With the blessings of Their Holinesses



Sri Chandrasekharendra Saraswathi Viswa Maha Vidyalaya

(University Established under section 3 of UGC Act 1956) Enathur, Kanchipuram

Accredited with Grade 'A' by NAAC

NANO TECHNOLOGY

COURSE MATERIAL (EIGHTH SEMESTER - MECHATRONICS)



(For the Academic year - 2021-2022)

PREPARED BY

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DEPARTMENT OF ELECTRONICS & INSTRUMENTATION ENGINEERING

| SEM VIII | | L | Т | Р | С |
|------------------------------|-----------------|------|-----|-------|-------|
| BRANCH : Mechatronics | NANO TECHNOLOGY | 3 | 0 | - | 3 |
| CODE : BMTF1880EM | | CATE | GOR | Y: 0] | EC IV |

(For Students admitted from 2018 onwards)

PREREQUISITE: Electronic devices and Linear Integrated circuits

COURSE OBJECTIVES

1. To provide a strong concept on the scientific revolutions & challenges in the field of nano electronics.

2. To provide knowledge on various molecular circuits, switches used & the limitations innano electronics architectures.

3. To provide knowledge on nano fabrication and complete knowledge on Optical & Soft lithography.

4. To provide information on spin polarization and its applications.

5. To study on various memory elements & sensors used in nano electronics.

UNIT I **INTRODUCTION**

Definition of Nano, Scientific revolution and its challenges, Future, Overview of Nanoelectronics.

UNIT II NANO ELECTRONICS & NANO-COMPUTER ARCHITECTURES (9 Hours)

Introduction to Nano-computers, Nano-computer Architecture, Quantum DOT cellular Automata (QCA), QCA circuits, Single electron circuits, molecular circuits, Logic switches - Interface engineering – Properties (Self-organization, Size-dependent) – Limitations.

UNIT III NANOELECTRONIC ARCHITECTURES (9 Hours)

Nanofabrication – Nano patterning of Metallic/Semiconducting nanostructures (e-beam/X-ray,Optical lithography, STM/AFM- SEM & Soft-lithography) - Nano phase materials - Self assembled Inorganic/Organic layers.

UNIT IV SPINTRONICS

Introduction, Overview, History & Background, Generation of Spin Polarization Theories of spin Injection, spin relaxation and spin dephasing, Spintronic devices and applications, spin filters, spin diodes, spin transistors.

UNIT V MEMORY DEVICES AND SENSORS

Nano ferroelectrics, ferroelectric random access memory (Fe-RAM) circuit design, ferroelectric thin film properties and integration, calorimetric sensors, electrochemical cells, surface and bulk acoustic devices, gas sensitive FETs.

(9 Hours)

(9 Hours)

(45 hrs)

(9 Hours)

COURSE OUTCOMES

At the end of the course the students will be able to

- CO1. Acquire knowledge on Challenges in the field of Nano Electronics.
- CO2. Acquire knowledge on nano electronics & computer architectures.
- CO3. Acquire knowledge on nano fabrication and structures.
- CO4. Acquire knowledge on spin polarization theories.
- CO5. Acquire knowledge on implementation of memory & sensors in nano electronics.

TEXTBOOKS

 Rainer Waser, Nano Electronics and Information Technology: Advanced ElectronicMaterials and Novel Devices, Third Edition, Wiley Publications, 2012.
Robert Puers, Nanoelectronics: Materials, Devices, Applications, Wiley publications, 2010

REFERENCES

- 1. Avik Ghosh, *Nanoelectronics: A Molecular View*, World Scientific Publishing Company, 2017.
- 2. David D. Awschalom, Spin Electronics, Springer, 2004
- 3. Karl Goser, JanDienstuhl, Nanoelectronics & Nano systems: From Transistor to Molecular & Quantum Devices, Springer, 2004.

<u>CHAPTER I</u> INTRODUCTION

Definition of Nano - Scientific revolution and its challenges - Future - Overview of Nano electronic

1. Definition of Nano

1.1.What is Nanotechnology?

Nanotechnology is the science and engineering of small things, in particular things that are less than 100 nanometres in size (in one direction). Nano is an SI prefix and comes from the Greek word for dwarf - *nanos*. One nanometre is 10^{-9} meters or about 3 atoms long.

To explore the size of the nanoscale in relation to other scales there are some great interactive sites such as Scale of the Universe, Power of Ten, and Nano Size Me.

Nanotechnology is often divided into two parts. Nanoscience - where researchers learn about the chemical and physical properties of materials at the nanoscale. Materials at 1-100 nm are called nanostructures. They are the smallest things that can be made. Nanotechnology - where researchers develop and apply materials at this scale to develop new products or methods; i.e., turning nanostructures into useable tools and applications.

We are talking about the "nano tidal wave". Not a single day passes without the press reporting on major innovations in this area. Large industrialized countries spend considerable amounts of money, around US\$10 billion per year, on this field of study. This should have a positive effect on the economy and on employment1. Microelectronics and the steady miniaturization of components has become commonplace. Moore's Law (a doubling of the number of transistors for the same surface every 18 months) illustrates this idea. This also makes us think of the production of chips in laboratories. With their engineers and technicians in uniform, these laboratories can be considered as the technological cathedrals of our times. Microcomputers, microprocessors, mobile phones and MP3 players with a USB connection are available to the general public. For several decades now, this technology has been largely submicronic, and the idea of nanoelectronics was created in the laboratories. The current

technological limits will soon be reached, even if ongoing innovations will push them beyond these limits. Emerging technologies such as carbon nanotubes will take over.



The nanoworld is the intermediary between the atom and the solid, from the large molecule or the small solid object to the strong relationship between surface and volume. Strictly speaking, the nanoworld has existed for a long time and it is up to chemists to study the structures and properties of molecules. They have learnt (with the help of physicists) to manipulate them and build more and more complex structures. Progress in observation tools (electron microscopes, scanning-tunnelling microscopes and atomic force microscopes) as well as in analysis tools (particularly X-ray, neutron and mass spectrometry) has been a decisive factor. The production of nanoscopic material is constantly improving, as is the case for the process of catalysis and surfaces used in the nanoworld. A substantial number of new materials with nano elements such as ceramics, glass, polymers and fibers are making their way onto the market and are present in all shapes and forms in everyday life, from washing machines to architecture.

Biology has been molecular for a long time. The areas of DNA, proteins, and cellular machinery are all subjects of multidisciplinary research. Investigations into these fields have been carried out by biologists, chemists, and physicists. Furthermore, the tools that have been developed have created new areas of specialization, such as bioinformatics. Observation, image-processing and simulation all benefit from the advances in information technology and, once more, conceptual progress goes hand in hand with technical expertise. The concept of the nanoworld is based on the convergence of a real mix of scientific and technological domains which once were separate. Even though the laws of quantum mechanics based on wave corpuscle duality are not directly visible in our everyday world, except for lasers and semi-

conductor components, they do govern the nanoworld. In the future, the quantum effects will be used in a large number of applications, and in objects with new properties, such as quantum cryptography, quantum computers, teletransportation, etc. The evolution of our know-how, and of technological innovations, is already having significant consequences. The Internet is the fruit of the union between information technology and telecommunications, just as biochips are for electronics and biology. Imaging on a molecular level revolutionized the techniques of medical examinations. The borders between chemistry, physics, mechanics and biology are disappearing with the emergence of new materials, such as intelligent systems, nanomachines, etc. This is where the nano tidal wave, which will have considerable impact on society, can be found. A comprehensive public debate is required on real or possible risks and their consequences. Will humanity be able to master these new applications or are we taking on an unfamiliar role?



1.2. Scientific Revolution and its Challenges

The breakthroughs in nanotechnology recent years have led scientists to predict that in the next five years, it will be possible to examine body fluids and filter them for minute bioparticles.

These bioparticles will then be used to reveals signs of diseases like cancer, even before they manifest any symptoms.

This is great news as diseases are easy to manage if they get diagnosed early. In the past, finding diseases was difficult as most of us would wait until we see symptoms. By this time the disease may already have progressed too far.

Nanotechnology is going to be a major driving force behind the impending technological revolution in the 21st century. Both private and public sector spendings are constantly increasing. The size of the market for nanotechnology products is already comparable to the biotechnology sector, while the expected growth rates over the next few years are far higher.

Nanotechnology manufacturing is a fundamentally new process in which structures are built from the bottom up, one atom at a time. Nanotechnology has the potential of producing new materials and products that may revolutionize all areas of life. Nanotechnology protagonists believe that nanotechnology will provide unsurpassed benefits for the society. Meanwhile, its antagonists believe that nanotechnology may pose serious health and environmental risks and advocate that the precautionary principle should govern the development and deployment of such products. Although it is difficult to predict precisely how nanotechnology will impact society, current understanding, under either the spectacular benefit or the serious risk scenarios, presages a huge impact on society in areas that include the environment, healthcare, energy, and electronics.



1.2.1. Challenges

The most immediate challenge in nanotechnology is that we need to learn more about materials and their properties at the nanoscale. Universities and corporations across the world are rigorously studying how atoms fit together to form larger structures. We're still learning about how quantum mechanics impact substances at the nanoscale.

Because elements at the nanoscale behave differently than they do in their bulk form, there's a concern that some nanoparticles could be toxic. Some doctors worry that the nanoparticles are so small, that they could easily cross the **blood-brain barrier**, a membrane that protects the brain from harmful chemicals in the bloodstream. If we plan on using nanoparticles to coat everything from our clothing to our highways, we need to be sure that they won't poison us.

Closely related to the knowledge barrier is the technical barrier. In order for the incredible predictions regarding nanotechnology to come true, we have to find ways to mass produce nano-size products like transistors and nanowires. While we can use nanoparticles to build things like tennis rackets and make wrinkle-free fabrics, we can't make really complex microprocessor chips with nanowires yet.

There are some hefty social concerns about nanotechnology too. Nanotechnology may also allow us to create more powerful weapons, both lethal and non-lethal. Some organizations are concerned that we'll only get around to examining the ethical implications of nanotechnology in weaponry after these devices are built. They urge scientists and politicians to examine carefully all the possibilities of nanotechnology before designing increasingly powerful weapons.

If nanotechnology in medicine makes it possible for us to enhance ourselves physically, is that ethical? In theory, medical nanotechnology could make us smarter, stronger and give us other abilities ranging from rapid healing to night vision. Should we pursue such goals? Could we continue to call ourselves human, or would we become transhuman -- the next step on man's evolutionary path? Since almost every technology starts off as very expensive, would this mean we'd create two races of people -- a wealthy race of modified humans and a poorer population of unaltered people? We don't have answers to these questions, but several organizations are urging nanoscientists to consider these implications now, before it becomes too late.

Not all questions involve altering the human body -- some deal with the world of finance and economics. If molecular manufacturing becomes a reality, how will that impact the world's economy? Assuming we can build anything we need with the click of a button, what happens to all the manufacturing jobs? If you can create anything using a replicator, what happens to currency? Would we move to a completely electronic economy? Would we even need money?

Whether we'll actually need to answer all of these questions is a matter of debate. Many experts think that concerns like grey goo and transhumans are at best premature, and probably unnecessary. Even so, nanotechnology will definitely continue to impact us as we learn more about the enormous potential of the nanoscale.

1.3.Benefits of Nanotechnology

Nanotechnology continues to improve and in many cases revolutionize many industry and technology sectors. The fact that materials can be tailored to extremely molecular levels to provide specific properties has meant that the science toolkit has the potential to be expanded considerably.

Use of nanotechnology will make it possible to make materials lighter, stronger, more reactive, more durable and superior electrical conductors. There is no limit when it comes to some of the improvement that can be made on materials.



Lighter cars, boats, airplanes and trucks will be a catalyst for large-scale fuel savings. At the same time, a combination of conductivity and lightweight makes carbon nanotube sheets ideal for electromagnetic or thermal management.

Some of the industries that continue to benefit from the technology include food safety, medicine, environmental science, energy, transportation and information technology among others.



1.4. Challenges and Risks Of Nanotechnology

The advances in nanotechnology have not been without questions from concerned quarters. There have been some concerns, and it will take some convincing to get all the naysayers on board. Here are some of the concerns:



(1) The Ethics Question

The use of this technology in medicine could mean that humans will be able to enhance themselves physically. The fact that not everyone will be able to afford it initially could lead to wealthy people being able to modify themselves and poorer people remaining the same. At the same time, should human beings be able to alter themselves?

(2) Impact on World Economy

Whenever there is a new technology, there are always concerns about its impact on jobs. Questions have been raised about the impact of nanotechnology on manufacturing jobs in the future.

At the same time, nanotechnology will make it possible for us to be able to replicate almost anything. This might have far-reaching consequences on the relevance of currency in its current form.

(3) <u>Nano safety</u>

The concept has also led to questions about the safety of the smaller "legacy" material and whether they might cause unforeseen safety hazards. It will be interesting to see how this

concern is addressed going forward. At the same time, it is important to note that toxic nanomaterials pose no greater threat in that form than their bulky counterparts.

(4) <u>Affordability</u>

It is going to be a challenge for this technology to be packaged and manufactured at such a scale that it reaches people from all walks of life across the world while simultaneously educating physicians and users on the benefits it brings. Silicon chips are a great way for the inexpensive manufacturing of technology.

1.4.1. Bottom line

It is fair to say that all these challenges will not all be solved at once. But it is concerns and grey areas like these that keep scientists on their toes to continue making improvements on innovations.

Although some of the concerns are outlandish and immature, it is clear that nanotechnology is here for the long haul.

As the nanoscale continues to prove its unlimited potential, we will continue to be impacted by nanotechnology in the immediate and long-term future.

1.5. Future

The future of nanomedicine is exciting! Nanomedicine involves the engineering of materials at the nanometre-scale for investigating fundamental biological problems and diagnosing and treating disease. We have witnessed significant investment by universities and companies in building the foundation for research activities in the field of nanomedicine in the last 20 years. This has led to the training of a workforce that understands the concepts of nanomedicine and works to move the field from "concept" to "reality". This workforce has built interdisciplinary teams including engineers, chemists, biologists, physicists, and clinicians to clinically translate nanotechnology to improve the lives of patients such that nanomedicine is now poised to revolutionize health care worldwide.

Nanomedicine research can be categorized as *in vitro* or *in vivo*. The *in vitro* applications of nanotechnology are much simpler to clinically translate in comparison to *in vivo* ones. *In vitro*,

nanotechnology is used in sensors to diagnose disease and study biological processes via isolated tissues, cells, or molecules from biological samples or fluids. The requirements for approval by health agencies are less arduous than those for *in vivo* applications. For example, in point-of-care diagnostic devices, a nanotechnology-based system needs to demonstrate improved clinical sensitivity or specificity over current tests or provide a new function that is not available with current methods. Additionally, the use of nanotechnology for basic research is already emerging. Nanoparticles such as quantum dots and gold nanoparticles are used for studying receptor–ligand interactions, cellular processing, or signal transduction. The major scientific barriers to the translation of nanoparticles for *in vitro* applications is low. In many cases, it requires a company to focus on commercializing many of the nanotechnologies that have been developed. The company is the link to end users for academic research. The *in vitro* use of nanotechnology for medical applications should be accelerating in the next 20 years.

In contrast, *in vivo* medical applications of nanotechnology are more challenging. The human body and the in vivo environment are extremely complex. The administered nanoparticles will interact with many different organs, cells, tissues, and biological fluids. These interactions could be permanent or transient, and in vivo kinetics of the nanoparticles could affect their biodistribution patterns. This, in effect, can influence their ability to target, diagnose, or treat diseased tissues or cause toxicity that leads to side effects. As nanoparticles are transported in the body, they interact with different biological compartments (i.e., organs, tissues, and cells). We can view these organs as bioreactors that can chemically alter the nanoparticle physicochemical properties as they transit through the body. These reactions can impact toxicity, elimination, or interactions with diseased tissue. Many researchers are starting to tease out these interactions systematically, in order to develop maps that guide the engineering of nanoparticles for use in the body. In contrast to the *in vitro* application, the complexities of these studies would suggest that translation could take much longer than the use of nanoparticles for in vitro applications. Yet, these studies are critical to control the in vivo transport and function of the nanoparticles. This will be important in rationally designing nanotechnology for use in the body.

In this special issue of *Accounts of Chemical Research*, we highlight a broad range of advances in the field of nanomedicine in the last 20 years. The issue is organized to encourage the community to think beyond academic proof-of-concept studies with a view to advancing these

studies to real-life medical products that help patients. This special issue of *Accounts of Chemical Research* is organized into (a) research toward rationale design of new nanomaterials for biology and medicine, (b) nanoparticle interactions with biological systems (nano-bio interaction), (c) imaging and sensing, (d) therapeutic proof-of-concept applications, and (e) clinical analysis.

1.6. Overview of Nano Electronics

Nanoelectronics is the term used in the field of nanotechnology for electronic components and research on improvements of electronics such as display, size, and power consumption of the device for the practical use. This includes research on memory chips and surface physical modifications on the electronic devices. Nanoelectronics cover quantum mechanical properties of the hybrid material, semiconductor, single dimensional nanotubes, nanowires, and so forth. Well-developed nanoelectronics can be applied in different fields, and are especially useful for detecting disease-causing agents and disease biomarkers. As a consequence, point-of-care detection became popularized due to the involvement of nanoelectronics.

The term *nanoelectronics* refers to the use of nanotechnology in electronic components. These components are often only a few nanometers in size. However, the tinier electronic components become, the harder they are to manufacture.

Nanoelectronics covers a diverse set of devices and materials, with the common characteristic that they are so small that physical effects alter the materials' properties on a nanoscale – interatomic interactions and quantum mechanical properties play a significant role in the workings of these devices. At the nanoscale, new phenomena take precedence over those that hold sway in the macro-world. Quantum effects such as tunnelling and atomistic disorder dominate the characteristics of these nanoscale devices

The first transistors built in 1947 were over 1 centimetre in size; the smallest working transistor today is 7 nanometers long – over 1.4 million times smaller (1 cm equals 10 million nanometers). The result of these efforts are billion-transistor processors where, once industry embraces 7nm manufacturing techniques, 20 billion transistor-based circuits are integrated into a single chip.

1.6.1. Nanoelectronic Devices

Spintronics

Besides transistors, nanoelectronic devices play a role in data storage (memory). Here, *spintronics* – the study and exploitation in solid-state devices of electron spin and its associated magnetic moment, along with electric charge – is already an established technology. Read more: "Graphene spintronics - from science to technology".



Spintronics also plays a role in new technologies that exploit quantum behavior for computing (read more: "Quantum computing moves forward with spintronics progress" and "The birth of topological spintronics").

Optoelectronics

Electronic devices that source, detect and control light – i.e. optoelectronic devices – come in many shapes and forms. Highly energy-efficient (less heat generation and power consumption) optical communications are increasingly important because they have the potential to solve one of the biggest problems of our information age: energy consumption.

In the field of nanotechnology, materials like nanofibers (see for instance: "Light-emitting nanofibers shine the way for optoelectronic textiles") and carbon nanotubes have been used and especially graphene has shown exciting potential for optoelectronic devices.

Displays

Display technologies can be grouped into three broad technology areas; Organic LEDs, electronic paper and other devices intended to show still images, and Field Emission Displays. For more, read our special section on Nanotechnology in Displays.

1.6.2. Wearable, flexible electronics

The age of wearable electronics is upon us as witnessed by the fast growing array of smart watches, fitness bands and other advanced, next-generation health monitoring devices such as electronic stick-on tattoos.

If current research is an indicator, wearable electronics will go far beyond just very small electronic devices or wearable, flexible computers. Not only will these devices be embedded in textile substrates but an electronics device or system could ultimately become the fabric itself. Electronic textiles (e-textiles) will allow the design and production of a new generation of garments with distributed sensors and electronic functions. Such e-textiles will have the revolutionary ability to sense, act, store, emit, and move – think biomedical monitoring functions or new man-machine interfaces – while ideally leveraging an existing low-cost textile manufacturing infrastructure (see for instance "wearing single-walled carbon nanotube electronics on your skin", a "temporary tattoo to monitor glucose levels" or "graphene nanosensor tattoo on teeth monitors bacteria in your mouth").



Optical image of the graphene wireless sensor biotransferred onto the surface of a tooth. (Image: McAlpine Group, Princeton University)

1.6.3. Nanoelectronics in Energy

Solar cells and supercapacitors are examples of areas where nanoelectronics is playing a major role in energy generation and storage. To learn more read our detailed sections on Nanotechnology in Energy and Graphene Nanotechnology in Energy.

1.6.3.1. Molecular Electronics

Distinct from nanoelectronics, where devices are scaled down to nanoscale levels, molecular electronics deals with electronic processes that occur in molecular structures such as those found in nature, from photosynthesis to signal transduction.

Molecular electronics aims at the fundamental understanding of charge transport through molecules and is motivated by the vision of molecular circuits to enable miniscule, powerful and energy efficient computers (see for instance: "Adding an optoelectronic component to molecular electronics").

CHAPTER 2

NANO ELECTRONICS & NANO-COMPUTER ARCHITECTURES

Introduction to Nano-computers, Nano-computer Architecture, Quantum DOT cellular Automata (QCA), QCA circuits, Single electron circuits, molecular circuits, Logic switches – Interface engineering – Properties (Self-organization, Size-dependent) – Limitations

2.1 Introduction to Nano Computer

A nanocomputer is a computer whose physical dimensions are microscopic. The field of nanocomputing is part of the emerging field of nanotechnology. Several types of nanocomputers have been suggested or proposed by researchers and futurists.

Electronic nanocomputers would operate in a manner similar to the way present-day microcomputers work. The main difference is one of physical scale. More and more transistor s are squeezed into silicon chips with each passing year; witness the evolution of integrated circuits (IC s) capable of ever-increasing storage capacity and processing power. The ultimate limit to the number of transistors per unit volume is imposed by the atomic structure of matter. Most engineers agree that technology has not yet come close to pushing this limit. In the electronic sense, the term nanocomputer is relative. By 1970s standards, today's ordinary microprocessors might be called nanodevices.

Chemical and biochemical nanocomputers would store and process information in terms of chemical structures and interactions. Biochemical nanocomputers already exist in nature; they are manifest in all living things. But these systems are largely uncontrollable by humans. We cannot, for example, program a tree to calculate the digits of pi , or program an antibody to fight a particular disease (although medical science has come close to this ideal in the formulation of vaccines, antibiotics, and antiviral medications). The development of a true chemical nanocomputer will likely proceed along lines similar to genetic engineering. Engineers must figure out how to get individual atoms and molecules to perform controllable calculations and data storage tasks.

Mechanical nanocomputers would use tiny moving components called nanogears to encode information. Such a machine is reminiscent of Charles Babbage 's analytical engines of the 19th century. For this reason, mechanical nanocomputer technology has sparked controversy; some researchers consider it unworkable. All the problems inherent in Babbage's apparatus, according to the naysayers, are magnified a millionfold in a mechanical nanocomputer.

Nevertheless, some futurists are optimistic about the technology, and have even proposed the evolution of nanorobots that could operate, or be controlled by, mechanical nanocomputers.

A quantum nanocomputer would work by storing data in the form of atomic quantum states or spin. Technology of this kind is already under development in the form of single-electron memory (SEM) and quantum dots. The energy state of an electron within an atom , represented by the electron energy level or shell, can theoretically represent one, two, four, eight, or even 16 bits of data. The main problem with this technology is instability. Instantaneous electron energy states are difficult to predict and even more difficult to control. An electron can easily fall to a lower energy state, emitting a photon; conversely, a photon striking an atom can cause one of its electrons to jump to a higher energy state.



2.2. Architectural Features & Compiler Analysis Techniques

Certain characteristics are common to most processors, and should be considered as candidates for reconfiguration. Characteristics such as the number of registers, functional units, memory units, cache and memory organization, branch history and prediction support, pipeline organization, and the instruction set architecture (ISA) should be considered. [14] Compilers currently retarget a source program to a target machine. With the flexibility of machine reconfiguration, the task of retargeting is made more powerful because the resulting target machine will be better suited to the specific characteristics and requirements of the source program. In analyzing the characteristics inherent in a given source program, the ability to detect instruction-level, tasklevel and coarse-grained parallelism will also guide the description of architectural features. For instance, the amount of instruction-level parallelism (ILP)

available in a program can impact the number of functional units that are specified, leading to improved performance. Rather than computer architects investing significant money and time in the design of an excellent general-purpose processor that does reasonably well running most source programs, the compiler itself can generate a well-tuned machine configured to match the individual source program, allowing each to maximize performance. The compiler has the responsibility of analyzing the source program and generating a suitable machine description based on the results of the analysis. There are extensive analyses available, although the majority is designed to optimize the program for a specific target machine [1]. Any analyses that measure or enable the measurement of variable liveness, inherent parallelism, branching behavior, common subexpressions, memory access patterns, cache utilization, register allocation opportunities, instruction scheduling opportunities, and many other characteristic-related metrics are candidates. All can provide information to guide the generation of a machine description that is suited to the source program. The key consideration is the ability to gather information about static characteristics or predictive behavior of the source to enable production of a best-fit machine description.

Compiler Design

The major goal of the initial work reported in this paper is the design of a compiler that generates as its output both an executable version of the original source program and the description of a machine on which the executable will run well. This study focuses on ILP architectures, although the concepts also apply more broadly to include coarse-grain approaches. Traditional compilers take the source code and translate it into a binary form suitable for a specific processor, optimized to run as well as possible on that target machine. Knowledge of the target machine is needed to perform machine-dependent optimizations. Our approach differs in that the configuration of the target machine is unknown when compilation begins. The machine configuration is extracted from the source program, based on its resource requirements. In this way, the resulting machine is an excellent fit to the program. To discover this machine description, the compiler must perform a number of analyses designed to reveal the needs of the program. For example, live variable analysis can be performed to help determine how many registers are needed. However, the number of registers needed also depends on the issue width of the target machine, which is determined by the inherent ILP in the program. Thus, there are numerous interactions to consider when analyzing a program and generating a machine description. Figure 1 illustrates the organization of the proposed

nanocompiler from a high level. Source code is processed by the Front end of the compiler, including machine-independent optimizations. The resulting intermediate form is passed to a Machine requirements analysis phase, which performs static analysis, providing metrics to the Machine description generation phase. The resulting machine description is used by the Processor generator phase to generate or reconfigure the target machine, and by the compiler Back end to perform machine-dependent optimizations and generate the executable code. The organization in Figure 1 also shows how information from the Processor generator and even runtime profiling information could be fed back into the Machine requirements analysis phase to enable iterative refinement of the machine description, and thus of the processor itself.

2.3. Quantum DOT cellular Automata (QCA):

In recent years, the use of CMOS technology is limited by high consumption, low speed, and density beyond 10 nm. To overcome these problems, a number of researchers have been ascertained to find the solution for this classical CMOS technology which is quantum-dot cellular automata (QCA) used for high-speed application.

Nowadays, QCA transistor-less technology, single electron transistor (SET), and carbon nanotube (CNT) are being used as an alternative to CMOS technology. The use of QCA on the nanoscale has a promising future because of its ability to achieve high performance in terms of clock frequency, device density, and power consumption. if it is compared to similar implementations with conventional VLSI technology. These advantages make the proposed QCA technology useful for high-performance electronic applications applied on mobile or autonomous devices where power consumption and real-time processing low are needed.

Recently, using QCA technology for electronic modules design has become widely used . In , memory circuits have been proposed. In , reversible full adder/subtractor and multiplier has been designed. In , a sequential circuits based on QCA technology has been proposed. In , a decoder circuit based on QCA technology has been developed.

In this chapter, we will describe the background of QCA technology. This new concept will take the great advantage of a physical effect called the Coulomb force. In the next, we will describe how the information can be propagated through QCA cell by clicking. Then, we will introduce the basic elements and gates used for QCA circuits. The proposed 2-input "XOR" circuit occupies small area of 0.006 μ m², low complexity of 10 cells as compared to previous

best designs. Besides, the proposed 3-input "XOR" design occupies only 0.008 μ m² whereas the previous best reported design occupies 0.0116 μ m² area. On the other hand, the proposed 3-input "XOR" gate has 32% less area than best reported design.

2.3.1. Background of QCA

In 1993, Craig Lent proposed a new concept called quantum-dot cellular automata (QCA). This emerging technology has made a direct deviation to replace conventional CMOS technology based on silicon . QCA generally uses arrays of coupled quantum dots in order to implement different Boolean logic functions. QCA or quantum-dot cellular automata as its name is pronounced uses the quantum mechanical phenomena for the physical implementation of cellular automata. In the general case, conventional digital technologies require a range of voltages or currents to have logical values, whereas in QCA technology, the position of the electrons gives an idea of the binary values . The advantages of this technology are especially given in terms of speed (range of terahertz), density (50 Gbits/cm²) and in terms of energy or power dissipation (100 W/cm²).

QCA is based essentially on a cell. Each cell represents a bit by a suitable charge configuration as shown in Figure 2.3.1.1. It consists of four quantum dots and two electrons charge. Under the effect of the force of Colombian repulsion, the two electrons can be placed only in two quantum sites diametrically opposite.



Figure 2.3.1.1 Basic QCA cell.

A QCA cell is composed of four points with one electron each in two of the four points occupying diametrically opposite locations. The question that arises in this case is why do electrons occupy quantum dots of opposite or diagonal corner To answer this question, it is enough to have an idea about the principle of the repulsion of Coulomb, which is less effective with respect to the electrons when they are in adjacent quantum dots. The points are coupled to one another by tunnel junctions.

Thus, the internal effect of the cell highlights two configurations possible; each one will be used to represent a binary state "0" or "1." A topology of QCA is a paving of cells QCA. The interaction between the cells makes it possible to transmit information which gives the possibility of replacing physical interconnection of the devices. The information (logic 0 or logic 1) can propagate from input to the output of the QCA cell only by taking advantage of the force of repulsion as shown in Figure 2.3.1.2.





Operations of a QCA wire propagation by application of logic 0 and logic 1 1 to a QCA cell at the input.

2.4. Clocking in QCA

Clocking is an important term in QCA design. In order to propagate the information through QCA without any random adjustments of QCA cells, it is necessary to make a clock to guarantee the same data putting from input to the output. According to <u>Figure 2.4.1</u> timing in QCA is obtained by clocking in four distinct periodic phases namely Switch, Release, Relax, and Hold.



Figure 2.4.1. Four phases of QCA clock zones.

Based on the position of the potential barrier, the arrays of QCA cells in each phase have different polarizations. There are four phases, and every phase has its own polarizations as shown in Table 2.4.1.

| Clock phase | Potential barrier | Polarization state of the cells |
|-------------|-------------------|---------------------------------|
| Hold | Held high | Polarized |
| Switch | Low to high | Polarized |
| Relax | Low | Unpolarized |
| Release | Lowered | Unpolarized |

Table 2.4.1. Operation of QCA clock phases.

From Table 2.4.1, during the "Switch" phase of the clock, the QCA cell begins without polarization and switches to polarized state while the potential barrier has been raised from low to high. In the "Hold" phase, the polarization state is preserved as the preceding phase and the potential barrier is high. From the "Release" phase, the potential barrier is lowered and the cells become unpolarized. In "Relax" phase, the potential barrier remains lowered and the cells keep at nonpolarized state. This phase, the cells are ready to switch again. This way information is propagated in QCA circuits by keeping the ground-state polarization all the time. Figure 2.4.2 illustrates the polarizations and interdot barriers of the QCA cells in each of the QCA clock zones.



Figure 2.4.2. Schematic of interdot barriers in QCA clock.

2.5. Basic QCA elements and gates

Many architectures of logic devices can be designed by using adequate arranging of QCA cells. The biggest advantage of this wireless technology is that the logic is carried by the cells themselves. The fundamental QCA logic is binary wire, inverter, and majority voter. These QCA logic gates are evaluated and simulated using the QCA Designer tool version 2.0.3.

2.5.1. Noninverter gate or binary wire

The great advantage of cell QCA is that all the close cells are aligned on a specific polarization, which depends on the input cell or the driver cell. Hence, by arranging the cells side-by-side according to the type "0" or "1" applied to the input cell, any logic can be transferred. Consequently, this gate can play the role of a wire or binary interconnection or noninverter gate as shown in Figure 2.5.1.1(a). The layout of each cell given by binary wire is represented in Figure 2.5.1.1(b).

The simulation results of the noninverter gate are presented in Figure 2.5.1.1(c). One waveform with one frequency is applied to the input (In), one waveform for the first clock (Clk 0), and one waveform for the binary wire outputs (Out). From simulation results of binary wire given by Figure 2.5.1.1(c), the expression from the output pulses of the noninverter gate can be deduced, which is given by Eq. (1):

$$Out = In. \overline{Clk}0$$
 ----- (1)



Figure 2.5.1.1.Binary wire, (a) representation, (b) QCA layout, and (c) simulation results.

2.5.2. Inverter gate

Thanks to the columbic interaction between electrons in neighboring cells, different types of the inverter gates in QCA were proposed. The principle operation of this gate is to invert the input signal applied. If the applied input is low then the output becomes high and vice versa, as shown in Figure 2.5.2.1(a) and 2.5.2.1(b). The input "In" is given to one of the ends and the output reversed will be obtained at the output "Out." The position of the electrons and the layout of each cell are represented in Figure 2.5.2.1(b). The principle of operation of this gate is based on the wire of input, which will be prolonged in two parallel wires and will polarize the cell placed at the end of these two wires, which implies the opposite polarization of this cell due to the Coulomb repulsion.

According to Figure 2.5.2.1(c), the simulation results of the inverter gate are presented. One waveform with one frequency is applied to the input (In), one waveform for the clock 0 (Clk 0), and one waveform for the inverter gate outputs (Out).



Figure 2.5.2.1.Inverter gate, (a) representation, (b) QCA layout, and (c) simulation results.

From simulation results of the output pulses inverter gate (Out) given by Figure 6(c), the expression of the inverter gate can be deduced as expressed in Eq. (2):

$$Out = \overline{In}. \overline{Clk}0 \qquad ----- (2)$$

2.5.3. QCA majority voter

In QCA circuits, the majority voter (MV) plays an important role for logic gates. It is only composed of five cells: three input cell, one output cell, and a center cell, which is the decision-making cell. These cells are arranged like a cross with three inputs (a, b, and c) and one output (Out). This gate is based on the majority logic value given at its input as shown in Figure 2.5.3.1(a). The layout of each cell given by MV is represented in Figure 2.5.3.1(b).

According to Figure 2.5.3.1(c), the simulation results of the majority voter (MV) gate are presented. Three waveforms with different frequencies are applied to the inputs (a, b, and c), one waveform for the clock 0 (Clk 0), and one waveform for the MV outputs (Out).



(c)

Figure 2.5.3.1. Majority voter (MV) gate, (a) QCA representation, (b) QCA layout, and (c) simulation results.

From simulation results of the output pulses of MV gate given by Figure 2.5.3.1(c), the expression of the MV gate can be given by Eq. (3):

$$Out = a.b + b.c + c.a$$
 ------ (3)

From the majority voter gate, depending on the input fixed to 0 or 1, other logical gates can be deduced such as AND/OR gates.

• On the one hand, when one of the inputs of MV is fixed to 1, the logical function of OR gate is obtained and can be expressed in Eq. (4):

Out=a+b when c=1 -----(4)

Figure 2.5.3.1 shows the representation, QCA layout, and simulation of OR gate.



Figure 2.5.3.1. OR gate, (a) QCA representation, (b) QCA layout, and (c) simulation results.

According to Figure 2.5.3.1(c), the simulation results of the OR gate are presented. Two waveforms with one frequency are applied to the inputs (a and b), one waveform for the clock 0 (Clk 0), and one waveform for the OR gate outputs (Out).

From simulation results of the output pulses OR gate (yellow) given by Figure 2.5.3.1(c), the expression of the inverter gate can be deduced as expressed in Eq. (5):

• On the other hand, when one of the inputs of MV is fixed to 0, the logical function of AND gate is obtained (Figure 2.5.3.2) and can be expressed in Eq. (6):



Figure 2.5.3.2.AND gate, (a) QCA representation, (b) QCA layout, and (c) simulation results.

According to Figure 2.5.3.2(c), the simulation results of the AND gate are presented. When there are two waveforms, with one frequency is applied to the inputs (a and b), one waveform given for the clock 0 (Clk 0), and one waveform for the AND gate outputs (Out).

From simulation results of the output pulses AND gate (yellow) given by Figure 2.5.3.2(c), the expression of the inverter gate can be deduced as expressed in Eq. (7):

$$Out = (a . b) . \overline{Clk}0 \qquad ----(7)$$

2.6. Novel proposed QCA elements and gates

2.6.1. Proposed structure of 2-input digital "XNOR" gate

The 2-input logical "XNOR" gate is a hybrid circuit based on Inverter gate and "Exclusive-OR" gate. The schematic of a simple digital "XNOR" gate is presented in Figure 2.6.1.1. This circuit has two inputs: "c" and "d," and one output "K."



Figure 2.6.1.1.Schematic of 2-input "XNOR" gate.

The truth table of this "XNOR" gate is shown in Table 2.

| c | d | K |
|---|---|---|
| 0 | 0 | 1 |
| 0 | 1 | 0 |
| 1 | 0 | 0 |
| 1 | 1 | 1 |

Table 2.6.1. Truth table of 2-input "XNOR" gate.

From Table 2.6.1, it can be deduced that when "c" and "d" are equal, the output "K" is equal to "1," and when "c" and "d" are different, the output "K" is equal to "0." Hence, the output "K" of the "Non-Exclusive-OR" ("XNOR") gate performs the following logic operation in Eq. (8):

$$K = c \odot d = \overline{cd + cd} \qquad ----- (8)$$

In this chapter, a novel architecture of two-input "non-Exclusive-OR" gate using QCA implementation is proposed. It is defined by a higher density and a small number of cells.

This novel structure of 2-input "XNOR" gate is composed of two inputs "c," "d," and one fixed logic "0," with one output "K." The structure and the QCA layout of the proposed design are shown in Figure 2.6.1.2.



Figure 2.6.1.2.The novel architecture of 2-input "XNOR" gate structure, (a) schematic of "XNOR" gate and (b) QCA layout of proposed "XNOR" gate.

The simulation results of the proposed 2-input logical "XNOR" gate are shown in Figure 2.6.1.3. Four waveforms are applied to the inputs: c, d, Clk 0 and Clk 1. One waveform for the digital "XNOR" gate outputs (K). It can be deduced that there is 0.5 clock delay of latency on the novel proposed 2-input "XNOR" gate constituted only by 10 cells with an area of 0.006 μ m².



Figure 2.6.1.3. The simulation result of the novel design of 2-input logical "XNOR" gate.

2.6.2. Proposed structure of 3-input digital "XNOR" gate

The 3-input logical "XNOR" gate is adapted of 2-input logical "XNOR" gate. The schematic of this digital "XNOR" gate is presented in Figure 2.6.2.1. This circuit has four inputs: "c," "d," "e," and one output "K."



Figure 2.6.2.1.Schematic of 3-input "XNOR" gate. (a) Schematic of "XNOR" gate and (b) QCA layout of proposed "XNOR" gate.

The truth table of this 3-input "non-Exclusive-OR" gate is shown in Table 2.6.2.1.

| с | d | e | k |
|---|---|---|---|
| 0 | 0 | 0 | 1 |
| 0 | 0 | 1 | 0 |
| 0 | 1 | 0 | 0 |
| 0 | 1 | 1 | 1 |
| 1 | 0 | 0 | 0 |
| 1 | 0 | 1 | 1 |
| 1 | 1 | 0 | 1 |
| 1 | 1 | 1 | |

Table 2.6.2.1. Truth table of 3-input "XNOR" gate.

From Table 2.6.2.1, it can be deduced that when the number of the input "1" is odd, the output "K" is equal to "0." In the case of the number of the input "1" is even, the output "K" is equal to "1." Hence, the output "K" of the XNOR gate can determine the parity and is given by the following logic operation in Eq. (9):

The simulation results of the proposed 3-input logical "XNOR" gate are shown in Figure 2.6.2.2. Three waveforms are applied to the inputs (c, d, and e) with the clock 0, clock 1, and

one waveform for the digital 3-input "XNOR" gate outputs (K). It can be deduced that there is 0.5 clock of latency on this novel proposed architecture 3-input "XNOR" gate constituted by 10 cells and with an area of $0.006 \ \mu m^2$.



Figure 2.6.2.2. The simulation result of the novel architecture of 3-input logical "XNOR" gate.

2.6.3. Proposed architecture of 2-input "XOR" gate

The 2-input logical "XOR" gate is a hybrid circuit, which is designed from 2-input logical "XNOR" gate. The schematic of "XOR" gate is presented in Figure 2.6.3.1. This circuit has two inputs: "c" and "d," and one output "K."



Figure 2.6.3.1.Schematic of 2-input "XOR" gate.

The truth table of this 2-input "Exclusive-OR" gate is shown in Table 2.6.3.1.

| С | d | K |
|---|---|---|
| 0 | 0 | 0 |
| 0 | 1 | 1 |
| 1 | 0 | 1 |
| 1 | 1 | 0 |

Table 2.6.3.1.Truth table of 2-input "XOR" gate.

From Table 4, it can be deduced that when "c" and "d" are different, the output "K" is equal to "1," and when "c" and "d" are equal, the output "K" is equal to "0." Hence, the output "K" of the "Exclusive-OR" ("XOR") gate performs the following logic operation in Eq. (10):

$$K = c \oplus d = \bar{c}d + c\bar{d} \qquad -----(10)$$

This novel design of 2-input "XOR" gate is composed of two inputs "c" and "d," and one fixed logic "0," with one output "K." The structure and the QCA layout of the proposed 2-input "XOR" gate are shown in Figure 2.6.3.2.



Figure 2.6.3.2.The architecture of novel design 2-input "XOR" gate structures: (a) schematic of 2-input "XOR" gate and (b) QCA layout of proposed 2-input "XOR" gate.

The simulation results of the proposed architecture of 2-input "XOR" gate are presented in Figure 2.6.3.3. Two waveforms are applied to the inputs (c and d), the clock 0, clock 1 and one waveform for "XOR" gate output (K). From <u>Figure 11</u>, it can be deduced that there is 0.5 clock of latency on this novel 2-input "XOR" gate, which is constituted by 10 cells with an area of 0.006 μ m².



Figure 2.6.3.3. The simulation result of the novel structure of 2-input "XOR" gate.

The proposed 2-input XOR circuit has lower computational complexity and better performances compared to the existing ones. Table 2.6.3.2 shows the comparison results of the proposed design for the XOR with the existing designs.

| Design | Cell count | Area (µm ²) | Latency |
|--------------------------------|------------|-------------------------|---------|
| 2-input XOR gate [27] | 67 | 0.06 | 1.25 |
| 2-input XOR gate [28] | 32 | 0.02 | 1 |
| 2-input XOR gate [29] | 28 | 0.02 | 0.75 |
| 2-input XOR gate [<u>30]</u> | 30 | 0.0233 | 0.75 |
| 2-input XOR gate [<u>31</u>] | 12 | 0.0116 | 0.5 |
| Proposed 2-input XOR | 12 | 0.006 | 0.5 |

Table 2.6.3.2. Comparison results of single layer 2-input XOR gates.

2.6.4. Proposed structure of 3-input "XOR" gate

The 3-input logical "XOR" gate is an adapted form of 3-input logical "XNOR" gate. The schematic of this digital "XOR" gate is presented in Figure 2.6.4.1. This circuit has only four inputs: "c," "d," "e," and one output "K."



Figure 2.6.4.1.The architecture of novel design 2-input "XOR" gate structures: (a) schematic of 2-input "XOR" gate and (b) QCA layout of proposed 2-input "XOR" gate.

The truth table of this 3-input "Exclusive-OR" gate is shown in Table 2.6.4.1.

| С | d | e | k |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 0 | 0 | 1 | 1 |
| 0 | 1 | 0 | 1 |
| 0 | 1 | 1 | 0 |
| 1 | 0 | 0 | 1 |
| 1 | 0 | 1 | 0 |
| 1 | 1 | 0 | 0 |
| 1 | 1 | 1 | 1 |

Table 2.6.4.1. Truth table of 3-input "XOR" gate.
From Table 2.6.4.1, it can be deduced that when the number of the input "1" is even, the output "K" is equal to "0". When the number of the input "1" is odd, the output "K" is equal to "1." Hence, the output "K" of the XNOR gate can determine the parity and is given by the following logic operation in Eq. (11):

 $K=c \oplus d \oplus e \qquad ----- (11)$

The simulation results of the proposed 3-input logical "XOR" gate are shown in Figure 2.6.4.2. Three different waveforms are applied to the inputs (c, d, and e), the clock 0 and clock 1 and one waveform for the digital 3-input "XNOR" gate outputs (K). It can be interpreted that there is 0.5 clock of latency on this novel proposed structure of 3-input? XOR? gate, which is composed of 12 cells with an area of 0.008 μ m².



Figure 2.6.4.2. The simulation result of the novel architecture of 3-input "XOR" gate.

Table 2.6.4.2 shows the comparison results of the proposed design for the 3-input XOR with the exist designs.

| Design | Cell count | Area (µm²) | Latency |
|---------------------------|------------|------------|---------|
| 3-input XOR gate [31] | 12 | 0.0116 | 0.5 |
| 3-input XOR gate [27] | 93 | 0.07 | 11.25 |
| Proposed 3-input XOR gate | 12 | 0.008 | 0.5 |

Table 2.6.4.2. Comparison results of single layer 3-input XOR gates.

2.7. Interface Engineering

As the microstructure of a material is refined from the micron scale to the nanoscale there is a significant increase in the interface density of the material. If the density of interfaces is high enough, the macroscopic deformation response can be influenced by the structure of the interface at the nanoscale. Shown below is a comparison of two interface types, cube-on-cube and incoherent twin. In the cube-on-cube interface structure the deformation systems are aligned across the interface as is indicated by the identical orientations of the Thomson tetrahedron on both sides of the bi-metallic interface. Alternatively the incoherent interface has a single aligned deformation plane as indicated. The mechanical response is shown for materials that consist predominantly of cube-on-cube and incoherent twin orientation illustrating the difference in material response that can be elicited based on interface structure.

Solidification rate dependent interface structures in Ag-Cu cast eutectic alloy



CHAPTER 3

NANOELECTRONIC ARCHITECTURE

Nanofabrication – Nano patterning of Metallic/Semiconducting nanostructures (e-beam/Xray, Optical lithography, STM/AFM- SEM & Soft-lithography) – Nano phase materials – Self assembled Inorganic/Organic layers

3.1. Nanofabrication

There is no single accepted definition of nanofabrication, nor a definition of what separates nanofabrication from microfabrication. To meet the continuing challenge of shrinking component size in microelectronics, new tools and techniques are continuously being developed. Component sizes that were in tens of micrometres became single-digit micrometers, and then hundreds of nanometers, and then went down to a few tens of nanometers where they stand today. As a result, what used to be called microfabrication was rebranded as nanofabrication, although the governing principles have remained essentially the same. The main driver of this technology has been the manufacture of integrated circuits, but there have been tremendous fallout benefits to other areas, including photonics.

Nanofabrication can be loosely divided into three major areas: thin films, lithography, and etching. Each of these are vast subject areas in and of themselves, but in this chapter we attempt to cover their essential concepts in a concise fashion for someone new to these areas. The goal is not to provide a working experience that allows one to walk into a laboratory and perform these tasks, but to provide an overall understanding of what these areas are as well as the pros and cons of the most commonly used techniques. Hopefully it will build a foundation for more specific training for anyone who wants to venture further into these areas.



Two very different paths are pursued. One is a top-down strategy of miniaturizing current technologies, while the other is a bottom-up strategy of building ever-more-complex molecular devices atom by atom. Top-down approaches are good for producing structures with long-range order and for making macroscopic connections, while bottom-up approaches are best suited for assembly and establishing short-range order at nanoscale dimensions. The integration of top-down and bottom-up techniques is expected to eventually provide the best combination of tools for nanofabrication. Nanotechnology requires new tools for fabrication and measurement.

3.1.1. Top-down approach

The most common top-down approach to fabrication involves lithographic patterning techniques using short-wavelength optical sources. A key advantage of the top-down approach—as developed in the fabrication of integrated circuits—is that the parts are both patterned and built in place, so that no assembly step is needed. Optical lithography is a relatively mature field because of the high degree of refinement in microelectronic chip manufacturing, with current short-wavelength optical lithography techniques reaching dimensions just below 100 nanometres (the traditional threshold definition of the nanoscale). Shorter-wavelength sources, such as extreme ultraviolet and X-ray, are being developed to allow lithographic printing techniques to reach dimensions from 10 to 100 nanometres. Scanning beam techniques such as electron-beam lithography provide patterns down to about 20 nanometres. Here the pattern is written by sweeping a finely focused electron beam across the surface. Focused ion beams are also used for direct processing and patterning of wafers, although with somewhat less resolution than in electron-beam lithography. Still-smaller features are obtained by using scanning probes to deposit or remove thin layers.

Mechanical printing techniques—nanoscale imprinting, stamping, and molding—have been extended to the surprisingly small dimensions of about 20 to 40 nanometres. The details of these techniques vary, but they are all based on making a master "stamp" by a high-resolution technique such as electron-beam lithography and then applying this stamp, or subsequent generations of it, to a surface to create the pattern. In one variation a stamp's surface is coated with a very thin layer of material (the "ink") that can then be deposited ("inked") directly onto the surface to reproduce the stamp's pattern. For example, the controlled patterning of a molecular monolayer on a surface can be achieved by stamping an ink of thiol functionalized organic molecules directly onto a gold-coated surface (molecules that contain a sulfur end

group, called a thiol, bond strongly to gold). In another approach the stamp is used mechanically to press the pattern into a thin layer of material. This surface layer is typically a polymeric material that has been made pliable for the moulding process by being heated during the stamping procedure. Plasma etching can then be used to remove the thin layer of the masking material under the stamped regions; any residual polymer is thus removed, and a nanoscale lithographic pattern is left on the surface. Still another variation is to make the relief pattern out of photoresist on a silicon wafer by optical or electron-beam lithography and then pour a liquid precursor—for example, polydimethylsiloxane, a form of silicone—over the pattern and then cure it. The result is a rubbery solid that can be peeled off and used as a stamp. These stamps can be inked and printed as described above, or they can be pressed to the surface and a liquid polymer allowed to flow into the raised regions of the mask by capillary action and cured in place. A distinction for this latter approach is that the stamp is flexible and can thus be used to print nanoscale features on curved surfaces.

These nanoscale printing techniques offer several advantages beyond the ability to use a wider variety of materials with curved surfaces. In particular, such approaches can be carried out in ordinary laboratories with far-less-expensive equipment than that needed for conventional submicron lithography. The challenge for all top-down techniques is that, while they work well at the microscale (at millionths of a metre), it becomes increasingly difficult to apply them at nanoscale dimensions. A second disadvantage is that they involve planar techniques, which means that structures are created by the addition and subtraction of patterned layers (deposition and etching), so arbitrary three-dimensional objects are difficult to construct.

3.1.2. Bottom-up approach

Bottom-up, or self-assembly, approaches to nanofabrication use chemical or physical forces operating at the nanoscale to assemble basic units into larger structures. As component size decreases in nanofabrication, bottom-up approaches provide an increasingly important complement to top-down techniques. Inspiration for bottom-up approaches comes from biological systems, where nature has harnessed chemical forces to create essentially all the structures needed by life. Researchers hope to replicate nature's ability to produce small clusters of specific atoms, which can then self-assemble into more-elaborate structures.

3.2. Nano Patterning

Techniques for fabricating on sub-micron length scales span a wide range, from sophisticated lithographic methods that have their origins in the semiconductor industry to more recent materials and chemical advances that rely on self-organization. For delineating patterns below 100 nm, several approaches have been proposed (and indeed demonstrated). These include nano-imprint lithography (including micro-contact printing, mold-assisted lithography, and hot embossing lithography), near-field optical lithography, direct patterning on a nanometer scale with scanning-probe microscopes, self-assembly of monolayers, pattern formation based on phase separation of polymers, etc. The search is on for nonphotolithographic methods that could provide technologically simpler and cheaper nanofabrication strategies. Some of these approaches are better suited for producing individual nano-structures for the investigation of nanometer-scale devices; the throughput is likely to always remain impracticably low for commercial application. Others such as nanoimprint lithography have the potential of high throughput due to parallel processing, do not require sophisticated tools, and allow nanoscale replication for data storage.



The natural length scales of polymer chains and their morphologies in the bulk, which lie in the nanometer domain, make polymers ideal building blocks for nanopatterning. Recent developments in the use of polymers for the fabrication of nanostructures via lithographic and self-assembling strategies have been reviewed.

3.2.1. e-beam / x-ray

Electron beam (E-beam) lithography is a technique for forming a photoresist (PR) pattern on a sample surface by bonding or cutting off polymers constituting a PR by irradiating high-energy electrons onto the surface of a sample coated with an E-beam reactive PR. Beginning from the scanning electron microscopy (SEM) technology in the 1950s, the E-beam lithography technique has been consistently developed towards the fabrication of smaller features with higher resolutions, based on tactful beam source deployment, use of an ultrafine-precision

staging and optical system, and resist enhancement. Careful tuning has also been investigated for application to various other materials, such as biological cells and soft polymers. Figure 3.2.1.1 illustrates several milestone achievements of various lithography methodologies developed by utilizing many diverse aids, such as laser, x-ray, UV, near-field scanning optical microscopy, self-assemble monolayer, dip-pen, and so on. Among them, and as recently achieving the reliable nanoscale patterning of sub-50nm resolution, E-beam lithography has now been a primary workhorse in semiconductor device.



Figure 3.2.1.1



Figure 3.2.1.2

Manufacturing that especially requires ultrafine pattering, for example, very large-scale integrated circuit (VLSI) production. It plays a key role in many steps, such as the production of a reticle (expanded mask) for a reduced projection exposure apparatus (stepper). The technology applied to the production of ultrafine patterns has achieved by far the highest resolution and capability for drawing the minimum line width in actual semiconductor manufacturing processes. The most important factors in implementing ultrafine patterns by using E-beam lithography include sensitivity of the PR, the spot size of the E-beam, electron scattering, the secondary electron range, the photosensitizer phenomenon, and mechanical stability. E-beam nanopatterning technology has been evolving with the development of a parallel process by using E-beam projection, from the conventional serial process such as probe lithography. Further improvements have also been conducted using the multi-beam process. Meanwhile, many research institutes have been developing new PRs with good resolution based on the studies on energy flow by increasing the voltage to reduce the spot size of the E-beam.

3.2.2. Optical Lithography

The fabrication of an integrated circuit (IC) requires a variety of physical and chemical processes performed on a semiconductor (e.g., silicon) substrate. In general, the various processes used to make an IC fall into three categories: film deposition, patterning, and semiconductor doping. Films of both conductors (such as polysilicon, aluminum, and more recently copper) and insulators (various forms of silicon dioxide, silicon nitride, and others) are used to connect and isolate transistors and their components. Selective doping of various regions of silicon allow the conductivity of the silicon to be changed with the application of voltage. By creating structures of these various components millions of transistors can be built and wired together to form the complex circuitry of a modern microelectronic device. Fundamental to all of these processes is lithography, i.e., the formation of three-dimensional relief images on the substrate for subsequent transfer of the pattern to the substrate.

The word lithography comes from the Greek *lithos*, meaning stones, and *graphia*, meaning to write. It means quite literally writing on stones. In the case of semiconductor lithography (also

called photolithography) our stones are silicon wafers and our patterns are written with a light sensitive polymer called a photoresist. To build the complex structures that make up a transistor and the many wires that connect the millions of transistors of a circuit, lithography and etch pattern transfer steps are repeated at least 10 times, but more typically are done 20 to 30 times to make one circuit. Each pattern being printed on the



wafer is aligned to the previously formed patterns and slowly the conductors, insulators, and selectively doped regions are built up to form the final device.

The importance of lithography can be appreciated in two ways. First, due to the large number of lithography steps needed in IC manufacturing, lithography typically accounts for about 30 percent of the cost of manufacturing. Second, lithography tends to be the technical limiter for further advances in feature size reduction and thus transistor speed and silicon area. Obviously, one must carefully understand the trade-offs between cost and capability when developing a lithography process. Although lithography is certainly not the only technically important and challenging process in the IC manufacturing flow, historically, advances in lithography have gated advances in IC cost and performance.

Optical lithography is basically a photographic process by which a light sensitive polymer, called a photoresist, is exposed and developed to form three-dimensional relief images on the substrate. In general, the ideal photoresist image has the exact shape of the designed or intended pattern in the plane of the substrate, with vertical walls through the thickness of the resist. Thus, the final resist pattern is binary: parts of the substrate are covered with resist while other parts are completely uncovered. This binary pattern is needed for pattern transfer since the parts of the substrate covered with resist will be protected from etching, ion implantation, or other pattern transfer mechanism.

The general sequence of processing steps for a typical photolithography process is as follows: substrate preparation, photoresist spin coat, prebake, exposure, post-exposure bake, development, and postbake. A resist strip is the final operation in the lithographic process, after the resist pattern has been transferred into the underlying layer. This sequence is shown diagrammatically in Figure 1-1, and is generally performed on several tools linked together

into a contiguous unit called a *lithographic cluster*. A brief discussion of each step is given below, pointing out some of the practical issues involved in photoresist processing. More on these topics will be discussed in detail in subsequent chapters.

1. Substrate Preparation

Substrate preparation is intended to improve the adhesion of the photoresist material to the substrate. This is accomplished by one or more of the following processes: substrate cleaning to remove contamination, dehydration bake to remove water, and addition of an adhesion promoter. Substrate contamination can take the form of particulates or a film and can be either organic or inorganic. Particulates result in defects in the final resist pattern, whereas film contamination can cause poor adhesion and subsequent loss of linewidth control. Particulates generally come from airborne particles or contaminated liquids (e.g., dirty adhesion promoter). The most effective way of controlling particulate contamination is to eliminate their source. Since this is not always practical, chemical/mechanical cleaning is used to remove particles. Organic films, such as oils or polymers, can come from vacuum pumps and other machinery, body oils and sweat, and various polymer deposits leftover from previous processing steps. These films can generally be removed by chemical, ozone, or plasma stripping. Similarly, inorganic films, such as native oxides and salts, can be removed by chemical or plasma stripping. One type of contaminant – adsorbed water – is removed most readily by a high temperature process called a *dehydration bake*.



Figure 3.2.2.1. Example of a typical sequence of lithographic processing steps (with no postexposure bake in this case), illustrated for a positive resist.

A dehydration bake, as the name implies, removes water from the substrate surface by baking at temperatures of 200°C to 400°C, usually for 30 to 60 minutes. The substrate is then allowed to cool (preferably in a dry environment) and coated as soon as possible. It is important to note that water will re-adsorb on the substrate surface if left in a humid (non-dry) environment. A dehydration bake is also effective in volatilizing organic contaminants, further cleaning the substrate. Often, the normal sequence of processing steps involves some type of high temperature process immediately before coating with photoresist, for example thermal oxidation. If the substrate is coated immediately after the high temperature step, the dehydration bake can be eliminated. A typical dehydration bake, however, does not completely remove water from the surface of silica substrates (including silicon, polysilicon, silicon oxide, and silicon nitride). Surface silicon atoms bond strongly with a monolayer of water forming silanol groups (SiOH). Bake temperatures in excess of 600°C are required to remove this final layer of water [1.1]. Further, the silanol quickly reforms when the substrate is cooled in a nondry environment. Since this approach is impractical, the preferred method of removing this silanol is by chemical means.

Adhesion promoters are used to react chemically with surface silanol and replace the -OH group with an organic functional group that, unlike the hydroxyl group, offers good adhesion to photoresist. Silanes are often used for this purpose, the most common being hexamethyl disilizane (HMDS) [1.2]. (As a note, HMDS adhesion promotion was first developed for fiberglass applications, where adhesion of the resin matrix to the glass fibers is important.) The HMDS can be applied by spinning a diluted solution (10-20% HMDS in cellosolve acetate, xylene, or a fluorocarbon) directly on to the wafer and allowing the HMDS to spin dry (HMDS is quite volatile at room temperature). If the HMDS is not allowed to dry properly dramatic loss of adhesion will result. Although direct spinning is easy, it is only effective at displacing a small percentage of the silanol groups. By far the preferred method of applying the adhesion promoter is by subjecting the substrate to HMDS vapor, usually at elevated temperatures and reduced pressure. This allows good coating of the substrate without excess HMDS deposition, and the higher temperatures cause more complete reaction with the silanol groups. Once properly treated with HMDS the substrate can be left for up to several days without significant

re-adsorption of water. Performing the dehydration bake and vapor prime in the same oven gives optimum performance.

2. Photoresist Coating

A thin, uniform coating of photoresist at a specific, well controlled thickness is accomplished by the seemingly simple process of spin coating. The photoresist, rendered into a liquid form by dissolving the solid components in a solvent, is poured onto the wafer, which is then spun on a turntable at a high speed producing the desired film. Stringent requirements for thickness control and uniformity and low defect density call for particular attention to be paid to this process, where a large number of parameters can have significant impact on photoresist thickness uniformity and control. There is the choice between static dispense (wafer stationary while resist is dispensed) or dynamic dispense (wafer spinning while resist is dispensed), spin speeds and times, and accelerations to each of the spin speeds. Also, the volume of the resist dispensed and properties of the resist (such as viscosity, percent solids, and solvent composition) and the substrate (substrate material and topography) play an important role in the resist thickness uniformity. Further, practical aspects of the spin operation, such as exhaust, temperature and humidity control, and spinner cleanliness often have significant effects on the resist film. *Figure 3.2.2.2* shows a generic photoresist spin coat cycle. At the end of this cycle a thick, solvent-rich film of photoresist covers the wafer, ready for post-apply bake.

Although theory exists to describe the spin coat process rheologically, in practical terms the variation of photoresist thickness and uniformity with the process parameters must be determined experimentally. The photoresist spin speed curve (*Figure 3.2.2.3*) is an essential tool for setting the spin speed to obtain the desired resist thickness. The final resist thickness varies as one over the square root of the spin speed and is roughly proportional to the liquid photoresist viscosity.



Figure 3.2.2.2. Pictorial representation of a simple photoresist spin coat cycle. If $w \ 1 > 0$, the dispense is said to be dynamic.



Figure 3.2.2.3. Photoresist spins speed curves for different resist viscosities showing how resist thickness varies as spin speed to the -1/2 power.

3. Post-Apply Bake

After coating, the resulting resist film will contain between 20 - 40% by weight solvent. The post-apply bake process, also called a softbake or a prebake, involves drying the photoresist after spin coat by removing this excess solvent. The main reason for reducing the solvent

content is to stabilize the resist film. At room temperature, an unbaked photoresist film will lose solvent by evaporation, thus changing the properties of the film with time. By baking the resist, the majority of the solvent is removed and the film becomes stable at room temperature. There are four major effects of removing solvent from a photoresist film: (1) film thickness is reduced, (2) post-exposure bake and development properties are changed, (3) adhesion is improved, and (4) the film becomes less tacky and thus less susceptible to particulate contamination. Typical prebake processes leave between 3 and 8 percent residual solvent in the resist film, sufficiently small to keep the film stable during subsequent lithographic processing.

Unfortunately, there are other consequences of baking most photoresists. At temperatures greater than about 70°C the photosensitive component of a typical resist mixture, called the photoactive compound (PAC), may begin to decompose [1.3,1.4]. Also, the resin, another component of the resist, can crosslink and/or oxidize at elevated temperatures. Both of these effects are undesirable. Thus, one must search for the optimum prebake conditions that will maximize the benefits of solvent evaporation and minimize the detriments of resist decomposition. For chemically amplified resists, residual solvent can significantly influence diffusion and reaction properties during the post-exposure bake, necessitating careful control over the post-apply bake process. Fortunately, these modern resists do not suffer from significant decomposition of the photosensitive components during prebake.

There are several methods that can be used to bake photoresists. The most obvious method is an oven bake. Convection oven baking of conventional photoresists at 90°C for 30 minutes was typical during the 1970s and early 1980s. Although the use of convection ovens for the prebaking of photoresist was once quite common, currently the most popular bake method is the hot plate. The wafer is brought either into intimate vacuum contact with or close proximity to a hot, high-mass metal plate. Due to the high thermal conductivity of silicon, the photoresist is heated to near the hot plate temperature quickly (in about 5 seconds for hard contact, or about 20 seconds for proximity baking). The greatest advantage of this method is an order of magnitude decrease in the required bake time over convection ovens, to about one minute, and the improved uniformity of the bake. In general, proximity baking is preferred to reduce the possibility of particle generation caused by contact with the backside of the wafer.

When the wafer is removed from the hotplate, baking continues as long as the wafer is hot. The total bake process cannot be well controlled unless the cooling of the wafer is also well

controlled. As a result, hotplate baking is always followed immediately by a chill plate operation, where the wafer is brought in contact or close proximity to a cool plate (kept at a temperature slightly below room temperature). After cooling, the wafer is ready for its lithographic exposure.

4. Alignment and Exposure

The basic principle behind the operation of a photoresist is the change in solubility of the resist in a developer upon exposure to light (or other types of exposing radiation). In the case of the standard diazonaphthoquinone positive photoresist, the photoactive compound (PAC), which is not soluble in the aqueous base developer, is converted to a carboxylic acid on exposure to UV light in the range of 350 - 450nm. The carboxylic acid product is very soluble in the basic developer. Thus, a spatial variation in light energy incident on the photoresist will cause a spatial variation in solubility of the resist in developer.

Contact and proximity lithography are the simplest methods of exposing a photoresist through a master pattern called a photomask (Figure 1-4). Contact lithography offers high resolution (down to about the wavelength of the radiation), but practical problems such as mask damage and resulting low yield make this process unusable in most production environments. Proximity printing reduces mask damage by keeping the mask a set distance above the wafer (e.g., 20 μ m). Unfortunately, the resolution limit is increased to greater than 2 to 4 μ m, making proximity printing insufficient for today's technology. By far the most common method of exposure is projection printing.



Figure 3.2.2.4. Lithographic printing in semiconductor manufacturing has evolved from contact printing (in the early 1960s) to projection printing (from the mid-1970s to today).

Projection lithography derives its name from the fact that an image of the mask is projected onto the wafer. Projection lithography became a viable alternative to contact/proximity printing in the mid-1970s when the advent of computer-aided lens design and improved optical materials allowed the production of lens elements of sufficient quality to meet the requirements of the semiconductor industry. In fact, these lenses have become so perfect that lens defects, called aberrations, play only a small role in determining the quality of the image. Such an optical system is said to be diffraction-limited, since it is diffraction effects and not lens aberrations which, for the most part, determine the shape of the image.

There are two major classes of projection lithography tools – scanning and step-and-repeat systems. Scanning projection printing, pioneered by the Perkin-Elmer company, employs reflective optics (i.e., mirrors rather than lenses) to project a slit of light from the mask onto the wafer as the mask and wafer are moved simultaneously by the slit. Exposure dose is determined by the intensity of the light, the slit width, and the speed at which the wafer is scanned. These early scanning systems, which use polychromatic light from a mercury arc lamp, are 1:1, i.e., the mask and image sizes are equal. Step-and-repeat cameras (called steppers for short) expose the wafer one rectangular section (called the image field) at a time and can be 1:1 or reduction. These systems employ refractive optics (i.e., lenses) and are usually quasi-monochromatic. Both types of systems (*Figure 3.2.2.5*) are capable of high-resolution imaging, although reduction imaging is required for the highest resolutions.

Scanners replaced proximity printing by the mid-seventies for device geometries below 4 to 5 μ m. By the early 1980s, steppers began to dominate as device designs pushed below 2 μ m. Steppers have continued to dominate lithographic patterning throughout the 1990s as minimum feature sizes reached the 250nm levels. However, by the early 1990s a hybrid step-and-scan approach was introduced by SVG Lithography, the successor to Perkin-Elmer. The step-and-scan approach uses a fraction of a normal stepper field (for example, 25mm x 8mm), then scans this field in one direction to expose the entire 4 x reduction mask. The wafer is then stepped to a new location and the scan is repeated. The smaller imaging field simplifies the design and manufacture of the lens, but at the expense of a more complicated reticle and wafer stage. Step-and-scan technology is the technology of choice today for below 250nm manufacturing.



Figure 3.2.2.5. Scanners and steppers use different techniques for exposing a large wafer with a small image field.

Resolution, the smallest feature that can be printed with adequate control, has two basic limits: the smallest image that can be projected onto the wafer, and the resolving capability of the photoresist to make use of that image. From the projection imaging side, resolution is determined by the wavelength of the imaging light (λ) and the numerical aperture (*NA*) of the projection lens according to the Rayleigh criterion:

$$R \propto \frac{\hat{\lambda}}{NA}$$

Lithography systems have progressed from blue wavelengths (436nm) to UV (365nm) to deep-UV (248nm) to today's mainstream high resolution wavelength of 193nm. In the meantime, projection tool numerical apertures have risen from 0.16 for the first scanners to amazingly high 0.93 NA systems today producing features well under 100nm in size.

Before the exposure of the photoresist with an image of the mask can begin, this image must be aligned with the previously defined patterns on the wafer. This alignment, and the resulting overlay of the two or more lithographic patterns, is critical since tighter overlay control means circuit features can be packed closer together. Closer packing of devices through better alignment and overlay is nearly as critical as smaller devices through higher resolution in the drive towards more functionality per chip.

Another important aspect of photoresist exposure is the standing wave effect. Monochromatic light, when projected onto a wafer, strikes the photoresist surface over a range of angles, approximating plane waves. This light travels down through the photoresist and, if the substrate

is reflective, is reflected back up through the resist. The incoming and reflected light interfere to form a standing wave pattern of high and low light intensity at different depths in the photoresist. This pattern is replicated in the photoresist, causing ridges in the sidewalls of the resist feature as seen in *Figure 3.2.2.6*. As pattern dimensions become smaller, these ridges can significantly affect the quality of the feature. The interference that causes standing waves also results in a phenomenon called *swing curves*, the sinusoidal variation in linewidth with changing resist thickness. These detrimental effects are best cured by coating the substrate with a thin absorbing layer called a bottom antireflective coating (BARC) that can reduce the reflectivity seen by the photoresist to less than 1 percent.



Figure 3.2.2.6. Photoresist pattern on a silicon substrate showing prominent standing waves.

5. Post-Exposure Bake

One method of reducing the standing wave effect is called the post-exposure bake (PEB). Although there is still some debate as to the mechanism, it is believed that the high temperatures used $(100^{\circ}\text{C} - 130^{\circ}\text{C})$ cause diffusion of the photoactive compound, thus smoothing out the standing wave ridges (*Figure 3.2.2.7*). It is important to note that the detrimental effects of high temperatures on photoresist discussed concerning prebaking also apply to the PEB. Thus, it becomes very important to optimize the bake conditions. It has also been observed that the rate of diffusion of the PAC is dependent on the prebake conditions. It is thought that the presence of solvent enhances diffusion during a PEB. Thus, a low temperature prebake results in greater diffusion for a given PEB temperature.

For a conventional resist, the main importance of the PEB is diffusion to remove standing waves. For another class of photoresists, called chemically amplified resists, the PEB is an essential part of the chemical reactions that create a solubility differential between exposed and unexposed parts of the resist. For these resists, exposure generates a small amount of a strong

acid that does not itself change the solubility of the resist. During the post-exposure bake, this photogenerated acid catalyzes a reaction that changes the solubility of the polymer resin in the resist. Control of the PEB is extremely critical for chemically amplified resists.



Figure 3.2.2.7. Diffusion during a post-exposure bake is often used to reduce standing waves. Photoresist profile simulations as a function of the PEB diffusion length: (a) 20nm, (b) 40nm, and (c) 60nm.

3.2.3. Soft Lithography

Soft lithography can be viewed as a complementary extension of photolithography. Originally, standard photolithography was mainly developed to deal with semiconductors used in the microelectronics industry. Photolithography is inherently well adapted to process photoresists.



Soft lithography, however, extends the possibilities of conventional photolithography. Unlike photolithography, soft lithography can process a wide range of elastomeric materials, i.e. mechanically soft materials. This is why the term "soft" is used. For instance, soft lithography is well suited for polymers, gels, and organic monolayers. PDMS, however, has been the most widely used material for the applications of soft lithography because of its useful properties including low cost, biocompatibility, low toxicity, chemical inertness, versatile surface chemistry insulating, as well as mechanical flexibility and durability, the PDMS can also be easily manipulated and making PDMS devices can require very few equipment.

It should be noted that the terminology soft lithography does not refer to a unique fabrication technique. Soft lithography actually encompasses a collection of fabrication methods that are all based on using a patterned layer of PDMS similar to the one exposed in Figure 1f. In order to provide a brief overview, the next sections of this tutorial will introduce some of the core techniques related to soft lithography.

3.3. Nano Phase Materials

Nanophase materials are materials with a grain size in the 1 to 100 nm range. Nanophase materials exhibit greatly altered mechanical properties compared to their normal, large-grained counterparts with the same chemical composition. For example, nanophase metals are up to five (5) times harder than the normal materials. While nanophase metals generally become harder and more brittle, nanophase ceramics become more ductile. In a typical nanophase material, 10 to 50% of the atoms are in grain boundary regions.

Nanophase materials can be made using a number of methods. The two main methods involve consolidation of nanometer sized particles or the creation of small grains using mechanical attrition. For the first method, small particles are created using techniques such as inert gas condensation or through the use of chemical processing. In the second case, larger particles are milled for a long period of time to create a very small grain size.

3.3.1 Self Assembly

Materials self-assembly is a key strategy for the design and fabrication of nanostructured systems and has become a fundamental approach for the construction of advanced materials and their application in the fields of nanomaterials and biotechnology. In nanomaterials self-assembly, the mutual interaction between disordered building blocks drive a material system toward the spontaneous formation of more ordered (or more organized) nano-structured systems. Main examples of the self-assembly method can be found in biomaterials, where the interaction of various macromolecular components and the integration of their actions allow the occurrence of highly specific functions of biological interest. For example, the folding of a polypeptide chain within a protein or the nucleic acids conformational changes into a variety of functional forms are important examples of self-assembly processes involved in many biological functions.

The construction and optimization of functional materials at the atomic and molecular level require a structural control and investigation at the nano-scale and have stimulated a parallel development of instrumentation techniques and observational methods on those size scales. Moreover, the development of multifunctional nanostructures and biomaterials using the recent concepts of nanoarchitectonics utilizes advanced processes for the self-assembly, such as supramolecular chemistry and host–guest processes.

The reversibility of the noncovalent forces allows a dynamic switching of the structure and morphology of the nanostructures in response to various (internal and external) stimuli, thus providing additional flexibility for the design and fabrication of versatile smart materials and functional nano-devices. Finally, the new structure and properties obtained by the precise engineering of chemical structures allow the modulation and control of morphology and the efficient use of noncovalent forces (and structure directing interactions) with the introduction of chirality, signal processing and recognition processes.

In this review we highlight the recent development of the self-assembly approaches with a focus on the main properties and recent applications. We present an organized overview, by analyzing the main parameters that sensitively influence the design of organic nanostructured systems, while putting into evidence challenges, limitations and emerging approaches in the various fields of nanotechology and biotechnology.



The nanotechnology self-assembly processes are based on the employment of cooperative interactions between basic units (called building blocks) and allow a suitable control of the formation processes by which multicomponent systems evolve towards novel equilibrium states through a spontaneous organization process. These cooperative interactions are established within an initial configuration of (disordered) building blocks. The combination of cooperative (non-covalent) forces with the multi-functionality of building blocks provides an excellent strategy for the preparation of novel, advanced nanomaterials. The various types of self-assembly processes of nanoscience have some common features that allow for the adoption of a conceptual scheme based on the following three stages.

3.3.2. Naturally Self-Assembled Inorganic-Organic (IO) Hybrid Systems and Applications

Inorganic-organic (IO) hybrid nanostructures have recently emerged as highly-promising systems for applications as optoelectronic devices, opening up a new dimension to nanotechnology, as unique replacement to their inorganic and organic counterparts. These hybrid systems have great advantage to combine distinct properties of inorganic and organic components within a single-molecular material. The art of combining dissimilar components to yield improved materials is not actually new: ancient building construction material, adobe, was made from a mixture of clay (inorganic) and straw (organic). Another classical example is *"blue Maya color"* developed in around 900 A.D., is an IO-hybrid composite. In fact the *Maya blue* is an inorganic-organic hybrid composed of *palygorskite* clay and organic indigo dye $C_{16}H_{10}N_2O_2$. The most characteristic beauty is its unusual stability; even after centuries of exposure to heat, humidity, and extreme atmospheric conditions, the color hardly faded.

Among various IO-hybrids, one of the most interesting and well-studied materials is a *perovskite* type hybrid. These self-organized materials are derived from the general structure form of AMX₃ where A is an organic moiety, M is a divalent metal (such as Pb^{2+} , Sn^{2+} , Ge^{2+} , Cu²⁺, Ni²⁺, Mn²⁺, Fe²⁺, Co²⁺, and Eu²⁺), and X is a halide (such as I, Br, and Cl). This simple 3D structure AMX₃ consists of corner-sharing MX_6 octahedra extended in three dimensions, where the "A" cations are located in the larger 12-fold coordinated voids between the octahedra. These self-assembling inorganic-organic perovskites adopt an alternating framework of semiconducting inorganic sheets and organic layers. The increasing interest is because of the ability to derive low-dimensional crystals, which show unique crystal structure and physical and optical properties, from parent 3D networks of AMX₃ from simple and effective natural self-assembly. These materials involve different types of interactions allowing the assembly of complex and highly-ordered structures with various bonding schemes. The chemical bonding involved in these IO-hybrid assembled systems are generally described as(i)covalent/ionic bonding within the inorganic network which favors the formation of sheets of corner-sharing metal halide octahedra,(ii)hydrogen/ionic bonding between the organic cations and the halogens in the inorganic sheets,(iii)various weak interactions like Van der Waals interactions between the organic R-groups. Many structural, electrical, thermochromic, and magnetic studies were carried out from almost a decade, to explore the advantages of IO-

hybrids over organic and inorganic counterparts [44–46], These hybrids have an advantage of structural flexibility to choose suitable organic spacers (usually monofunctional or difunctional amines). The crystallographic orientation and the thickness of the perovskite sheets can be tailored as per the choice of appropriate organic cations. In other words, inorganic units can be self-organized into low-dimensional crystals of zero-(0D), one-(1D) and two-(2D) dimensional networks. In 0D networks, MX₆ octahedra are isolated and are surrounded with the organic spacers. In 1D networks, metal halides (MX₆ octahedra) are extended as a chain along one direction with corner/edge/face shared to form 1D hybrid. Similarly, inorganic networks. In 2D, inorganic layers are stacked alternatively with orientation along a specific crystal direction.



Figure 3.3.2.1. Schematic of MX₆ octahedra and the organic moiety of the basic AMX₃ perovskite unit cell and three-dimensional network formed by AMX₃ perovskite unit cells.



Figure 3.3.2.2. Schematic of 2D, 1D, and 0D IO-hybrid derived from parent AMX₃ type 3D IO-hybrid.

During synthesis, the organic moieties, apart from controlling the dimensionality, can also alter the crystallographic orientation of the parent network. For example, based on the organic moiety interaction with metal halide network, the resultant network can deviate from oriented 2D network to 1D dimensional oriented hybrid structures also. Under special circumstances, based on organic moiety conformation, the metal halides may self-assemble into either edge sharing or face sharing of metal halide octahedra, forming various low dimensional inorganic halide networks of different orientations. Based on such different networks, these hybrids show marked variation in their structural and optical features.

Several studies were carried out in the recent past to prove the potential ability of IO-hybrids in photonic applications: electro-absorption and electroluminescence, photoconductive devices, optical nonlinear devices, stark effect magneto- absorption, and spontaneous magnetization. Apart from linear optical studies, high-optical excitation effects such as ultrafast dynamics of excitons, observation of higher-order excitons (biexciton and triexciton), and even an attempt of biexciton lasing were also reported. Photonic devices such as thin film transistors (TFTs), inorganic-organic field-effect transistors (IOFETs), inorganic-organic light emitting diodes (IOLEDs), and scintillators were also been successfully demonstrated .

<u>CHAPTER 4</u> <u>SPINTRONICS</u>

Introduction, Overview, History & Background, Generation of Spin Polarization Theories of spin Injection, spin relaxation and spin dephasing, Spintronic devices and applications, spin filters, spin diodes, spin transistors.

4.1. Introduction:

In a narrow sense Spintronics refers to spin electronics, the phenomena of spin-polarized transport in metals and semiconductors. The goal of this applied Spintronics is to find effective ways of controlling electronic properties, such as the current or accumulated charge, by spin or magnetic field, as well as of controlling spin or magnetic properties by electric currents or gate voltages. The ultimate goal is to make practical device schemes that would enhance functionalities of the current charge based electronics. An example is a spin field effect transistor, which would change its logic state from ON to OFF by flipping the orientation of a magnetic field. In a broad sense Spintronics is a study of spin phenomena in solids, in particular metals and semiconductors and semiconductor hetero-structures. Such studies characterize electrical, optical, and magnetic properties of solids due to the presence of equilibrium and non-equilibrium spin populations, as well as spin dynamics.

4.2. Overview:

The spin-electronics also called Spintronics, where the spin of an electron is controlled by an external magnetic field and polarize the electrons. These polarized electrons are used to control the electric current. The goal of Spintronics is to develop a semiconductor that can manipulate the magnetism of an electron. Once we add the spin degree of freedom to electronics, it will provide significant versatility and functionality to future electronic products. Magnetic spin properties of electrons are used in many applications such as magnetic memory, magnetic recording (read, write heads), etc.

The realization of semiconductors that are ferromagnetic above room temperature will potentially lead to a new generation of Spintronic devices with revolutionary electrical and optical properties. The field of Spintronics was born in the late 1980s with the discovery of the "giant magnetoresistance effect". The giant magnetoresistance (GMR) effect occurs when a magnetic field is used to align the spin of electrons in the material, inducing a large change in the resistance of a material. A new generation of miniature electronic devices like computer

chips, light-emitting devices for displays, and sensors to detect radiation, air pollutants, light and magnetic fields are possible with the new generation of Spintronic materials.

In electronic devices, information is stored and transmitted by the flow of electricity in the form of negatively charged subatomic particles called electrons. The zeroes and ones of computer binary code are represented by the presence or absence of electrons within a semiconductor or other material. In Spintronics, information is stored and transmitted using another property of electrons called spin. Spin is the intrinsic angular momentum of an electron, each electron acts like a tiny bar magnet, like a compass needle, that points either up or down to represent the spin of an electron. Electrons moving through a nonmagnetic material normally have random spins, so the net effect is zero. External magnetic fields can be applied so that the spins are aligned (all up or all down), allowing a new way to store binary data in the form of one's (all spins up) and zeroes (all spins down). The effect was first discovered in a device made of multiple layers of electrically conducting materials: alternating magnetic field was applied to the device, the spin of its electrons went from all up to all down, changing its resistance so that the device acted like a valve to increase or decrease the flow of electrical current, called Spin Valves.





Spins can arrange themselves in a variety of ways that are important for Spintronics devices. They can be completely random, with their spins pointing in every possible direction and located throughout a material in no particular order (upper left). Or these randomly located

spins can all point in the same direction, called spin alignment (upper right). In solid state materials, the spins might be located in an orderly fashion on a crystal lattice (lower left) forming a nonmagnetic material. Or the spins may be on a lattice and be aligned as in a magnetic material (lower right).

The first scheme of Spintronics device based on the metal oxide semiconductor technology was the first field effect spin transistor proposed in 1989 by Suprio Datta and Biswajit Das of Purdue University. In their device, a structure made from indium–aluminum-arsenide and Indiumgallium- arsenide provides a channel for two dimensional electron transport between two ferromagnetic electrodes. One electrode acts as an emitter and the other as a collector. The emitter emits electrons with their spins oriented along the direction of electrodes magnetization, while the collector acts as a spin filter and accepts electrons with the same spin only. In the absence of any change to the spins during transport, every emitted electron enters the collector.This device is explained in further detail under the topic of spin transistors.



Figure 4.2.2

Datta-Das spin transistor was the first Spintronic device to be proposed for fabrication in a metal-oxide- semiconductor geometry familiar in conventional microelectronics. An electrode made of a ferromagnetic material (purple) emits spin-aligned electrons (red spheres), which pass through a narrow channel (blue) controlled by the gate electrode (gold) and are collected

by another ferromagnetic electrode (top). With the gate voltage off, the aligned spins pass through the channel and are collected at the other side (middle). With the gate voltage on, the field produces magnetic interaction that causes the spins to precess, like spinning tops in a gravity field. If the spins are not aligned with the direction of magnetization of the collector, no current can pass. In this way, the emitter- collector current is modulated by the gate electrode. As yet, no convincingly successful application of this proposal has been demonstrated.

3. History and Background:

In the information era, a new promising science has been strongly addressed called Spintronics, the contracted form of spin based electronics. The 2007 Nobel Prize for physics, with whom A. Fert and P. A. Grunberg have been awarded, is another clear signal that the importance of Spintronics for society is worldwide understood. In the far 1933 the physicist F. Mott published his innovative concept of spin dependent conduction. Only forty years later experimental evidence of current spin polarisation was reported by P. Tedrow and R. Meservey, carrying out experiments of tunneling between ferromagnetic metals and superconductors. In 1975 experiments on a Fe/GeO/Co junction led to the discovery of tunneling magnetoresistance (TMR) by M. Julliere, only verified in 1995 by T. Miyazaki and N. Tezuka and J. S. Moodera. In1988 experiments on layered thin films of FMs alternated to a non-magnetic metal (NM) led to the simultaneous and independent discovery of the giant magnetoresistance (GMR) by A. Fert and P. A. Grunberg. Nowadays the principal application of Spintronics devices is the magnetic data storage with an information density growth rate faster than the corresponding Moore law.

Spintronics dates to the 1960s and was discovered by a group at IBM headed by Leo Esaki, a Japanese physicist who would later go on to win a share of the Nobel Prize I 1973 for discovering the phenomenon of electronic tunneling. Esaki and his team conducted a study which showed an antiferromagnetic barrier of EuSe sandwiched between metal electrodes exhibits a large magnetoresistance.

Subsequent advances of semiconductor thin film deposition techniques such as molecular beam epitaxy led to the development of semiconductor quantum structures, which prompted studies of magnetic multilayers. Ensuing studies of magnetic multilayers resulted in the discovery of giant magne- toresistance (GMR) in 1988. This effect was used to make magnetic sensors,

which boosted the areal density of information stored on hard disk drives and led to the 2007. Nobel Prize in Physics awarded to Albert Fert and Peter Grunberg. Since then rapid progress has continued to enhance both the role and the potential of Spintronics.

4.3. Generation of Spin Polarization Theories of:-

4.3.1 Spin Injection:

The present microelectronics technology rests on charge-based device concepts, which are realized by means of semiconductors, mostly silicon. In addition, semiconductors also strongly interact with light and thus provide optical functionalities (optoelectronics). Combining independent spin and charge control in a single device promises a wide range of new phenomena and applications. To successfully incorporate spins into existing semiconductor technology, however, one has to resolve several issues such as the efficient injection, transport, control and manipulation, and detection of spin-polarized currents. Despite recent successes, the all-electrical spin injection and detection still remains the holy grail of spin electronics.



Figure 4.3.1.1

Rotation of the spin polarization in a field-effect type device due to the Rashba effect.

Realizing new functionalities in spintronic devices requires the spin control and manipulation of the charge carriers passing through the semiconductor. This manipulation can be achieved, for example, by the Rashba effect. This effect is due to a spin-orbit like interaction, which is generated by an electric field in a system with broken inversion symmetry Fig. It rotates the

spin quantization axis of the charge carriers traversing the electric field. A simple device following the field-effect transistor (FET) scheme was proposed by Datta and Das. This proposal has stimulated a broad research activity, leading to a variety of competing device concepts, for example, based on bipolar circuit schemes.

Electrons which can be labelled as spin up and spin down. The total number of electrons is assumed to be preserved. If the electron densities are $n\uparrow$ and $n\downarrow$ for the spin up and spin down states, the total particle density is, $n = n\downarrow + n\downarrow$. While the spin density is, $s = n\downarrow -n\downarrow$.

Let probability of w that a spin is flipped in the time of τ , so that the spin flip rate is w/ τ . We will assume that w <<1. The actual spin flip probability during the relaxation time τ is typically 10-3 to 10-6 ; so that electrons need to experience thousands scatterings before spin flips. Therefore the density spin polarization as well as the current spin polarization is given by, $Pn = n\uparrow -n\downarrow/n = s/$, $Pj = j\uparrow -j\downarrow/nj = js/j$. This will be useful in our model of spin injection.

4.3.2. Spin Injection Standard Model



Figure 1: Scheme of our spin-injection geometry.

The standard model of spin injection has its roots in the original proposal of Aronov (1976). The thermodynamics of spin injection has been developed by Johnson and Silsbee, who also formulated a Boltzmann-like transport model for spin transport across ferromagnet non-magnet (F/N) interfaces. Our goal is to find the current spin polarization, Pj(0) in the normal conductor. We will assume that the lengths of the ferromagnet and the nonmagnetic regions are greater than the corresponding spin diffusion lengths. The spin injection scheme is illustrated in Fig. 1. The ferromagnetic conductor (F) forms a junction with the nonmagnetic conductor (N). The contact region (C) is assumed to be infinitely narrow, forming the discontinuity at x = 0. It is assumed that the physical widths of the conductors are greater than the corresponding spin

diffusion lengths. We assume that at the far ends of the junction, the non-equilibrium spinvanishes. We now look at the three regions separately. The ferromagnet, contact, and normal conductor regions are identified. The electric current splits into the spin up and spin down components, each passing through the corresponding spin-resolved resistors.



Figure 4.3.2.1. The equivalent circuit of the standard model of spin injection in *F/N* junctions.

i. Ferromagnet :

Current spin polarization at x = 0 in the ferromagnet is, $pjF \ 0 = p\sigma F + (4 \ 1/ j)(\sigma f \uparrow \sigma f \downarrow / \sigma f)$, Where effective resistance of the ferromagnet, $RF = \sigma f / 4\sigma f \uparrow \sigma f \downarrow (LsF)$. (6) This is not the electrical resistance of the region, only an effective resistance that appears in the spinpolarized transport and is roughly equal to the actual resistance of the region of size LsF.

ii. Nonmagnetic Conductor :

Since in the nonmagnetic conductor $P\sigma = 0$, and $\sigma N \downarrow = \sigma N \uparrow$, the current spin polarization in the nonmagnetic conductor then becomes, $pjN(0) = -(1/j)(1/\sigma N)$, where, effective resistance of the nonmagnetic region, $RF = LsF/\sigma N$.

iii. Contact:

The conductance spin polarization is, $P\sum (0) = \sum \uparrow -\sum \downarrow /\sum$ Where, $\sum = \sum \uparrow +\sum \downarrow$ is the conductance, while spin conductance is $\sum = \sum \uparrow -\sum \downarrow$ and the effective resistance of the contact is, $Rc = \sum /4\sum \downarrow \sum \uparrow$, Current spin polarization, at the contact given by, $pjc (0) = P\sum + (1/j)(4\sum \downarrow \sum \uparrow / \sum)$.Let assume spin current continuity at the contact: Pj=Pjf=Pjn=Pjc.

The above equalities are justified if spin-flip scattering can be neglected in the contact. For contacts with paramagnetic impurities, we would need to take into

account contact spin relaxation which would lead to spin current discontinuity. This assumption of the low rate of spin flip scattering at the interface should also be carefully reconsidered when analyzing room temperature spin injection experiments. Using the spin current continuity equations, we can solve our algebraic system and readily obtain for the spin injection efficiency, $pj = RF \ p\sigma F + RcP\Sigma/(RF+Rc+RN)$.

The standard model of spin injection can be summarized by the equivalent electrical circuit shown in Fig. 2. Spin up and spin down electrons form parallel channels for electric current. Each region of the junction is characterized by its own effective resistance, determined by the spin diffusion lengths in the bulk regions, or by the spin-dependent conductance in the contact.

4.3.3. Spin relaxation:

Hanle spin precession: by applying an out-of-plane magnetic field, the magnetic field induced spin precession at a Larmor frequency.



$$R_{NL} \propto \pm \int_0^\infty \frac{1}{\sqrt{4\pi Dt}} \exp\left[-\frac{L^2}{4Dt}\right] \cos(\omega_L t) \exp(-t/\tau_s) dt$$

diffusion constant

spin life time

$$D = 2.5 \times 10^{-2} \text{ m}^2 \text{s}^{-1}$$

$$\tau_s = 84 \text{ ps}$$

$$\lambda_G = \sqrt{D\tau_s} = 1.5 \text{ }\mu\text{m}$$

Hanle curve, depends on

- Spin precession
- Spin diffusion
- Spin relaxation



The ferromagnetic contacts can theoretically introduce spin relaxation through a number of mechanisms:

 \succ Roughness of the Co film could produce inhomogeneous local magnetic fields that vary with the morphology, which will generate spin relaxation through inhomogeneous spin precession about the spatially-varying local fields.

 \succ Interfacial spin scattering: possible because of the direct contact between the FM and graphene for the transparent and pinhole contacts.

> Hanle measurement: with metallic Co in contact with graphene, the spins diffuse from the graphene to the Co with a characteristic escape time τ esc.

➤ Due to the conductance mismatch between Co and graphene, the escape time can become comparable to or less than the actual spin lifetime!

$$\tau_s^{-1} = \tau_{sf}^{-1} + \tau_{esc}^{-1}$$

 \succ More accurate measurement of the true spin life- time in graphene is made possible by the insertion of good tunnel barriers to reduce the out-diffusion of spins.



4.3.4. Spin Dephasing

First, we study the spin dephasing in the samples as a function of experimental parameters. To suppress the effects of spin diffusion out of the pump spot in these measurements, the experiments are performed using the larger spot size of 40 μ m, with full overlap of pump and

probe beams. Figure 1 (a) and (b) show typical Hanle- MOKE traces measured on sample B and C for different excitation densities of the pump laser. (color online) (a) and (b) Hanle-MOKE traces measured for different excitation densities on sample B and C at a nominal temperature of 4 K. (c) Spin lifetime τ_s (filled circles) and MOKE signal amplitude at zero magnetic field (filled stars) for sample B as a function of excitation density. The solid lines are fits to Eq. 8 (spin lifetime) and Eq. 4 (signal amplitude) with Io = 0.052 W/cm2.(d) Spin lifetime τ_s for sample C as a function of excitation density.



Figure. 4.3.4.1

While in sample B, it is clearly visible that the linewidth of the Hanle curve increases significantly with the excitation density, only a small narrowing of the Hanle curve is observed in sample C for an even larger range of excitation densities. The spin lifetimes for both samples, extracted from the linewidth of the Hanle curves, are shown in Figs. 1(c) and (d). Here, sample B shows a behaviour already observed previously in sample A: the spin lifetime excitation density, it reaches values of more than 100 ns. The solid black line in Fig. 1 (c) corresponds to a fit to the dependence of the spin lifetime using Eq. (8). Additionally, the signal amplitude, which corresponds to S_z (0) in Eq. (5), saturates at low excitation densities, the solid red line corresponds to a fit to the signal amplitude data using Eq. (4). For both fit curves, the same saturation amplitude $I_0 = 0.052 \text{ W/cm}^2$ was used. This radiation intensity corresponds to
the photo induced hole density $\sim 4 \times 10^{\circ}$ cm² for a QW absorbance $\eta \sim 2$ percent, which was determined experimentally for similar QW samples, and a hole lifetime of 1 ns. The observed behaviour may be explained as follows. The quantum wells in samples A and B are macroscopically symmetric and the BAP mechanism of spin dephasing plays an important role, which leads to a decrease of the spin lifetime τ_s with increasing the excitation density, see Eq. (8). The samples differ mainly in the maximum value of τ_s that can be reached in the limit of low excitation density, and in the excitation density for which saturation of the signal amplitude occurs. By contrast, in sample C, the spin lifetime increases with the pump excitation density. From this, we infer that the dominant dephasing mechanism for this sample, under the experimental conditions in this measurement series, is the Dyakonov-Perel mechanism.



Figure 4.3.4.1 (a) Spin lifetime as a function of sample temperature for sample A. (b) Spin lifetime as a function of sample temperature for sample C.

In both measurement series, an excitation density of 0.27 Wcm^2 was used.

In this regime, the optically generated holes serve as scattering centers, reducing the momentum relaxation time, and thereby increasing the spin lifetime. Additionally, the increased excitation density leads to local heating, which aids the ionization of remote dopants. We will show below that the dominant dephasing mechanism in sample C changes with temperature.

We now look at the temperature dependence of the spin lifetime, which is given in Fig. 2 for samples A and C. While for sample A, the spin lifetime monotonously decreases with

temperature, sample C shows a pronounced maximum of the spin lifetime at about 20 K. Such a drastic change of the spin lifetime with temperature was recently observed by resonant spin amplification in a similar sample. The reason for this behaviour lies in the complex growth structure of our samples: while the sample design is optimized to yield a highly symmetrical modulation doping, leading to a vanishing Rashba spin-orbit field, we observe that in some wafers, at low temperatures, the remote donors are not fully ionized. This leads to a reduced carrier concentration, but more importantly, it also gives an asymmetric ionization of the dopant layers below and above the quantum well, resulting in a pronounced Rashba field.

This leads to spin precession also for the out-of-plane spin component and makes the DP mechanism dominant. With increasing temperature, the remote dopant layers become fully ionized, increasing the carrier concentration, and also significantly reducing the Rashba field. Now, the DP mechanism is suppressed for the out-of-plane spin orientation. The decrease of the spin lifetime with temperature, which is observed in sample A for the whole temperature range investigated, and in sample C for temperatures above 18 K, where ionization of remote dopants is complete, stems from the BAP mechanism. This mechanism becomes more efficient with increasing temperature because of reduced Pauli blocking and increased electron-hole scattering rates.



Figure.4.3.4.1 (a) Photoluminescence spectra of sample A measured for different values of above-barrier illumination power. (b) Spin lifetime as a function of above-barrier

Illumination power for sample A at a sample temperature of 18 K. An excitation density of $^{-2}$ 0.27 Wcm⁻² was used for the pump laser. (c) and (d) Spin lifetime as a function of above barrier illumination power for sample C at a sample temperature of 4 K (c) and 50 K (d). In both measurement series, an excitation density of 0.54 Wcm⁻² was used for the pump laser.

Next, we investigate the effects of above-barrier illumination on the spin dynamics. The generation of electron-hole-pairs in the barriers leads to a redistribution of the donor electrons in a two-step process: while optically generated holes in the valence band can easily move from the barrier layers into the QW, there is a potential barrier for electrons in the conduction band which is formed by the modulation doping. The holes may then recombine with electrons in the QW, effectively transferring electrons from the 2DES back to the dopant layers and reducing the carrier density. This process is also known as optical gating and may even lead to inversion of the carrier type. We can directly observe this effect in PL measurements, as shown in Fig. 3(a) for sample A. If no above-barrier illumination is used, the PL from the 2DES shows a typical, shark-fin like shape. The width of the PL peak corresponds to transitions in the QW from the lowest-lying energy states in the conduction band up to the Fermi energy of the 2DES, therefore, the PL width can be used to monitor the carrier density in the 2DES. By increasing the power of the above-barrier illumination, the width of the PL is reduced significantly.

To study the effect of optical gating on the spin dynamics, Hanle measurements were performed for a fixed pump intensity, with varying above-barrier illumination power, for samples A and C. The spin lifetimes extracted from the Hanle curves are plotted in Figs. 3(b)-(d). In sample A, where the BAP mechanism plays an important role, we see a decrease of the spin lifetime with the above-barrier illumination. Here, the reduction of the carrier density in the 2DES reduces Coulomb screening of the photogenerated holes, increasing the electron-hole scattering rate. Therefore, the BAP mechanism becomes more effective, leading to a reduction of the spin life-time. By contrast, sample C shows a different behaviour at low temperatures, evidenced by Fig. 3(c): here, the spin lifetime increases with the above-barrier illumination power. This finding supports the interpretation that, at low temperatures, the spin dephasing in sample C is dominated by the DP mechanism. Therefore, the reduction of the carrier density (and the Fermi energy, accordingly) leads to a slowdown of the spin dephasing due to a reduction of the spin orbit effective magnetic field as well as a decrease of the scattering time t*p. The first effect is caused by the fact that, in QWs, the effective field is proportional to the electron wave vector.

The latter results from a reduction of the Coulomb screening and decrease of the electronelectron scattering time $\tau_{\rho\rho}$, cf. Eq. (10).

Additionally, the above-barrier illumination of sample C may reduce the asymmetry in the ionization of the remote dopants at low temperatures, leading to a reduction of the Rashba spinorbit field. This effect was observed recently in RSA measurements on a similar sample. We note that, at higher temperatures, the dependence of the spin lifetime on the above-barrier illumination changes, as Fig. 3(d) shows. Here, we see a similar behaviour as in sample A, indicating that the BAP mechanism becomes dominant in sample C at higher temperatures due to vanishing of the regular Rashba field in the structure with fully ionized dopants

4.4. Spintronic devices and Applications:

Recording devices, such as computer hard disks, already employ the unique properties of the materials. Data are recorded and stored any tiny areas of magnetized iron or chromium oxides. A "read head" can read this information by detecting minute changes in the magnetic field as the disk rotates underneath it. This induces changes in the magnetoresistance. Recent discovery of Tunneling Magnetoresistance (TMR) has lead to the idea of magnetic tunnel junction that has been utilized for the MRAM (Magnetic Random Access Memory). Here, one has two magnetic layer separated by an insulating metal oxide layer. Electrons are able to tunnel from one layer to other only when magnetizations of the layers than in the standers GMR devices, known as "spin valves". Spintronics devices, combining the advantages of magnetic materials and semiconductors, are expected to be fast, non-volatile and consume less power. They are smaller than s 100 nanometers in size, more versatile and more robust than the conventional ones making up silicon chips and circuit elements The potential market is expected to be worth hundreds.

(i) Giant magneto resistance (GMR):-

Magnetism is an intrinsic physical property associated with the spins of electrons in a material. Magnetism is already exploited in recording devices Such as computer hard disks. Data are recorded and stored as tiny areas of magnetized iron or chromium oxide. To access the information, a read head detects the minute changes in magnetic field as the disk spins underneath it. Spintronics burst on the scene in 1988 when French and German physicists discovered a much more powerful effect called "giant magneto resistance" (GMR). It results

from subtle electron-spin effects in ultra-thin "multilayer" of magnetic materials, which cause huge changes in their electrical resistance when a magnetic field is applied. The basic GMR device consists of a three-layer sandwich of a magnetic metal such as cobalt with a nonmagnetic metal filling such as silver. A current passes through the layers consisting of spinup and spin-down electrons. Those oriented in the same direction as the electron spins in a magnetic layer pass through quite easily while those oriented in the opposite direction are scattered. If the orientation of one of the magnetic layers can easily be changed by the presence of a magnetic field then the device will act as a filter, or "spin valve", letting through more electrons when the spin orientations in the two layers are the same and fewer when orientations are oppositely aligned. The electrical resistance of the device can therefore be changed dramatically. GMR is 200 times stronger than ordinary magneto resistance. IBM soon realized that read heads incorporating GMR materials would be able to sense much smaller magnetic fields, allowing the storage capacity of a hard disk to increase from 1 to 20 gigabits.

(ii) Magnetic random access memory (MRAM):-

The magnetic version of a random access memory (RAM) used in the computer is -,,MRAM". The advantage of magnetic random access memory (MRAM) is that it is ,,non-volatile" - information isn't lost when the system is switched off.

4.4.1 Spintronics Applications

Spintronics is an emerging science yet a very trendy one. It has become popular in a very short span of time and is used in many applications such as:

- It is widely used in mass storage devices due to its capacity for compressing a massive amount of data into a very small area.
- It has become a very effective tool to detect cancer in medical science.
- Spintronic devices are an ancillary to digital electronics. Hard drives being the foremost example of the same.
- Semiconductor spintronics, when integrated with conventional technology, can be used as spin valves and spin polarizers.
- Spin transistors are known to run on electron spin as incorporating a two-state quantum system.
- Electron spin resonance (ESR) spectroscopy that is applied in Chemistry and Physics.

- This technology is applied in chemistry in the form of Nuclear magnetic resonance spectroscopy.
- Spin based computers apply modern nanofabrication techniques where electron motion gets quantized in almost all the directions while conducting electrons are limited to nanometer distance.
- Electron transport in DNA is one of the remarkable research that is being done in this field.

4.5. Spin Filters:

The search for an applicable spin-filtering layer has successfully produced very large TMR values using a large Zeeman splitting in the magnetic semiconductors EuO and EuS. Spin filtering has also been reported using europium and chromium calcogenides rock-salt, *e.g.*, EuO and EuSe, and the spinels, *e.g.*, CdCr₂S₄ and CdCr₂Se₄, For example, EuS shows a TMR ratio of up to 110% at 2 K, which disappears above $T_C \sim 16.8$ K. Larger TMR ratios has been reported using coherent tunnelling with a MgO barrier as detailed in tunnelling magnetoresistance, of which lattice matching can be precisely controlled by Al doping.

4.6. Spin Diodes:

Since DMS show a large Zeeman splitting and ferromagnetism, DMS can be used as a spin aligner to inject spin-polarised carriers, *i.e.*, spin-polarised electrons for *n*-SC or holes for *p*-SC. The spin polarisation of the injected carriers is detected optically through circularly polarised EL from the SC (*e.g.*, GaAs), which are called spin LEDs. With FM *p*-GaMnAs as a spin aligner, spin-polarised hole injection has been reported at low temperature. At forward bias, spin-polarised holes from the *p*-GaMnAs as well as unpolarised electrons from the *n*-GaAs layer are injected into the InGaAs QW, so that the recombination of the spin-polarised holes can create circularly polarised EL emission from the QW. However, as the spin relaxation time for the holes is much shorter than that for the electrons, the spin polarisation signal through the recombination process in the GaAs is very small (about $\pm 1\%$). On the other hand, using paramagnetic *n*-BeMnZnSe with large Zeeman splitting as a spin aligner, highly efficient electron spin injection has been achieved with the applied field of ~ 30 kOe (spin polarisation in EL ~ 90%). This is because the spin diffusion length of the electrons has been reported to be above 100 µm in the GaAs. Similar results have been obtained using CdMnTe, ZnMnSe, ZnSe and MnGe but only at low temperatures (typically *T* < 80 K). Since RT ferromagnetism

has been predicted in several DMS compounds but not yet observed, spin injection at RT with a DMS may be achievable in the near future.

GMR devices, known as "spin valves". Spintronic

4.7. Spin Transistors:



Figure 4.7.1 For the cases where there is high concentrations of carriers (i.e. (Ga, Mn)As where Mn ions behave as acceptors and provide magnetic moment)

The basic idea of spin transistor, as proposed by Suprio Datt and Biswajit Das, is to control the spin the spin orientation by applying a gate voltage, as shown in fig.1. A spin –FET, as depicted below, consists of ferromagnetic electrodes and semiconductor channels that contain a layer of electrons and a gate electrode attached to the semiconductor. The source and drain electrodes are ferromagnetic (FM) metals. The spin-polarized electrons are injected from the FM source electrode (FMs), and after entering the semiconductor channels they begin to rotate. The rotation can be controlled by an applied electric field through the gate electrode. If the spin orientation of the electron channels is aligned to FM drain (FMd) electrode, electrons are able to flow into the FM drain electrode. However, if the spin orientation is flipped in the electron layer electrons cannot enter the drain electrode. In this way, with the gate electrode the orientation of the electron spin can be controlled head's electrical resistance, also known as "read head" can read this information by detecting creases with temperature, sample C shows a pronounced creases with increasing excitation density. For the lowedensity, it reaches values of more than 100 ns.

CHAPTER 5

MEMORY DEVICES AND SENSORS

Nano ferroelectrics, ferroelectric random access memory (Fe-RAM) circuit design, ferroelectric thin film properties and integration, calorimetric sensors, electrochemical cells, surface and bulk acoustic devices, gas sensitive FETs.

5.1. Nano ferroelectronics

Ferroelectric RAM (FeRAM, F-RAM or FRAM) is a random-access memory similar in construction to DRAM but using a ferroelectric layer instead of a dielectric layer to achieve non-volatility. FeRAM is one of a growing number of alternative non-volatile random-access memory technologies that offer the same functionality as flash memory. The F-RAM chip contains a thin ferroelectric film of lead zirconate titanate, commonly referred to as PZT. The atoms in the PZT change polarity in an electric field, thereby producing a power efficient binary switch. However, the most important aspect of the PZT is that it is not affected by power disruption or magnetic interference, making F-RAM a reliable nonvolatile memory. FeRAM's advantages over Flash include: lower power usage, faster write performance and a much greater maximum read/write endurance (about 1010 to 1014 cycles). FeRAMs have data retention times of more than 10 years at +85 °C (up to many decades at lower temperatures). Market disadvantages of FeRAM are much lower storage densities than flash devices, storage capacity limitations and higher cost. Like DRAM, FeRAM's read process is destructive, necessitating a write-after-read architecture.

5.2. F-RAM USAGE

Currently ferroelectric RAM is not as widely used as many of the more established technologies including DRAM and Flash. These technologies have become well entrenched and their use is widespread.

As developers often tend to rely on trusted technologies that are guaranteed to deliver the performance they require, they are often reluctant to use technologies like FRAM that are not guaranteed to deliver. Also issues like memory density that limit the size of memory available have caused them not to be so widely used.

However FRAM technology is now being embedded into chips using CMOS technology to enable MCUs to have their own FRAM memories. This requires fewer stages than the number

required for incorporating Flash memory onto MCU chips, thereby providing some significant cost reductions

5.3. Circuit diagram



Figure. 5.1 Circuit Diagram

5.3.1. Ferroelectric Thin Film

Ferroelectric thin films deposited by a sol-gel process show multidomains and/or grained structure, which is similar to bulk ceramics. Their ferroelectric properties are also similar to those of bulk ceramics. The strain in sol-gel thin films is relaxed due to the presence of a grain and/or domain boundary. Sputtered ferroelectric thin films also show this behavior if the films include the domain and/or grain-structures.

If the thin films include strain, the strain modifies the ferroelectric properties. A typical example is the shift of Curie temperature. The two-dimensional compressive strain induced by the mismatch in the lattice parameter or the thermal expansion coefficient between the film and the substrate will elevate the Curie temperature.

Continuous single-crystal thin films show a diffused temperature anomaly in their dielectric properties. The diffused temperature anomaly is passively observed in thin epitaxial ferroelectric films and in epitaxial films on vicinal substrates. Typical examples are shown in Figure. Thin ferroelectric films and epitaxial films on vicinal substrates are coherent and tightly bonded to substrate surfaces. This results in a diffused temperature anomaly. The diffused temperature anomaly is also observed in the lattice parameter.

| Function | Devices: Materials | Miscellaneous |
|----------------------|--|--|
| Ferroelectricity | FEDRAM ^a : PZT, PLZT | Nonvolatile |
| | FESRAM ^b : BPZT, SBT | High Ps, Pr |
| | FEMFET ^c : BMF | PZT>20 μC/cm ² |
| High permittivity | Capacitor for high count DRAM: SBT, ST, PZT, PLT | High permittivity |
| | | PZT:500-2000 |
| Pyroelectricity | IR detector: PT, PLT | Sensitive/low noise |
| | | PLT: <i>γ</i> =5.5×10 ⁻⁴ C/m ² K |
| Piezoelectricity | BAW/SAW: ZnO, AlN | High coupling for SAW |
| | Filter: PZT,PLT | ZnO/sapphire: K ² =5% |
| | Resonator | High-temperature stability |
| | Oscillator | ZnO/glass: TCD ^e =0 |
| | Delay line | |
| Electrostriction | Actuator: PLT, PZT | High sensitivity |
| | MEMS ^d : ZnO | |
| Acousto-optics | Integrated optics: ZnO, LN | Low working voltage |
| | Channel switch: PLT | High-speed operation |
| | Modulator: PLZT | |
| Electro-optics | Integrated optics: LT, LN | Pockels effect (linear EO) |
| | Coupler: BTO | LN, LT, BTO, PLZT |
| | Channel switch: PLT | Kerr effect (quadratic EO) |
| | Modulator: PLZT | PLT, PLZT |
| | Optical shutter | <i>R</i> =1×10 ⁻¹⁶ m ² /V ² (6328 Å) |
| | EO disk memory | |

Table 7.1. Ferroelectric Thin Films and Devices

BPZT:BaTiO₃-PbZrO₃, SBT:SrBi₂Ta₂O₉, BST: (Ba,Sr)TiO₃, BTO:Bi₄Ti₃O₁₂, LN:LiNbO₃, BMF:BaMgF₄.

а

С

d

Ferroelectric dynamic random access memory. b

- Ferroelectric static random access memory.
- Ferroelectric memory field effect transistor.
- Micro-electromechanical system.
- e Temperature coefficient of delay.

5.4. Calorimetric sensor



A simple colorimetric sensor array technique was developed for the detection of various different nanoparticles (NPs) in aqueous solutions. The sensor array consists of five different cross-reactive chemoresponsive dyes, whose visible absorbances change in response to their interactions with NPs. Although no single dye is specific for any one NP, the pattern of color changes for all dyes provides a unique molecular fingerprint for each type of NP studied. Based on the responses of various dyes, a semiquantitative determination of concentration of each type of NP could also be accomplished with excellent sensitivity (<100 ng/mL). A variety of chemically distinct NPs were unambiguously identified using standard chemometric approaches, including gold nanospheres (2 through 40 nm diameter), gold nanorods (2.4 and 3.5 aspect ratios), and multifunctional carbon nanospheres without errors in 112 trials. This colorimetric approach may pave the way for a fast, reliable, and inexpensive method to detect noise pollution and to characterize the physicochemical properties of NPs.

Calorimetric sensors are based on measurement of the heat produced by the molecular recognition reaction and the amount of heat produced is correlated to the reactant concentration. The principle of the calorimetric sensors is the determination of the presence or concentration of chemical species by the measurement of the enthalpy change produced by any chemical reaction or physisorption process that releases or absorbs heat. We talk about exothermic reactions if heat is generated and endothermic reactions if it is absorbed.

What is a Calorimetric Sensors?

Calorimetric sensors have been described for enzyme reactions for detecting glucoses, urea, gases, etc. The thermal conductivity gas sensor has long been employed as a detector in gas chromatography (GC) and works on the basis of a heated W-Re wire filament to measure relatively high concentrations in gases.

Calorimetric sensors or chemoresistors can be classified in low-temperature chemoresistors and high-temperature chemoresistors.

Low-temperature chemoresistors consist of chemically sensitive layers applied over interdigitated electrodes on an insulating substrate. Examples of the chemically sensitive layers are: metal phthalocyanines, conducting polymers such as poly (pyrrol) and poly (aniline). These types of chemoresistors are used in the detection of ethanol, methanol and other organic volatile molecules.

High-temperature chemoresistors consist of micromachined semiconductor hotplates with a sensing film on a thermally insulated inorganic membrane. ZnO, InO, GaO, SnO are usually employed as sensitive materials. Gaseous electron donors (H) or electron acceptors (NOx) adsorb on metal oxides and form surface states, which can exchange electrons with the semiconductor.

Calorimetric Sensors Classification

Another way to classify the calorimetric sensors is taking into account the different ways of transducing heat variations:

Catalytic sensors or pellistors, which use a platinum coil used as heater and temperature sensors (resistance thermometer) and contain a catalyst to enhance a combustion process. The heated catalyst permits gas oxidation at reduced temperatures and at concentrations below the lower explosive limit. Some of the applications are: monitoring/detection of flammable gas hazards, CH_4 (methane), H_2 , C_3H_8 (propane), CO and organic volatiles.

Thermistor based sensors, these devices detect with high accuracy changes in the electrical resistance that result from temperature changes. If a linear relationship between resistance and temperature is assumed (i.e. a first-order approximation), the following expression results:

$\varDelta R = k \varDelta T$

Where ΔR is the change in resistance, ΔT , the change in temperature and *k* a first-order temperature coefficient of resistance. Thermistors can be classified in two types depending on the sign of *k*. If *k* is positive, the resistance increases with increasing temperature, and the device is called a positive temperature coefficient (PTC) thermistor. If *k* is negative, the resistance decreases with increasing temperature, and the device is called a negative temperature coefficient (NTC) thermistor. These sensors use composite oxides. Negative Temperature Coefficient (NTC) Thermistors use sintered metal oxides like titanium oxide and Positive Temperature Coefficient (PTC) Thermistors use Ba/Pb titanate.

Pyroelectric sensors, which are based on the phenomenon of pyroelectricity, the ability of certain materials to generate an electrical potential when they are heated or cooled (gallium nitride (GaN), cesium nitrate (CsNO₃), polyvinyl fluorides, derivatives of phenylpyrazine, cobalt phthalocyanine, Lithium tantalate (LiTaO₃), etc.).

Seebeck-effect based sensors, which transform temperature differences directly into electricity.

Thermal-flow based sensors and bimorph effect cantilevers.



Figure 5.2 Calorimetric Sensors Concept

5.5 Electrochemical Cells:

An **electrochemical cell** is a device capable of either generating electrical energy from chemical reactions or using electrical energy to cause chemical reactions. The electrochemical cells which generate an electric current are called voltaic or galvanic cells and those that generate chemical reactions, via electrolysis for example, are called electrolytic cells. A common example of a galvanic cell is a standard 1.5 volt cell meant for consumer use.

A *battery* consists of one or more cells, connected in parallel, series or series-and-parallel pattern.



Figure 5.3 A demonstration electrochemical cell setup resembling the Daniell cell. The two half-cells are linked by a salt bridge carrying ions between them. Electrons flow in the external circuit.

Electrolytic Cell

An electrolytic cell is an electrochemical cell that drives a non-spontaneous redox reaction through the application of electrical energy. They are often used to decompose chemical compounds, in a process called electrolysis—the Greek word lysis means *to break up*.

Important examples of electrolysis are the decomposition of water into hydrogen and oxygen, and bauxite into aluminium and other chemicals. Electroplating (e.g. of copper, silver, nickel or chromium) is done using an electrolytic cell. Electrolysis is a technique that uses a direct electric current (DC).

An electrolytic cell has three component parts: an electrolyte and two electrodes (a cathode and an anode). The electrolyte is usually a solution of water or other solvents in which ions are dissolved. Molten salts such as sodium chloride are also electrolytes. When driven by an external voltage applied to the electrodes, the ions in the electrolyte are attracted to an electrode with the opposite charge, where charge-transferring (also called faradaic or redox) reactions can take place. Only with an external electrical potential (i.e. voltage) of correct polarity and sufficient magnitude can an electrolytic cell decompose a normally stable, or inert chemical compound in the solution. The electrical energy provided can produce a chemical reaction which would not occur spontaneously otherwise.



Figure 5.4 Nineteenth century electrolytic cell for producing oxyhydrogen.

Galvanic cell or Voltaic cell:

A galvanic cell, or voltaic cell, named after Luigi Galvani or Alessandro Volta respectively, is an electrochemical cell that derives electrical energy from spontaneous redox reactions taking place within the cell. It generally consists of two different metals connected by a salt bridge, or individual half-cells separated by a porous membrane.

Volta was the inventor of the voltaic pile, the first electrical battery. In common usage, the word "battery" has come to include a single galvanic cell, but a battery properly consists of multiple cells.



Figure 5.5 Galvanic cell with no cation flow

Primary Cell:

A primary cell is a Galvanic battery that is designed to be used once and discarded, in contrast to a secondary cell (rechargeable battery), which can be recharged with electricity and reused. In general, the electrochemical reaction occurring in the cell is not reversible, rendering the cell unrechargeable. As a primary cell is used, chemical reactions in the battery use up the chemicals that generate the power; when they are gone, the battery stops producing electricity and is useless. In contrast, in a secondary cell, the reaction can be reversed by running a current into the cell with a battery charger to recharge it, regenerating the chemical reactants. Primary cells are made in a range of standard sizes to power small household appliances such as flashlights and portable radios.

Primary batteries make up about 90% of the \$50 billion battery market, but secondary batteries have been gaining market share. About 15 billion primary batteries are thrown away worldwide every year, virtually all ending up in landfills. Due to the toxic heavy metals and strong acids or alkalis they contain, batteries are hazardous waste. Most municipalities classify them as such and require separate disposal. The energy needed to manufacture a battery is about 50 times greater than the energy it contains. Due to their high pollutant content compared to their small energy content, the primary battery is considered a wasteful, environmentally unfriendly technology. Due mainly to increasing sales of wireless devices and cordless tools, which cannot be economically powered by primary batteries and come with integral rechargeable batteries, the secondary battery industry has high growth and has slowly been replacing the primary battery in high end products.

Secondary Cell:

A secondary cell, commonly referred to as a *rechargeable battery*, is an electrochemical cell that can be run as both a galvanic cell and an electrolytic cell. This is used as a convenient way to store electricity: when current flows one way, the levels of one or more chemicals build up (charging); while it is discharging, they reduce and the resulting electromotive force can do work.

A common secondary cell is the lead-acid battery. This can be commonly found as car batteries. They are used for their high voltage, low costs, reliability, and long lifetime. Lead-acid batteries

are used in an automobile to start an engine and to operate the car's electrical accessories when the engine is not running. The alternator, once the car is running, recharges the battery.

Fuel Cell:

A *fuel cell* is an electrochemical cell that converts the chemical energy from a fuel into electricity through an electrochemical reaction of hydrogen fuel with oxygen or another oxidizing agent. Fuel cells are different from batteries in requiring a continuous source of fuel and oxygen (usually from air) to sustain the chemical reaction, whereas in a battery the chemical energy comes from chemicals already present in the battery. Fuel cells can produce electricity continuously for as long as fuel and oxygen are supplied.

The first fuel cells were invented in 1838. The first commercial use of fuel cells came more than a century later in NASA space programmes to generate power for satellites and space capsules. Since then, fuel cells have been used in many other applications. Fuel cells are used for primary and backup power for commercial, industrial and residential buildings and in remote or inaccessible areas. They are also used to power fuel cell vehicles, including forklifts, automobiles, buses, boats, motorcycles and submarines.



Figure 5.6 Scheme of a proton-conducting fuel cell

There are many types of fuel cells, but they all consist of an anode, a cathode, and an electrolyte that allows positively charged hydrogen ions (protons) to move between the two sides of the fuel cell. At the anode a catalyst causes the fuel to undergo oxidation reactions that generate protons (positively charged hydrogen ions) and electrons. The protons flow from the

anode to the cathode through the electrolyte after the reaction. At the same time, electrons are drawn from the anode to the cathode through an external circuit, producing direct current electricity. At the cathode, another catalyst causes hydrogen ions, electrons, and oxygen to react, forming water. Fuel cells are classified by the type of electrolyte they use and by the difference in startup time, which ranges from 1 second for proton-exchange membrane fuel cells (PEM fuel cells, or PEMFC) to 10 minutes for solid oxide fuel cells (SOFC). A related technology is flow batteries, in which the fuel can be regenerated by recharging. Individual fuel cells produce relatively small electrical potentials, about 0.7 volts, so cells are "stacked", or placed in series, to create sufficient voltage to meet an application's requirements. In addition to electricity, fuel cells produce water, heat and, depending on the fuel source, very small amounts of nitrogen dioxide and other emissions. The energy efficiency of a fuel cell is generally between 40 and 60%; however, if waste heat is captured in a cogeneration scheme, efficiencies up to 85% can be obtained.

The fuel cell market is growing, and in 2013 Pike Research estimated that the stationary fuel cell market will reach 50 GW by 2020.

Half-cell:

An electrochemical cell consists of two half-cells. Each *half-cell* consists of an electrode and an electrolyte. The two half-cells may use the same electrolyte, or they may use different electrolytes. The chemical reactions in the cell may involve the electrolyte, the electrodes, or an external substance (as in fuel cells that may use hydrogen gas as a reactant). In a full electrochemical cell, species from one half-cell lose electrons (oxidation) to their electrode while species from the other half-cell gain electrons (reduction) from their electrode.



Figure 5.7 The Bunsen cell, invented by Robert Bunsen.

A *salt bridge* (e.g., filter paper soaked in KNO₃, NaCl, or some other electrolyte) is often employed to provide ionic contact between two half-cells with different electrolytes, yet prevent the solutions from mixing and causing unwanted side reactions. An alternative to a salt bridge is to allow direct contact (and mixing) between the two half-cells, for example in simple electrolysis of water.

As electrons flow from one half-cell to the other through an external circuit, a difference in charge is established. If no ionic contact were provided, this charge difference would quickly prevent the further flow of electrons. A salt bridge allows the flow of negative or positive ions to maintain a steady-state charge distribution between the oxidation and reduction vessels, while keeping the contents otherwise separate. Other devices for achieving separation of solutions are porous pots and gelled solutions. A porous pot is used in the Bunsen cell (right).

Equilibrium Reaction

Each half-cell has a characteristic voltage. Various choices of substances for each half-cell give different potential differences. Each reaction is undergoing an equilibrium reaction between different oxidation states of the ions: When equilibrium is reached, the cell cannot provide further voltage. In the half-cell that is undergoing oxidation, the closer the equilibrium lies to the ion/atom with the more positive oxidation state the more potential this reaction will provide. Likewise, in the reduction reaction, the closer the equilibrium lies to the ion/atom with the more oxidation state the higher the potential.

Cell Potential

The cell potential can be predicted through the use of electrode potentials (the voltages of each half-cell). These half-cell potentials are defined relative to the assignment of 0 volts to the standard hydrogen electrode (SHE). (See table of standard electrode potentials). The difference in voltage between electrode potentials gives a prediction for the potential measured. When calculating the difference in voltage, one must first rewrite the half-cell reaction equations to obtain a balanced oxidation-reduction equation.

- 1. Reverse the reduction reaction with the smallest potential (to create an oxidation reaction/overall positive cell potential)
- 2. Half-reactions must be multiplied by integers to achieve electron balance.

Cell potentials have a possible range of roughly zero to 6 volts. Cells using water-based electrolytes are usually limited to cell potentials less than about 2.5 volts due to high reactivity of the powerful oxidizing and reducing agents with water that is needed to produce a higher voltage. Higher cell potentials are possible with cells using other solvents instead of water. For instance, lithium cells with a voltage of 3 volts are commonly available.

The cell potential depends on the concentration of the reactants, as well as their type. As the cell is discharged, the concentration of the reactants decreases and the cell potential also decreases.

5.6. Surface and Bulk Acoustic Devices

SURFACE ACOUSTIC WAVES • A surface acoustic wave (SAW) is an acoustic wave traveling along the surface of a material exhibiting elasticity, with an amplitude that typically decays exponentially with depth into the material. • Acoustic waves (also known as sound waves) are a type of longitudinal waves that propagate by means of adiabatic compression and decompression.

SAWs were first explained in 1885 by Lord Rayleigh thus waves are named as Rayleigh waves • Rayleigh waves have a longitudinal and a vertical shear component that can couple with any media in contact with the surface. This coupling strongly affects the amplitude and velocity of the wave, allowing SAW sensors to directly sense mass and mechanical properties.

The velocity of acoustic waves is typically 3000m/s, which is much lower than the velocity of the electromagnetic waves. • SAW devices use SAWs in electronic components to provide a number of different functions, including delay line (Propagation delay, the length of time taken for something to reach its destination) filters, correlators and AC to DC converters. • SAW filters are now used in mobiles and provide significant advantages in performance, cost, and size over other filter technologies such as quartz crystals (based on bulk waves), LC filters, and waveguide filters.

Surface acoustic wave devices provide wide-range of applications with the use of electronic system, including delay lines, filters, correlators and DC to DC converters. The possibilities of these SAW device could provide potential field in radar system, communication systems.

Application in Electronic Components

This kind of wave is commonly used in devices called *SAW devices* in electronic circuits. SAW devices are used as filters, oscillators and transformers, devices that are based on the transduction of acoustic waves. The transduction from electric energy to mechanical energy



Figure 5.8 Schematic picture of a typical SAW device design

Electronic devices employing SAWs normally use one or more interdigital transducers (IDTs) to convert acoustic waves to electrical signals and vice versa by exploiting the piezoelectric effect of certain materials, like quartz, lithium niobate, lithium tantalate, lanthanum gallium silicate, etc. These devices are fabricated by substrate cleaning/treatments like polishing, metallisation, photolithography, and passivation/protection (dielectric) layer manufacturing. These are typical process steps used in manufacturing of semiconductor like silicon integrated circuits.

All parts of the device (substrate, its surface, metallisation material type, thickness of metallisation, its edges formed by photolithography, layers - like passivation coating the metallisation) have effect on the performance of the SAW devices because propagation of Rayleigh waves is highly dependent on the substrate material surface, its quality and all layers in contact with the substrate. For example in SAW filters the sampling frequency is dependent on the width of the IDT fingers, the power handling capability is related to the thickness and materials of the IDT fingers, and the temperature stability depends not only of the temperature behaviour of the substrate but also on the metals selected for the IDT electrodes and the possible dielectric layers coating the substrate and the electrodes.

SAW filters are now used in mobile telephones, and provide technical advantages in performance, cost, and size over other filter technologies such as quartz crystals (based on bulk waves), LC filters, and waveguide filters specifically at frequencies below 1.5-2.5 GHz depending on the RF power needed to be filtered. Complementing technology to SAW for frequencies above 1.5-2.5 GHz is based on thin-film bulk acoustic resonators (TFBAR, or FBAR).

Much research has been done in the last 20 years in the area of surface acoustic wave sensors.^[6] Sensor applications include all areas of sensing (such as chemical, optical, thermal, pressure, acceleration, torque and biological). SAW sensors have seen relatively modest commercial success to date, but are commonly commercially available for some applications such as touchscreen displays.

SAW Device Applications in Radio and Television

SAW resonators are used in many of the same applications in which quartz crystals are used, because they can operate at higher frequency. They are often used in radio transmitters where tunability is not required. They are often used in applications such as garage door opener remote controls, short range radio frequency links for computer peripherals, and other devices where channelization is not required. Where a radio link might use several channels, quartz crystal oscillators are more commonly used to drive a phase locked loop. Since the resonant frequency of a SAW device is set by the mechanical properties of the crystal, it does not drift as much as a simple LC oscillator, where conditions such as capacitor performance and battery voltage will vary substantially with temperature and age.

SAW filters are also often used in radio receivers, as they can have precisely determined and narrow passbands. This is helpful in applications where a single antenna must be shared between a transmitter and a receiver operating at closely spaced frequencies. SAW filters are also frequently used in television receivers, for extracting subcarriers from the signal; until the analog switchoff, the extraction of digital audio subcarriers from the intermediate frequency strip of a television receiver or video recorder was one of the main markets for SAW filters.

Early pioneer Jeffery Collins incorporated surface acoustic wave devices in a Skynet receiver he developed in the 1970s. It synchronised signals faster than existing technology.

They are also often used in digital receivers, and are well suited to superhet applications. This is because the intermediate frequency signal is always at a fixed frequency after the local oscillator has been mixed with the received signal, and so a filter with a fixed frequency and high Q provides excellent removal of unwanted or interference signals.

In these applications, SAW filters are almost always used with a phase locked loop synthesized local oscillator, or a varicap driven oscillator.

SAW in Geophysics:

In seismology surface acoustic waves could become the most destructive type of seismic wave produced by earthquakes,^[9] which propagate in more complex media, such as ocean bottom, rocks, etc. so that it need to be noticed and monitored by people to protect living environment.

SAW in Quantum Acoustics:

SAWs play a key role in the field of quantum acoustics (QA) where, in contrast to quantum optics (QO) which studies the interaction between matter and light, the interaction between quantum systems (phonons, (quasi-)particles and artificial qubits) and acoustic waves is analysed. The propagation speed of the respective waves of QA is five orders of magnitude slower than that of QO. As a result, QA offers a different perspective of the quantum regime in terms of wavelengths which QO has not covered. One example of these additions is the quantum optical investigation of qubits and quantum dots fabricated in such a way as to emulate essential aspects of natural atoms, e.g. energy-level structures and coupling to an electromagnetic field. These artificial atoms are arranged into a circuit dubbed 'giant atoms', due to its size reaching 10^{-4} – 10^{-3} m. Quantum optical experiments generally made use of microwave fields for matter-light interaction, but because of the difference of wavelength between the giant atoms and microwave fields, the latter of which has a wavelength ranging between 10^{-2} – 10^{-1} m, SAWs were used instead for their more suitable wavelength (10^{-6} m).

Within the fields of magnonics and spintronics, a resonant coupling between spin waves and surface acoustic waves with equal wave-vector and frequency allows for the transfer of energy from one form to another, in either direction. This can for example be useful in the construction of magnetic field sensors, which are sensitive to both the intensity and direction of external magnetic fields. These sensors, constructed using a structure of magnetostrictive and piezoelectric layers have the benefit of operating without batteries and wires, as well as having a broad range of operating conditions, such as high temperatures or rotating systems.

Single Electron Control



Figure 5.9 Animation of an electron transported via a surface acoustic wave.

Even at the smallest scales of current semiconductor technology, each operation is carried out by huge streams of electrons. Reducing the number of electrons involved in these processes, with the ultimate goal of achieving single electron control is a serious challenge. This is due to the electrons being highly interactive with each other and their surroundings, making it difficult to separate just one from the rest. The use of SAWs can help with achieving this goal. When SAWs are generated on a piezoelectric surface, the strain wave generates an electromagnetic potential. The potential minima can then trap single electrons, allowing them to be individually transported. Although this technique was first thought of as a way to accurately define a standard unit of current, it turned out to be more useful in the field of quantum information. Usually, qubits are stationary, making the transfer of information between them difficult. The single electrons, carried by the SAWs, can be used as so called flying qubits, able to transport information from one place to another. To realise this a single electron source is needed, as well as a receiver between which the electron can be transported. Quantum dots (QD) are typically used for these stationary electron confinements. This potential minimum is sometimes called a SAW QD. The process, as seen in the GIF on the right, is typically as follows. First SAWs are generated with an interdigital transducer with specific dimensions between the electrodes to get the favourable wavelengths. Then from the stationary QD the electron quantum tunnels to the potential minimum, or SAW QD. The SAWs transfer some kinetic energy to the electron, driving it forward. It is then carried through a one dimensional channel on a surface of piezoelectric semiconductor material like GaAs. Finally, the electron tunnels out of the SAW QD and into the receiver QD, after which the transfer is complete. This process can also be repeated in both directions.

SAW and 2D Materials:

As acoustic vibrations can interact with the moving charges in a piezoelectric semiconductor through the strain-induced piezoelectric field in bulk materials, this acoustoelectric (AE) coupling is also important in 2D materials, such as graphene. In these 2D materials the two-dimensional electron gas has band gap energies generally much higher than the energy of the SAW phonons traveling through the material. Therefore the SAW phonons are typically absorbed via intra-band electronic transitions. In graphene these transitions are the only way, as the linear dispersion relation of its electrons prevents momentum/energy conservation when it would absorb a SAW for an inter-band transition.

Often the interaction between moving charges and SAWs results in the diminishing of the SAW intensity as it moves through the 2D electron gas, as well as re-normalizing the SAW velocity. The charges take over kinetic energy from the SAW and lose this energy again through carrier scattering.

Aside from SAW intensity attenuation, there are specific situations in which the wave can be amplified as well. By applying a voltage over the material, the charge carriers may obtain a higher drift speed than the SAW. Then they pass on a part of their kinetic energy to the SAW, causing it to amplify its intensity and velocity. The converse works as well. If the SAW is moving faster than the carriers, it may transfer kinetic energy to them, and thereby losing some velocity and intensity.

SAW in Microfluidics:

In recent years, attention has been drawn to using SAWs to drive microfluidic actuation and a variety of other processes. Owing to the mismatch of sound velocities in the SAW substrate and fluid, SAWs can be efficiently transferred into the fluid, creating significant inertial forces and fluid velocities. This mechanism can be exploited to drive fluid actions such as pumping, mixing, and jetting. To drive these processes, there is a change of mode of the wave at the liquid-substrate interface. In the substrate, the SAW wave is a transverse wave and upon entering the droplet the wave becomes a longitudinal wave. It is this longitudinal wave that creates the flow of fluid within the microfluidic droplet, allowing mixing to take place. This technique can be used as an alternative to microchannels and microvalves for manipulation of substrates, allowing for an open system.

This mechanism has also been used in droplet-based microfluidics for droplet manipulation. Notably, using SAW as an actuation mechanism, droplets were pushed towards two or more outlets for sorting. Moreover, SAWs were used for droplet size modulation, splitting, trapping, tweezing, and nano fluidic pipetting. Droplet impact on flat and inclined surfaces has been manipulated and controlled using SAW.

PDMS (polydimethylsiloxane) is a material that can be used to create micro channels and microfluidic chips. It has many uses, including in experiments where living cells are to be tested or processed. If living organisms need to be kept alive, it is important to monitor and control their environment, such as heat and pH levels; however, if these elements are not regulated, the cells may die or it may result in unwanted reactions. PDMS has been found to absorb acoustic energy, causing the PDMS to heat up quickly (exceeding 2000 Kelvin/second). The use of SAW as a way to heat these PDMS devices, along with liquids inside micro channels, is now a technique that can be done in a controlled manner with the ability to manipulate the temperature to within 0.1 °C.

SAW in Flow Measurement:

Surface acoustic waves can be used for flow measurement. SAW relies on the propagation of a wave front, which appears similar to seismic activities. The waves are generated at the excitation centre and spread out along the surface of a solid material. An electric pulse induces SAWs that propagate like the waves of an earthquake. them to generate Interdigital transducer acts as sender and as receiver. When one is in sender mode, the two most distant ones act as receivers. The SAWs travel along the surface of the measuring tube, but a portion will couple out to the liquid. The decoupling angle depends on the liquid respectively the propagation velocity of the wave which is specific to the liquid. On the other side of the measuring tube, portions of the wave will couple into the tube and continue their way along its surface to the next interdigital transducer. Another portion will be coupled out again and travels back to the other side of the measuring tube where the effect repeats itself and the transducer on this side detects the wave. That means excitation of any one transducer here will lead to a sequence of input signals on two other transducers in the distance. Two of the transducers send their signals in the direction of flow, two in the other direction.

5.7. Bulk Acoustic Wave Devices

A BAW resonator is like a simple capacitor. An acoustic wave could be generated when a differential voltage is applied on two electrodes, and it will produce acoustic reflection to the surfaces. In this case, the resonance is produced by the excitation of wave to the thickness direction and determined by the properties of piezoelectric film and electrodes

5.7.1. Comparison between Saw Devices and Baw Devices

SAW devices work at low frequency (below 1GHz). At higher frequency its power handling capacity becomes less. They are quite sensitive to temperature change • Unlike SAW devices, BAW filters have the ability of occupying good performance above 2GHz frequency with less loss in a tiny size. In addition, BAW devices are far less sensitive to temperature changes even at broad bandwidths.

SAW and BAW device coverage includes delay lines and filters operating at selected frequencies in the range from about 10 MHz to 11 GHz. Modeling with single-crystal piezoelectric and layered structures; resonators and low-loss filters; comb filters and multiplexers; antenna duplexers; harmonic devices; filters for pulse compression. Filters acoustic and acoustoelectric correlators for radar, spread spectrum, and packet radio; acousto-optic processors for Bragg modulation and spectrum analysis. Real-time Fourier-transform and cestrum processors for radar and sonar. • Filters for microwave digital radio; clock-recovery filters for fiber communications.

5.8. Gas-sensitive FETs

Gas-sensitive FETs based on nanomaterials such as carbon nanotubes (CNTs), nanowires (NWs), graphene, and transition metal chalcogenides have also been investigated because the high surface-to-volume ratios of nanomaterials are attractive for improving sensor properties.

Introduction:

The importance and demand for sensing gases, vapors, and volatile organic compounds (VOCs) have been increasing in fields such as diagnostics environmental monitoring for industrial, agricultural, home safety, and so on. Various types of gas sensors and sensor arrays have been researched and developed, including field-effect transistor (FET)-based sensors.

Following the report of pioneering work on catalytic-gate FETs, research on FET-based gas sensors has been extended to various types of gas-sensitive FETs. In this chapter, catalytic-gate FETs, suspended-gate FETs (SGFETs), and solid electrolyte-based FETs are introduced. Gas-sensitive FETs based on nanomaterials such as carbon nanotubes (CNTs), nanowires (NWs), graphene, and transition metal chalcogenides have also been investigated because the high surface-to-volume ratios of nanomaterials are attractive for improving sensor properties.

For recognition of gaseous and volatile analytes from sensing results, two main methods have been used. The conventional recognition method uses selective sensors with specific receptors designed for selective interaction with target analytes. Another recognition method uses a combination of cross-reactive sensor arrays and pattern recognition methods. These crossreactive sensor arrays consist of gas sensors that are responsive to a broad range of analytes and have differential sensitivities. To date, various gas sensors have been applied in sensor arrays, including gas-sensitive FETs. In this chapter, research on the combination of FET-based sensor arrays and pattern recognition methods is briefly reviewed.

Gas-sensitive FETs and Field-Effect Devices combined with catalytic metal gates:



Figure 5.10 Schematic illustrations of the (a) structure and (b) threshold voltage shift of a Pd-gate FET sensitive to hydrogen

Catalytic-gate FETs are one of types of gas-sensitive FETs. In 1975, Lundström et al. first reported a Pd-gate FET sensitive to hydrogen. Pioneering research on catalytic-gate FETs

opened up the field of FET-based gas sensors and other gas-sensitive field-effect devices such as capacitor-based and Schottky diode-based sensors. Catalytic-gate filed-effect devices feature a nanoscale layer of catalytic metals, such as palladium and platinum, as a gate electrode on insulating layers in a metal-insulator-semiconductor (MIS) structure. Figure 1 shows reported schematic illustrations of this structure and the threshold voltage shift of a Pd-gate FET that is sensitive to hydrogen. In initial reports of catalytic-gate FETs, Pd as a catalytic-gate electrode was deposited onto the insulating layer of the MIS structure of the FET. Figure 2 shows changes observed in the threshold voltage on hydrogen introduction to Pd-gate FETs. The gas-sensitive mechanisms of catalytic-gate FETs and catalytic-gate field-effect devices have been described in earlier reviews.



Figure 5.11 Changes in the threshold voltage toward H2 at different concentrations at 150°C

Porous metal gates in catalytic-gate field-effect devices have allowed for important progress in NH3 sensing. Figure 3 shows reported TEM observations of 3- and 7-nm-thick Pt layers evaporated onto SiO2. These thin Pt layers consist of discontinuous metals. The choice of catalytic materials, the structure of the catalytic layer, and the operating temperature affect the sensitivity and selectivity of catalytic-gate field-effect devices. Furthermore, the type of insulating materials used in the MIS structure also influences the responsive properties of gassensitive field-effect devices.



Figure 5.12 Transmission electron micrographs of 3- and 7-nm thick porous Pt metal layers on SiO2.

For operation at high temperatures, silicon carbide (SiC)-based FETs have been investigated. SiC is a wide-bandgap semiconductor, and can be used as a substrate for the MIS structure instead of the conventional Si substrate. SiC can be used at high temperatures and harsh environments because of its chemical inertness. SiC-based FETs have been applied to the sensing of CO, NH3, NO2, and SO2. As with conventional catalytic-gate FETs using an Si substrate, the catalytic-gate material used in SiC-based FETs influences the sensitivity and selectivity of the sensor.

Catalytic-gate devices consisting of high-electron mobility transistors (HEMTs) have also been studied for operation at high temperature. For example, GaN/AlGaN heterostructures that exhibit two-dimensional electron gas (2DEG) induced by spontaneous and piezoelectric polarization at the interface of the heterostructure have been applied to a catalytic-gate HEMT as a gas sensor. In this report, the GaN/AlGaN-based HEMT combined with a Pt gate electrode was operated at about 400°C for sensing of H2, CO, C2H2, and NO2.

MODEL MCQ: (Question & Answers)

- 1. Nanomaterials are the materials with at least one dimension measuring less than
 - a) 1 nm
 - b) 10 nm
 - c) 100 nm
 - d) 1000 nm
 - Ánswer: c
- 2. A material with one dimension in Nano range and the other two dimensions are large is called ______
 - a) Micro-material
 - b) Quantum wire
 - c) Quantum well
 - d) Quantum dot
 - Answer: c
- 3. The colour of the nano gold particles is _____
 - a) Yellow
 - b) Orange
 - c) Red
 - d) Variable
 - Answer: d
- 4. The melting point of particles in nano form _____
 - a) Increases
 - b) Decreases
 - c) Remains same
 - d) Increases then decreases
 - Answer: b
- The first talk about nano-technology was given by _________
 a) Albert Einstein
 - b) Newton
 - c) Gordon E. Moore
 - d) Richard Feynman
 - Answer: d
- 6. Which of the processes of materials was not described as Nanotechnology? a) Separation
 - b) Creation
 - c) Processing
 - d) Consolidation
 - Answer: b
- 7. The initial tools used to help launch the nanoscience revolution were _____
 - a) Binoculars
 - b) Microscope
 - c) Scanning probe instruments
 - d) Interferometer
 - Answer: c
- 8. The size of atoms is nearly _____
 - a) 0.01 nm
 - b) 0.1 nm
 - c) 1 nm

| d) 10 mm | |
|---|--|
| | |
| Allsweit 0 0 What's the procedure in Tan down febrication method? | |
| 9. What's the procedure in Top-down labrication method? | |
| a) Nano-particles -> Powder -> Dulk | |
| b) Powder -> Bulk -> Nano-particles | |
| c) Bulk -> Powder -> Nano-particles | |
| d) Nano-particle $->$ Bulk $->$ Powder | |
| Answer: c | |
| 10. Which of the following is an example of Bottom Up approach? | |
| | |
| b) Colloidal dispersion | |
| c) Milling | |
| a) Etching | |
| Answer: D | |
| 11. For milling operations, what kind of environment is preferred? | |
| a) Acture b) Desig | |
| b) Basic | |
| d) Insert | |
| a) Inert | |
| Allswell u | |
| 12. What kind of metals are used for mining operations? | |
| a) Soft and electic | |
| a) Hard and brittle | |
| d) Hard and electic | |
| A new or a | |
| Allswell C 12 CVD stands for | |
| a) Carbon vanour density | |
| a) Carbon vapour density | |
| a) Chemical vapour densition | |
| d) Carbon vapour deposition | |
| Answer: c | |
| 14 Chemical solution deposition is also known as | |
| a) Sol-gel | |
| h) CVD | |
| c) Plasma spraving | |
| d) Laser pyrolysis | |
| Answer: a | |
| 15 Typical precursor used in sol-gel are | |
| a) Metal oxides | |
| b) Metal dioxides | |
| c) Metal alkoxides | |
| d) Metal fluorides | |
| Answer: c | |
| 16. Particles of ZrO_2 , Y_2O_2 and Nano whiskers have been produced by | |
| a) Sol-gel | |
| b) CVC | |
| c) Plasma spraving | |
| d) Laser pyrolysis | |
| Answer: b | |
| | |

17. Which gas serves as buffer gas in Laser ablation? a) Nitrogen b) Oxygen c) Helium d) Neon Answer: c 18. The configuration of Buckminsterfullerene is a) 12 Hexagons and 22 Pentagons b) 18 Hexagons and 15 Pentagon c) 20 Hexagon and 12 Pentagon d) 15 Hexagon and 15 Pentagon Answer: c 19. C₆₀ is soluble in _____ a) Water b) Ammonia c) HCl d) Benzene Answer: d 20. CNTs stands for a) Carbon Nanotubes b) Carbon Nanotechnology c) Carbon Nanoscience and technology d) Carbon Nine Technology Answer: a 21. CNTs are capped on both ends with which carbon nanostructure? a) Graphite b) Diamond c) C₆₀ d) Benzene Answer: c 22. For the synthesis of CNTs, the quartz tube is heated up to _____ a) 1000°C b) 1200°C c) 1400°C d) 1600°C Answer: b 23. The metallic tubes have which kind of structure? a) Armchair b) Chiral c) Boat d) Achiral Answer: a 24. The main purpose of CNTs in fuel cells is _____ a) Production of energy b) Active medium c) Catalyst d) Storage Answer: d 25. Carbon nanotubes are poor transmitters of electromagnetic radiations due to their

a) High conductivity

b) Large surface area

c) High porosity

d) Chemical Stability

Answer: a

26. The figure shows a FET using CNT. Identify CNT.



d) There is no such property Answer: b 32. The colour of the nano gold particles is _____ a) Yellow b) Orange c) Red d) Variable Answer: d 33. On both ends of the CNTs, which carbon nanostructure is placed? a) Graphite b) Diamond c) C₆₀ d) Benzene Answer: c 34. Quantum dots can be used in a) Crystallography b) Optoelectronics c) Mechanics d) Quantum physics Answer: b 35. Vesicle is a type of _____ a) Nanostructure b) Nanoparticle c) Nanocrystal d) Supramolecular system Answer: d 36. Which property of Nanomaterials make them suitable to be used for elimination of pollutants? a) High purity b) Better thermal conductivity c) Enhanced chemical activity d) Small size Answer: c 37. Nano crystalline materials synthesised by sol-gel technique results in a foam like structures called _ a) Gel b) Aerosol c) Foam d) Aerogel Answer: d 38. Which nanomaterial is used for cutting tools? a) Fullerene b) Aerogel c) Tungsten Carbide d) Gold Answer: c 39. A Carbon monoxide sensor made of zirconia uses which characteristic to detect any change? a) Capacitance b) Resistivity

- c) Activity
- d) Permeability
- Answer: c

40. Which components of an automobile are envisioned to be coated with zirconia? a) Spark plugs

- b) Liners
- c) Tyres
- d) Brakes
- Answer: b
- 41. The main purpose of CNTs in fuel cells is _____
 - a) Production of energy
 - b) Active medium
 - c) Catalyst
 - d) Storage
 - Answer: d
- 42. Zirconia is a hard, brittle _____
 - a) Metal
 - b) Non-metal
 - c) Composite
 - d) Ceramics
 - Answer: d
- 43. Nanoscale aluminium oxide increases the _____
 - a) Conductivity
 - b) Resistance
 - c) Ductility
 - d) Stability
 - Answer: b
- 44. Which of the following are applications of quantum dots?
 - a) Immunolabelling and fluorescence imaging.
 - b) Drug delivery.
 - c) As tags for other drug carries.
 - d) All the above.
 - Answer: d
- 45. Which one of the following is used in making nanowires?
 - a) ZnO.
 - b) TiO.
 - c) H2O.
 - d) MnO.
 - Answer: a