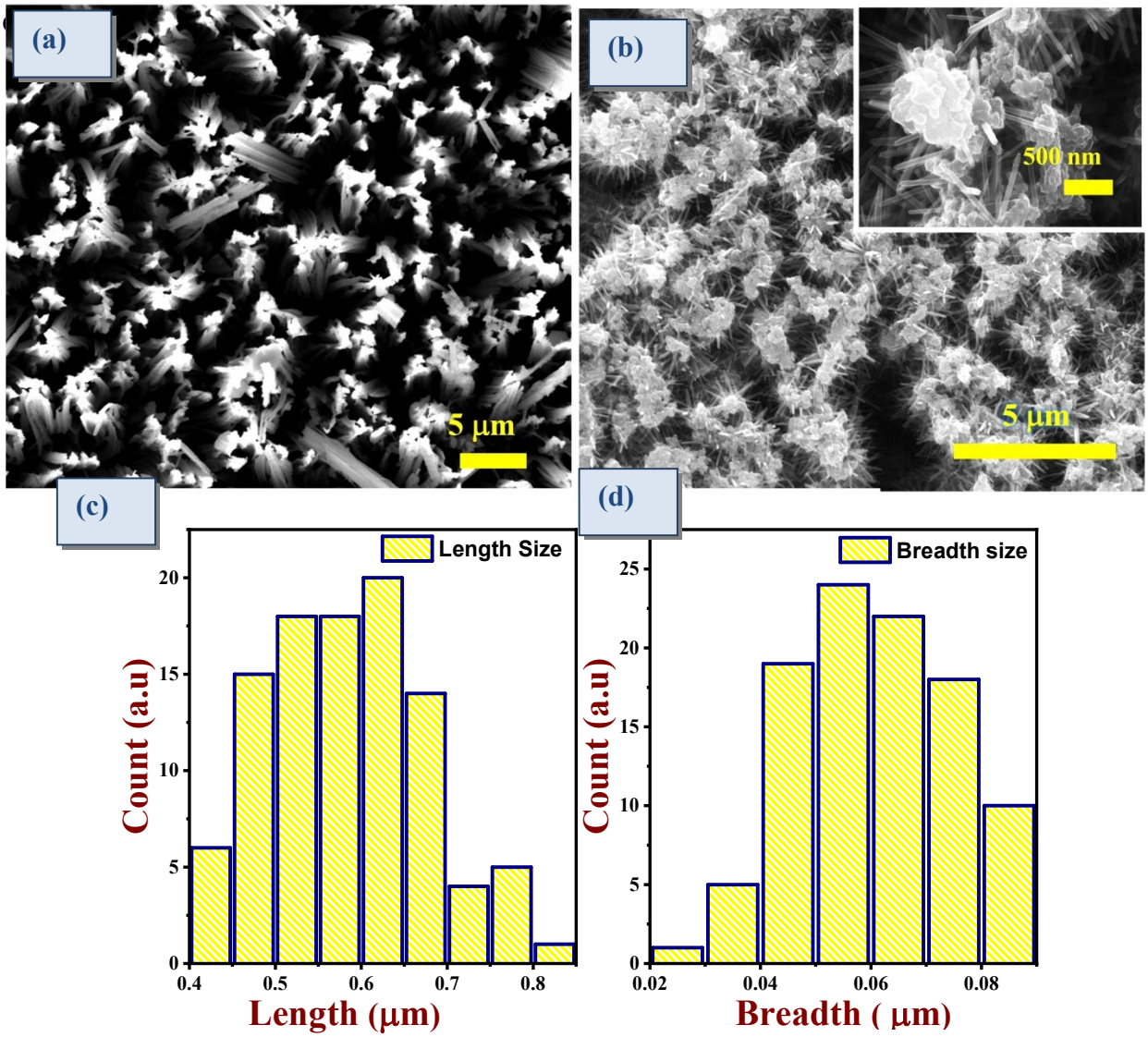

Fig7. 5(a) FESEM images of silicon nanowire, (b) FESEM images of low magnification and high magnification (insets) of sample ST2, Fig(c) Lengthwise particle size distribution of ST2, & Fig (d) Breadth wise particle size distribution of ST2

The influence of time on the Silicon nanowire-titanium dioxide was investigated in this paper to understand how the structure (length and breadth) would change. The morphologies of Si-TiO_2 under different times (2 hours, 3 hours, 4 hours) were characterized by FESEM.

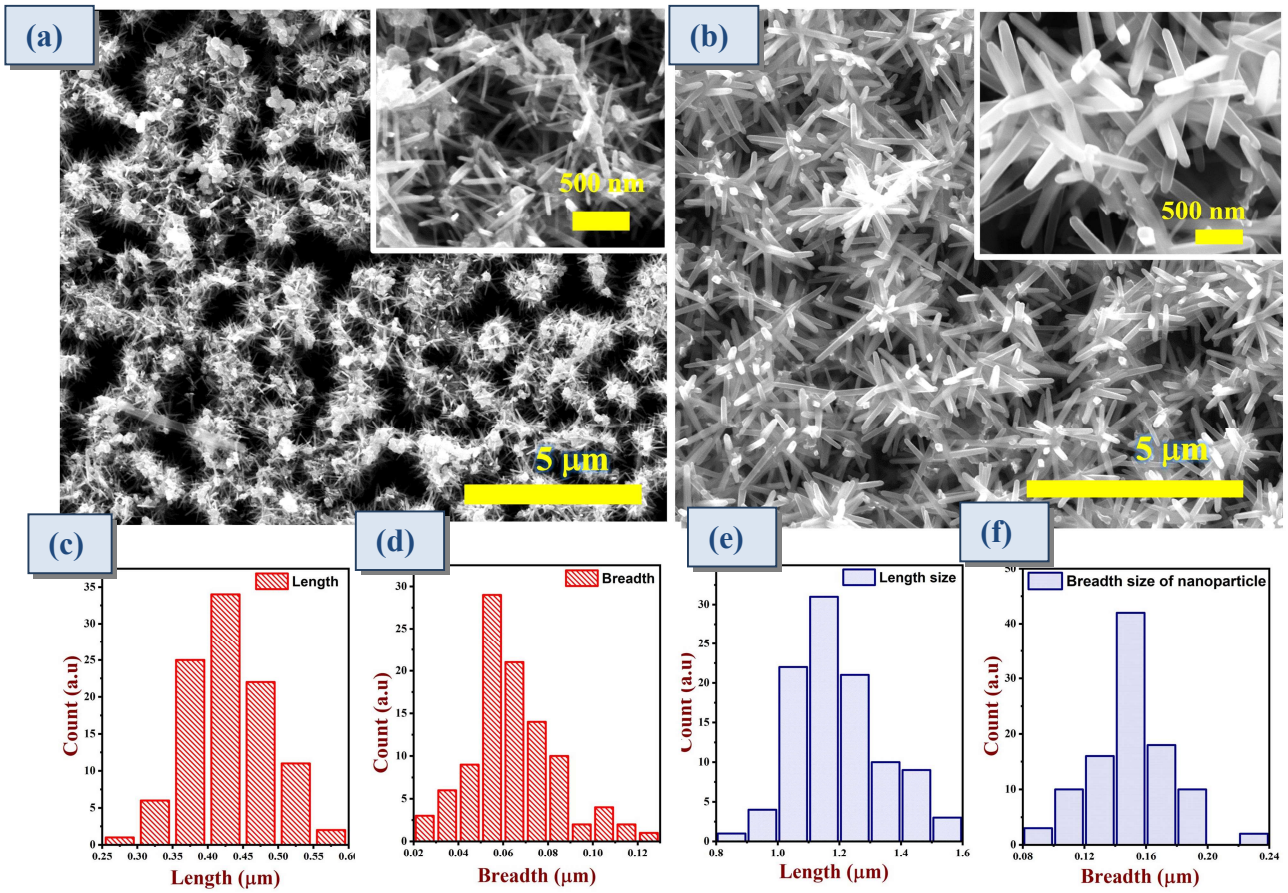

Fig7. 6(a)FESEM images of low magnification and high magnification (insets) of sample ST3 , Fig(b) FESEM images of low magnification and high magnification (insets) of sample ST4, Fig(c) & Fig(e) Particle size distribution lengthwise of ST3 and ST4, Fig(d) & Fig(f) Particle size distribution breadth wise of ST3 and ST4

The FESEM images of SiNWs synthesized with different hydrothermal synthesis process times with high magnified and cross-sectional images are shown in Fig7. 5(a) & (b). It can be seen comprehensively that SiNWs are formed uniformly over the entire field. From cross-sectional images, it can be seen that the diameters of the samples are not more than 5–20 nm although the length and breadth change with hydrothermal synthesis time, thus changing the aspect ratio of the SiNWs.

It was observed that the morphologies of ST 4 is better than ST 3 and ST 2. So, we can say the morphology of all these different samples was prepared by changing the time scale showed

different crystal structures. Thus, morphology is the main factor to impact catalytic activity. The surface morphology and structure of pure silicon nanowire and SiNW/TiO_2 heterojunction are displayed here by a field emission scanning microscope (FESEM)

7.3.Bond Structure Analysis:

FTIR ANALYSIS:

FTIR analysis means Fourier transform infrared spectroscopy. It is basically a technique used to done to characterize various types of organic, inorganic, and polymeric samples such as molecular bonds, chemical properties, etc. This type of analysis is used to obtain the infrared spectrum of absorption or emission spectra of a solid, liquid, powder, or gaseous sample over a wide spectral range with the help of an infrared source of light. FTIR is used to confirm the nature of the reaction intermediate and identification of various functional groups which participate in the formation of Si/TiO_2 heterojunction. The surface configuration of four different samples was categorized by FTIR transmittance analysis. The FTIR spectra show the characteristic peaks of Ti--O and the Ti—O--T stretching vibration in the range of 400–700 cm−1. The results also show that the peak at 3450 cm−1 is caused by a Ti--OH band. These results are almost identical to the report of Nakamura et al. the report provide further confirmation of the effect of TiO_2 implementation on the surface of SiNW arrays. Si—O—Si bridge between 1,000 cm^{-1} to 1,300 cm^{-1} is visible. Additionally, a prominent signal is obtained between 3,000 to 3,650 cm^{-1}. This signal attributed to SiO—H bond. The stretching point of O_3Si—H is at 2,258 cm^{-1} is comparatively weak. The peak at 1443 may be attributed to C—H plane bending.

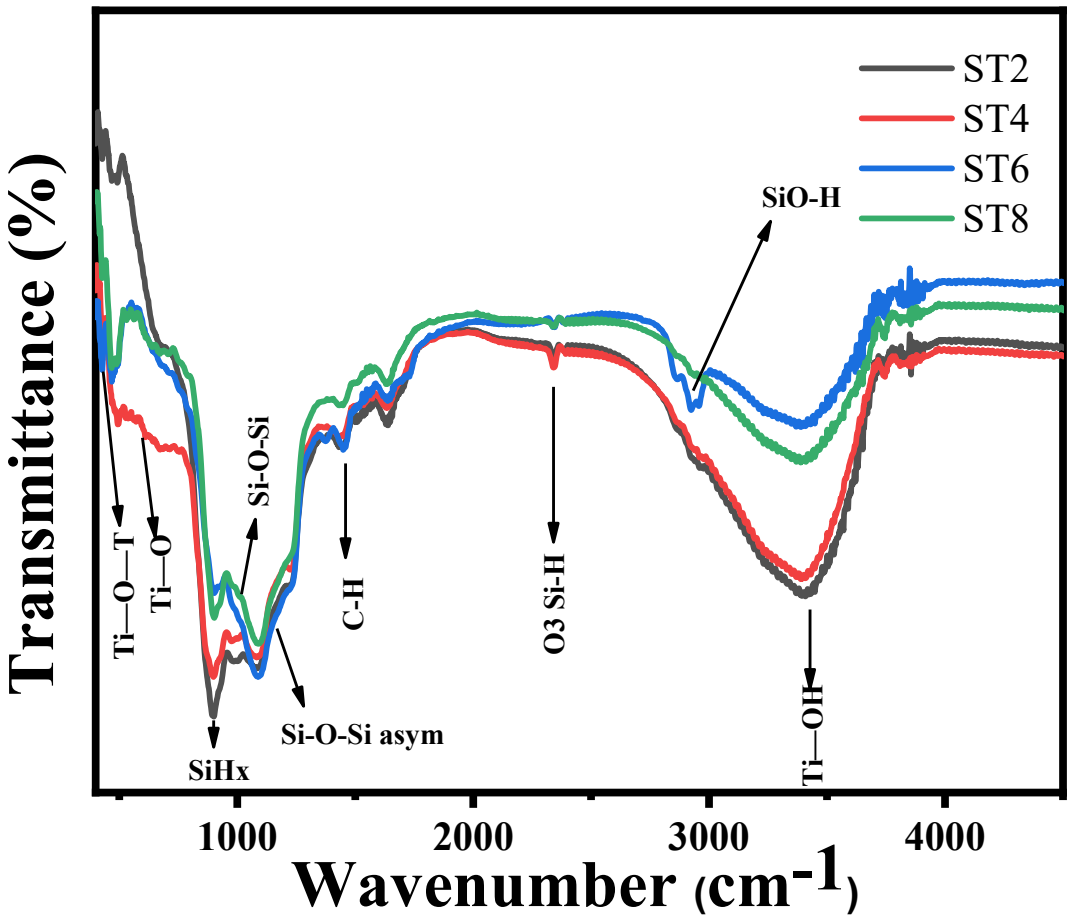

Fig7. 7. FTIR Spectroscopy of Samples ST 2, ST4,ST6,ST8

This C—H bond hardly can be avoided because it is a natural bond that emerges from environmental contamination. The peak at 1732 cm^{-1} is related to the atmospheric or environmental impact and this peak showed the presence of a C=O bond.

7.4. HRTEM analysis:

Detailed analysis of the microstructure is represented by the HRTEM image of SiNWs synthesizes at60 min etching time in fig. The sample grid is prepared by scraping the SiNWs from the silicon substrate and sonicating it in a small amount of ethanol and then it is dropcasted on the grid.

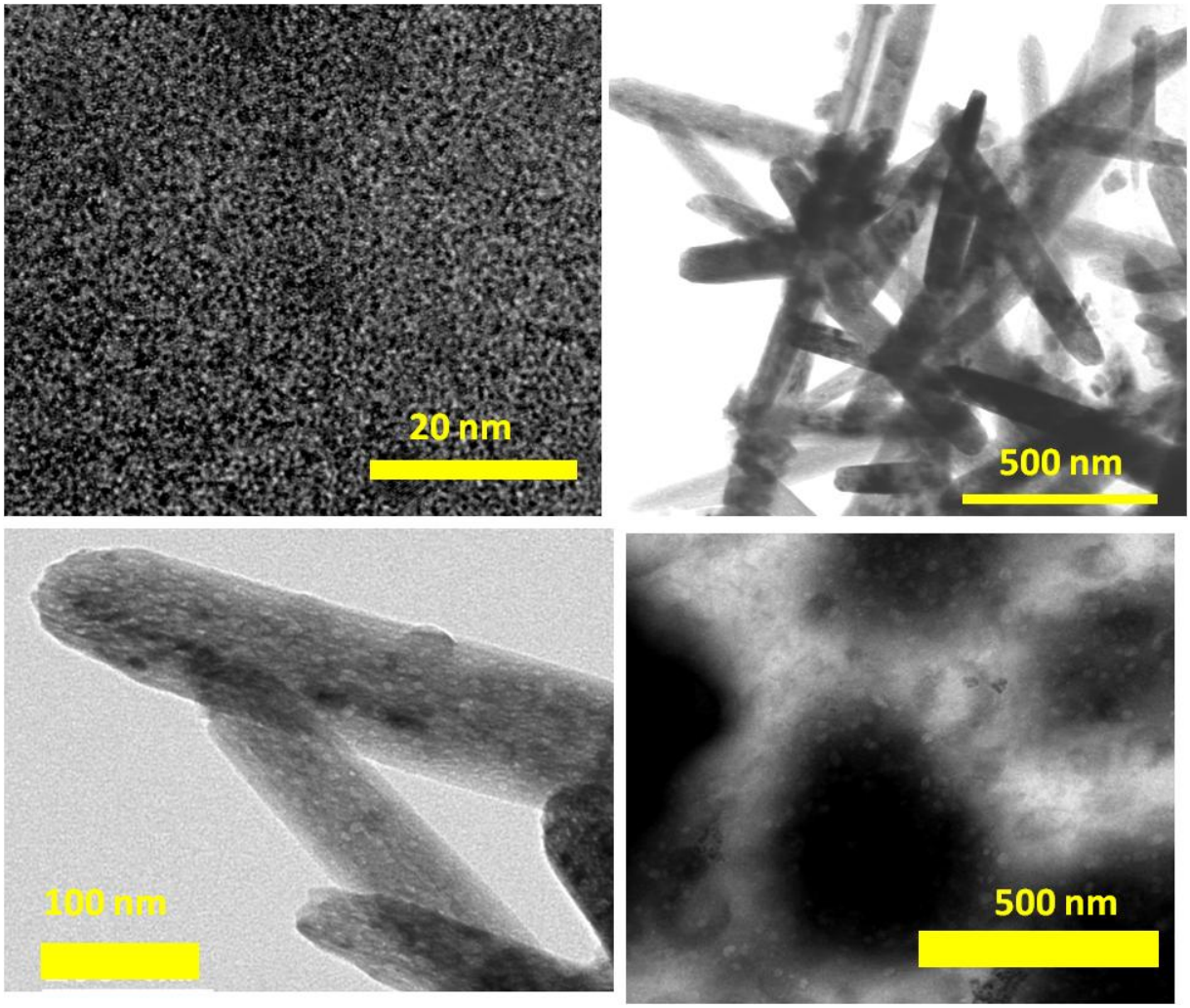

Fig7. 8. (a) TEM image of SiNW 60, (b) & (c) TEM image of SiNW/TiO_2 heterojunction at different scales with (d) lattice image

Though the TEM image displays the size of the nanowires can be clearly seen to be around 100nm. From the fig 7.8(a) and (d) it is evident that the SiNWs formed are porous in nature. Balasundaram et al. [15] previously reported that with increase of etching time and heating, the porosity increases. The formation of the pores result in the decrease in mechanical strength of silicon nanowire as suggested by liu et al. which may also be a reason for the agglomeration of the wires. The concentration of oxidizing agent i.e. H_2O_2 may also play an important role in increment of porosity.

7.5. ELECTRICAL STUDIES:

Figure7. 9. shows the current-voltage (I-V) characteristics under the illumination of TiO_2 thin film with different synthesis times. The forward current changes with the deposition time of TiO_2. It is clearly noticed that the Si/TiO_2 samples ST2, ST4, and ST6 demonstrate exact junction behavior as a practical diode.

Diodes always follow the rules of thermionic emission. Thermionic emission is the surface emission. It releases electrons from heated material. Thermionic emission is extensively used as a source of electrons in traditional television picture tubes, electric bulbs, etc. When exterior heat energy is activated then the operation by which free electrons are generated from the surface of a metal is called the thermionic emission. Current flowing through the forward junction of a diode can be determined by the thermionic equation:

$$\boldsymbol{I=I_O \exp\left(\frac{qV}{\eta kT}\right) - 1}$$

Where$I$denotes the net current flowing through the device, I_O denotes the reverse saturation current, q represents the absolute value of charge of an electron, V denotes the applied voltage across the two terminals of the diode, ηdenotes the ideality factor, k denotes the Boltzmann's constant, T denotes the absolute temperature.

The forward current varies with the deposition time and for the sample ST 2 and ST 4 current increases with voltage but in case of ST 6 current is slightly not continuous with increasing voltage. Thus, four hours of Titanium dioxide (TiO_2) deposition on porous silicon nanowire is considered to be the best for revealing the finest forward characteristics.

The ideality factor and Schottky Barrier Height can be determined from the following equation.

$$\boldsymbol{\eta = \frac{q}{kT}\left[\frac{dV}{d(lnI)}\right]}$$

Where, $\boldsymbol{\eta}$is ideality factor which is dimensionless. It can be determined from the slope of the linear region of the forward bias lnI-V characteristics through the above relation.

$$I_o = AA^*T^2 exp(-\frac{q\varphi Iv}{kT})$$

Where, $I_o$denotes the reverse saturation current, A represents the diode area, A^* represents the effective Richardson constant and Φ_{IV} represents the Schottky Barrier Height(SBH). Here p-type Silicon is used for experiment and for p-type silicon the value of effective Richardson constant is $32A/cm^2K^2$.

TiO_2 in its pure form (n-type semiconductor) possesses indirect energy band gaps of rutile, anatase, and brookite phases of 3.02, 3.2, and 2.96 eV respectively and rutile phase fermi level is lower than the anatase by ~0.1 eV .

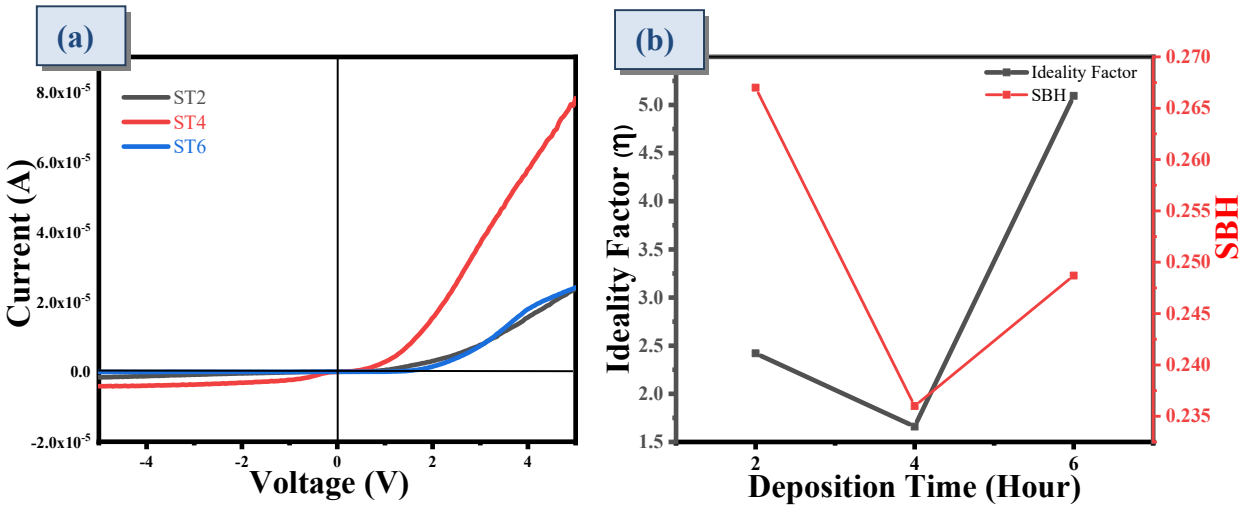

Fig7. 9 (a) Dark IV characteristics for samples ST 2, ST4, and ST 6, (b) the ideality factor and Schottky barrier height change with the deposition time (HOUR) variation of TiO_2 nanoparticles on SiNW

It can be clearly deduced from the graph of ideality factor, SBH with respect to deposition time that the ideality factor increases with deposition time, and the Schottky Barrier Height (SBH) decreases with deposition time. The ideality factor of p-n junction diode is used to establish the sharp meticulous relationship between the practical and ideal diode. It shows how closely the practical diode follows the ideal diode. The ideality factor reduces from 2.43 to 1.66 and SBH

reduces from 5.19 to 1.85 respectively for the samples ST 2 and ST 4. Moreover, the ideality factor for the sample ST 6 again rises to 5.08 and the SBH rises to 3.22. So, ST 4 behaves as the best diode as the ideality factor is close to 1 (unity).

It can be concluded that TiO_2 nanoparticles are less and unevenly distributed on Silicon nanowire in the sample ST 2 whereas in case of sample ST 4 TiO_2 nanoparticles are distributed evenly and it forms a proper junction. With the increase in deposition timing, the thickness of TiO_2 on silicon nanowire increases to such a high level that the effective contact area between TiO_2 and SiNWs decreases resulting to form a poor junction.

7.6. I-V CHARACTERIZATION:

The techniques for the measurement of the electrical behaviour of laminated composites are the two-probe method and four probe methods. The room temperature current-voltage (I-V) measurement under DARK and U-V light were performed to determine the diode characteristics of the produced Si/TiO_2 heterojunction device.

The resistance of the segment between the voltage contacts can be calculated through Ohm'slaw:

$$V = I * R$$

Where, V and I are the voltage and current from the voltage and current contacts, respectively.

From the graph (Fig7. 10(a-f)) of I-V measurement, it is seen that the heterojunction device has a diode characteristic. The Si/TiO_2heterojunction diode was shown to have good light sensitivity from I-V characteristics (DARK & U-V). These properties indicate that Si/TiO_2 heterojunction device has a fast and highly stable photodiode characteristic. According to the I-V result, it can be concluded that the photodiode device is suitable for different applications for light detection and optical communication purpose in UV visible range. TiO_2/p-type Si structure has a photodiodes behavior. The transient photocurrent technique is used to reveal the

photoconduction mechanism of the Si/TiO_2 structure.The downward curvature region of the forward bias I-V characteristics at high bias voltages results from the diode series resistance Rs of the neutral region of the semiconductor substrate. Therefore, as can be seen from Fig7. 10(a-c) (I V Graph), the forward bias I-V characteristics of p-type Si/TiO_2 photodiodes under UV light intensity are not exactly linear because they have occurred at high bias voltage region where the diode series resistance affects. The series resistance (R_s) can be determined from dV/d(lnI) versus the current graph plot. The forward biased I-V plot deviates from linearity due the series resistance, the interfacial insulator layer, and the N_{ss} when the applied voltage is sufficiently large.

As can be seen from the calculations, the ideality factor η values have increased due to light intensity from the UV rays with respect to the diode under dark conditions. Electrons in the valance band have been invigorating for the conductance band by the photon energy, which has the actual adequate energy. This situation can be caused to increase the current, particularly under reverse bias. The TiO_2 thin film material has been affected by the UV light illumination, and characteristics of varied conditions. The changes in characteristics of the photodetector are associated with the interface states and interfacial layer between semiconductor and metal.

Amidst all the samples of the SiNW/TiO heterostructures, the highest photocurrent is acquired for ST4. ST2 having low and inconsistent coverage of TiO_2 nanoparticles on the surface SiNWs have lower photocurrent than ST4. In case of ST6, photocurrent is also reduced as shown in the I-V characteristics. This reduction in photocurrent may be a consequence of two reasons. Firstly, the TiO_2 nanoparticle can be grown highly on the surface of a silicon nanowire and secondly, the thickness can be the barrier to entering the photogenerated charge carriers. The thickness may be acted as a resistance.

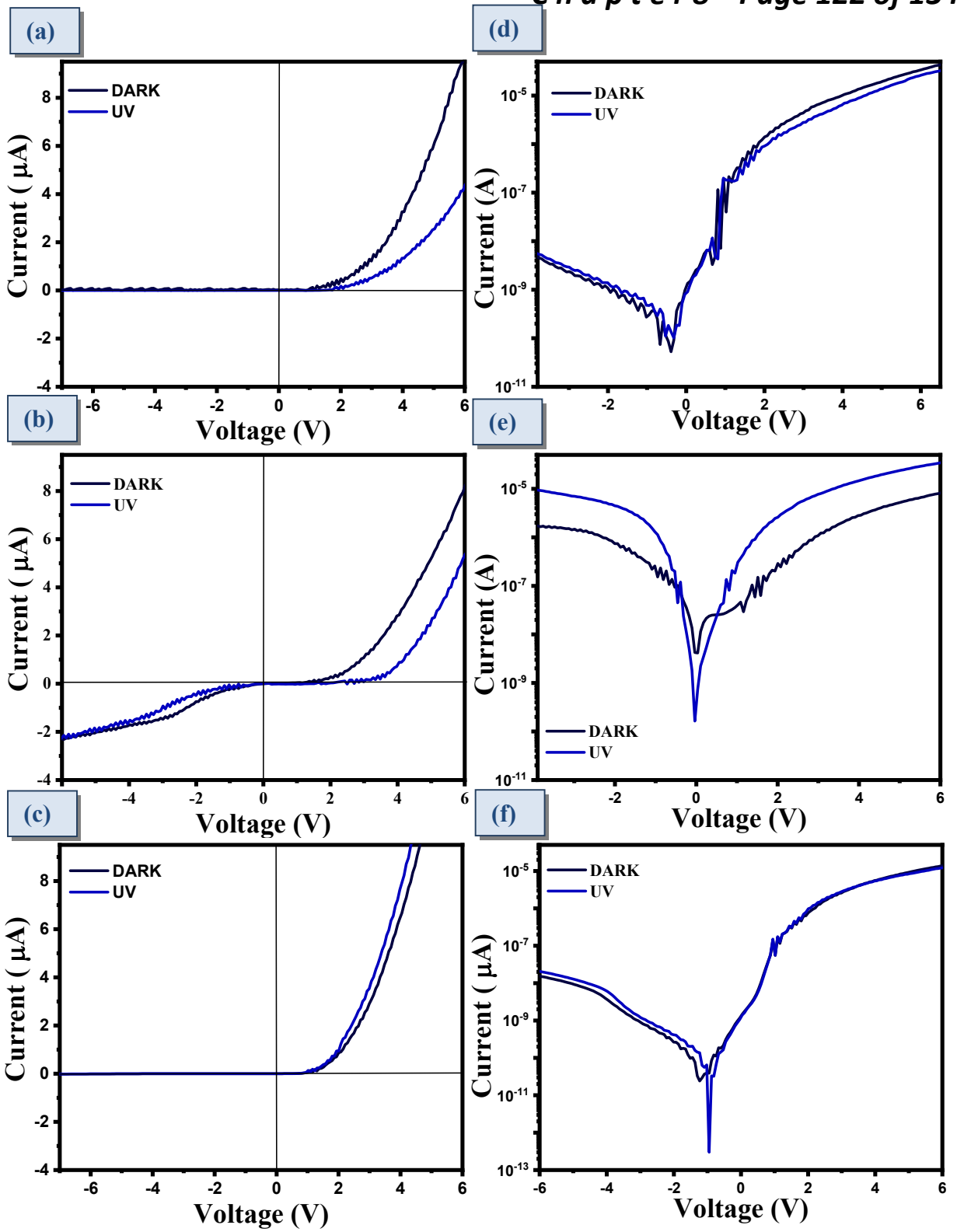

Fig7. 10(a-c) I-V Characteristics under DARK and UV light for ST2, ST4, and ST6, (d-f) logarithmic I-V curve of the samples ST2, ST4, and ST6

7.6. SWITCHING CHARACTERISTICS:

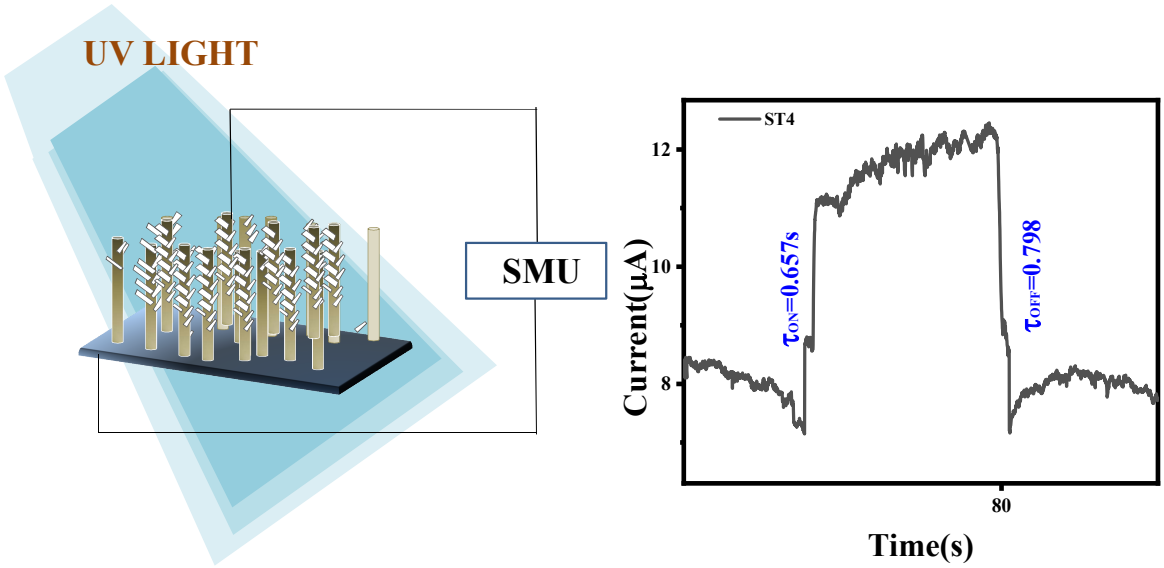

Fig7. 11(a) Schematic for measurement of response speed of samples, (b) Enlarge photo response of for ST4

It has been noticed that the produced Si/TiO_2 heterojunction device shows diode characteristics with a good rectification ratio.

As the current obtained under UV irradiation is greater than in dark conditions, the UV responses of the heterostructures are further investigated and the results are depicted inFig7. 12. An alternate on-time and off-time of 20 s were maintained for UV irradiation. Among all the samples of the p-SiNW/n-TiO_2 heterojunctions, the best photocurrent is obtained for ST4. ST2 having uneven coverage of TiO_2 nanoparticles on the surface Silicon nanowires have lower photocurrent than ST4. Additionally, ST6 also does not show a higher photocurrent due to its higher thickness. ST6 sometimes shows steep current increasing but its stability is not good rather than ST4. The best sample shows the highest ratio of photocurrent to dark current I_p/I_d. The average photocurrent and dark current obtained for ST4 are 12 μA and 6 μA respectively. For determining the capability to follow high frequency switching the switching response of p-n junction devices are determined and evaluated.

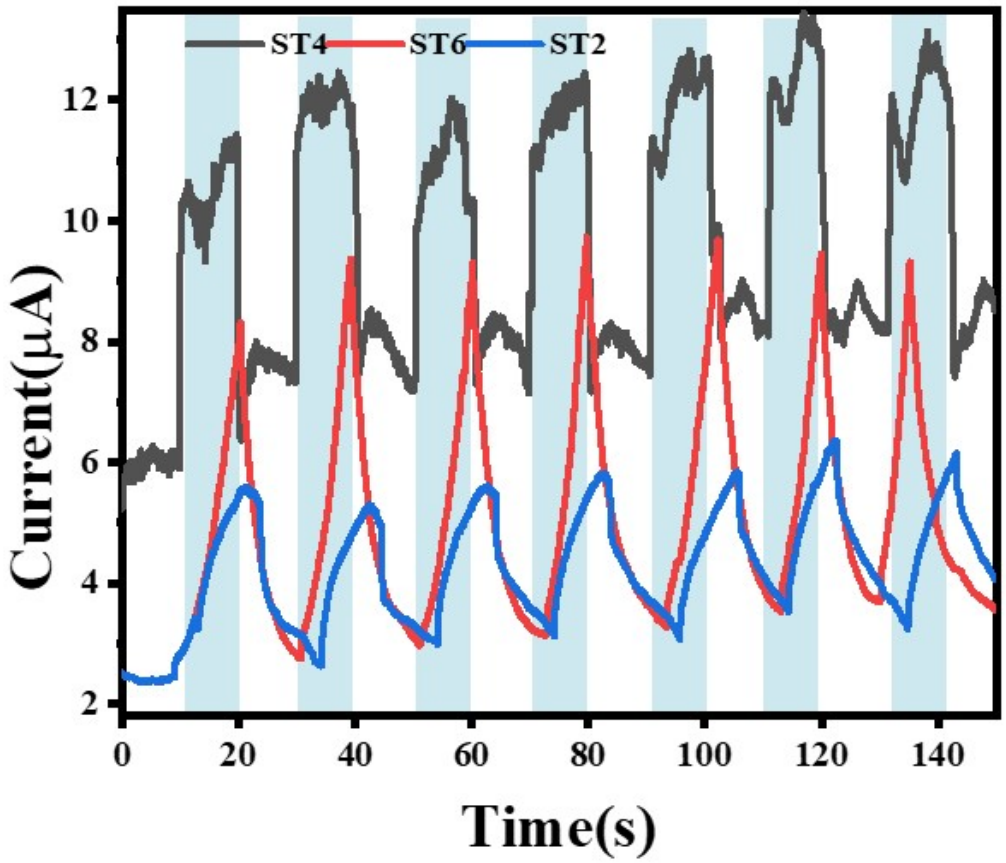

Fig7. 12: UV photoresponse of measurement of the samples ST2, ST4 & ST6

The following two equations are used to calculate the responsivity (R) and detectivity (D) of the device depending on the intensity of the incident UV light [37].

$$R = \frac{Ip - Id}{Pin}$$

And

$$D = A^{1/2} R/(2qI_d)^{1/2}$$

where I_d, I_p, P_{in}, q and A are used to represent dark current, photo current, power of incident light, charge of an electron, and effective area of the device respectively.

The maximum responsivity obtained for ST4 is 240 mA/W for the low intensity of 2.5μW/cm2 . At low intensity the value of responsivity is high due to the low concentration of photogenerated electron hole pairs. With increasing light intensity the photogenerated charge carriers increases. This leads to scattering of charge carriers resulting in power dissipation in the form of heat and it decreases the responsivity of the device.

The ST4 sample showed the highest detectivity of 1.051×10^{12}at a light intensity of 2.5 μW/cm2 . The enhancement of the photoresponsivity and detectivity of the device can be attributed to the inbuilt electric field and the proper band alignment of the SiNW/TiO_2 heterojunction.

7.8. Charge transfer mechanism of Si/TiO heterojunction:

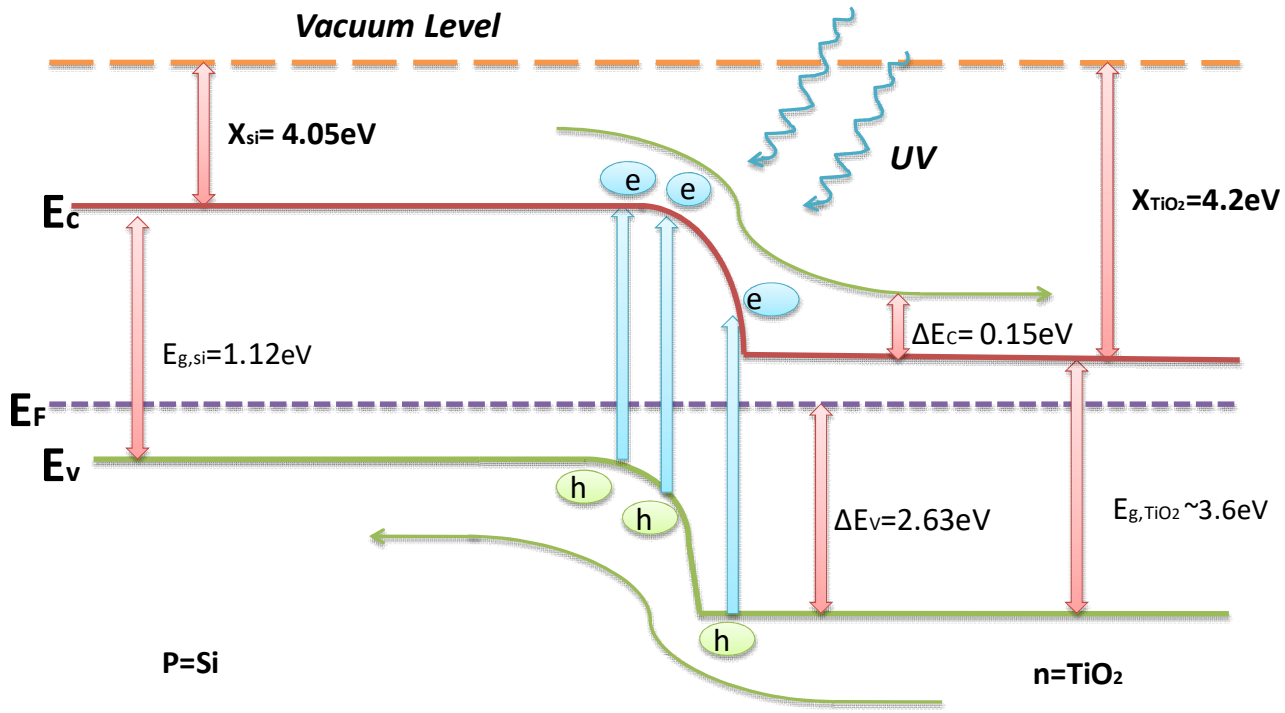

Fig7. 13: Charge transfer mechanism of Si/TiO heterojunction

The band diagram of the SiNW/TiO_2 heterojunction isbased on Anderson's model [34]. It is shown in Fig7. 13. The expected transport procedure of the photogenerated charge carriers is

explained in the band diagram. Silicon has a band gap and electron affinity of 1.12 eV and 4.05 eV [35, 36] respectively, while TiO_2 has 3.6 eV and 4.2 eV respectively. Therefore the valence band offset present is 2.63eV while the conduction band offset is 0.15 eV. When the reverse biased condition is applied the minority carriers contribute to the current flow in dark condition and under the UV ray. Again, electron and hole pairs are generated in the space charge region under illumination due to the absorption of energy from photons having higher energy than that of the semiconductor band gap energy.

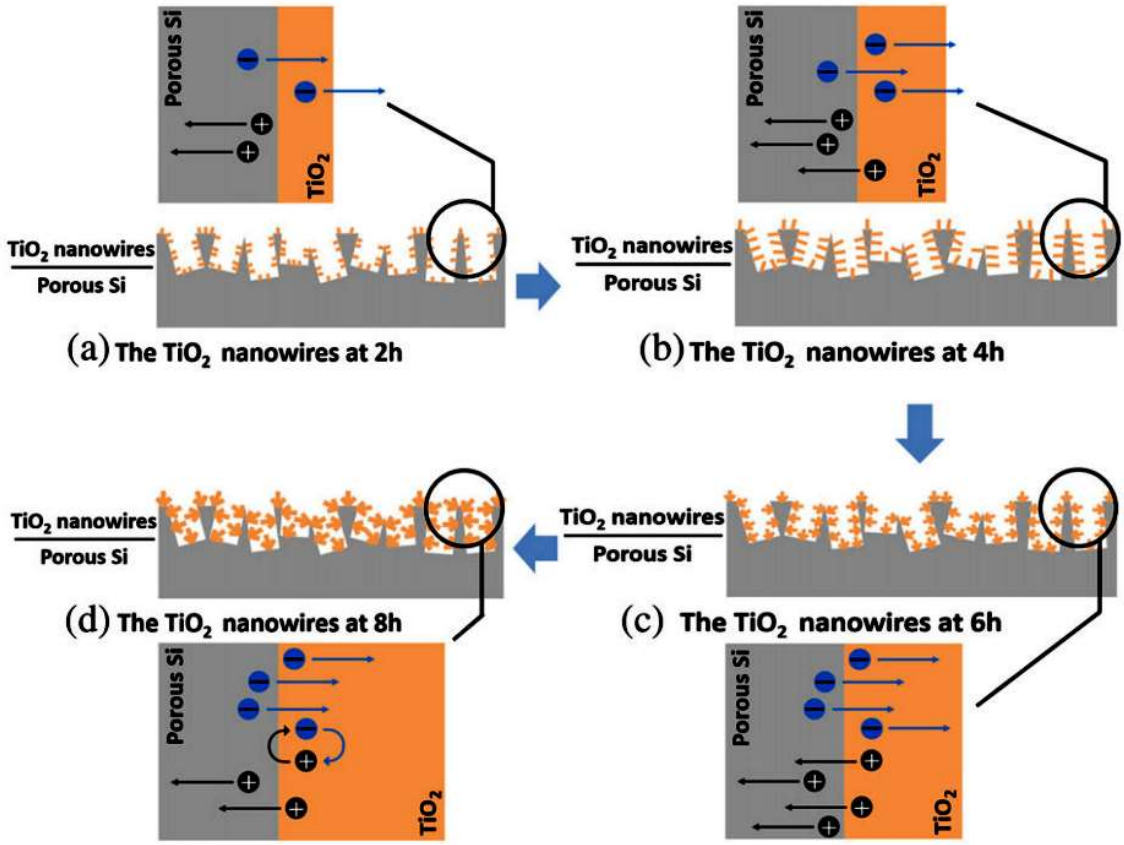

Fig7. 14: The schematic diagram of separation of electron-hole pairs of SiNWs/TiO_2 heterojunction at different deposition times.

The surface morphology of Si/TiO_2 nanowire varies with the hydrothermal synthesis timing. At optimum scale (Fig b) enough electron-hole pairs are generated. So, the recombination rate is low but in case of 2 hours, 4 hours, and 8-hour deposition it does not show favorable conditions

for preparing p-n junction photodiode. In case of 2 hours hydrothermal synthesis technique, enough electron-hole pairs cannot be generated. If the amount of TiO_2 is very thick as shown in case of 6 hours and 8-hour deposition, the crowded electron-hole pairs are not advantageous for transferring and diffusing of the electrolyte. The electron-hole pairs recombine before transmission. That's why four-hour hydrothermal synthesis is more beneficial than other deposition times.

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CHAPTER:8

Conclusion and Future Prospects

8.1.Conclusion:

The whole work indicates toward good field emission property of porous silicon nanowires and good switching characteristics of Silicon nanowire with Titanium dioxide (TiO_2). Here,SiNW is synthesized at 60°C temperature. Important basic characterizations are carried out. As the etching time increases, the length of the nanowire increases and diameter decreases. Thus, SiNW 60 showed highest current density at high applied potential though the other properties like turn on field, threshold voltage or enhancement factors are not improved. In that case, SiNW 60 is the optimum one for good field emitter property.

The photodiode performances of atomic layer deposited as TiO_2 on silicon nanowire structure were investigated using I-V and XRD measurements. Some parameters such as responsivity, detectivity, power efficiency for photovoltaic properties of the device were calculated from I-V measurements under different illumination conditions. And also, the barrier height and ideality factor which are important parameters for the diodes, were calculated from I-V characteristics of device under dark and various light intensity. Moreover, the heterojunction diode was shown to have good light sensitivity.

Porous SiNWs/TiO_2 nanowire photodiode were prepared by a combination of hydrothermal synthesis and MACE. We found that the porous SiNWs/TiO_2 nanowire photodiode obtained at 4 hour showed the highest photocurrent and UV light detection.It can be seen that the barrier height values decrease while ideality factor increases with increasing light power.

8.2. Future Prospects:

It is believed that the porous Si/TiO_2 nanowire photodiode might offer a great potential in environmental, energy and other domains. The results obtained in the study described may provide some useful guidance for similar research. The result analyzes that TiO_2/Si structure can be used for the photovoltaic and some optoelectronic applications for light detection. As the result shows in this project the light sensitivity, detectivity of SiNW/TiO_2 photodiode so it can be used as optical communication purposes in the UV–Visible range for industrial purposes.

Due to wide work function of TiO_2 the heterojunction Si/TiO_2 shows outstanding photoelectric response and rectification characteristic. The rutile phase reveal high refractive index, high optical absorptivity that is accountable for its application in optical communication devices such as isolators, modulators and switches. This idea can be further used in SiNW/TiO_2 photoelectrocatalysis work.