CHAPTER 1
INTRODUCTION

The revolution in nanotechnology resulted in nanocarbon technology which is finding now in every aspect of life. This novel technology finds in the development of smart systems, helps in the preventive healthcare system along with extended facilities during diagnosis as well for treatment. This chapter gives a brief introduction on the thesis titled as ‘Characterization of Nanocarbon thin films’, which includes the area of research, the motivation towards the research work, the objectives and organization of the thesis.

1.1 Nanocarbon Technology

Nature and its unique designs make economic use of materials by optimizing the design of the entire structure or system to meet various needs. The Designs found in nature are the result of millions of years; just in case of a human being, the heart helps to pump the blood, ear helps to hear the sound. The nature is self-generating and most of the designs or models in science and technology are based on the study of natural objects. The development referring to the nature is possible because of advanced facilities available in science, technology and engineering. The developed complex knowledge based systems are beyond just simple mimicking of nature [1, 2].

The transfer of technology from nature to engineering is referred as Biomimetic (also known as bio-mimicry), and it focus on characterizing the structure and mechanics of natural materials and duplicate these structures and mechanisms into new, high-performance engineering materials [4, 5]. Biomimetic is a biologically inspired technology [1-7], for example mimicking of a heart resulted in the design of sophisticated pumps referred as heart pumps [6], and mimicking sensory organs like eye referred as bionic eye [7].

Nature has organic or inorganic or polymeric types of materials (may be nanomaterial’s or bulk materials). The materials available in the nature are highly ordered, self-generating,
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hierarchical, multifunctional, adaptive, self-repairing and biodegradable structures. But the incomplete understanding of natural biochemical or biosynthesis processes resulted in difficulties to mimic the nature materials or systems [2]. The possibilities exist for the synthesis of materials by mimicking biological systems are: (i) direct use of organisms for the synthesis (ii) use wholly synthetic methods, and (iii) use some modification of the biological processing technique [1-7]. Especially the second approach expects the self-aligning nanostructures, with special characteristics.

The innovations in the material science evolved a series of carbon allotropes have found having good characteristics comparably. The flexible and stretchable electronics have been intensively explored for enabling new applications otherwise unachievable with the conventional Silicon technology. Engineering of functional systems at the molecular scale resulted in the development of new era called Nanotechnology [8, 9]. The advances in computing power, materials modeling, coupled with significant advances in characterization tools such as Atomic Force Microscopy (AFM), Scanning Tunneling Microscopy (SCM), Transmission Electron Microscopy (TEM), Raman Spectroscopy, Electron Energy Loss Spectroscopy (EELS), have provided a few additional factors that have enabled the design and development of self-aligned nano-materials for specific applications [10].

The design of nanosystems or nano devices are challenging still, where one has to consider the surface to volume ratio. This is also an important factor in case of dimension reduction [11]. The characteristic of material drastically changes with change in the surface to volume ratio, this is observed in many cases. The allotrope of carbon such as diamond is one of the hard materials as well it is excellent electrical insulator. But nanocarbon allotropes are also found to be metallic, semiconducting or insulating. Thus, the scientists focus, from microelectronics has turned towards nanoelectronics [9, 10].
The research interest is now focused on maintaining the increase of performances by alternate means other than just scaling the dimensions (is referred as “equivalent scaling”). The equivalent scaling achieved with the incorporation of non-digital functionalities such as RF communication, power control, passive components, sensors, and actuators. Thus “More-than-Moore” (MtM) technology fulfill a specific function such as transducing a physical signal into an electrical one, by allowing heterogeneous integration [9].

Figure 1.1 ITRS: Dual trend map includes More Moore and More-than-Moore [9].

Shown in figure 1.1 is the dual trend approach includes miniaturization and incorporation of non-digital functions. The "More-than-Moore" approach allows for the non-digital functionalities to migrate from the system board-level into the package (SiP) or onto the chip (SoC). In addition, to this the associated complex embedded software might also need to be modified. Thus the “More-than-Moore” is to extend the use of the silicon-based technology
developed in the microelectronics industry to provide new, non-digital functionalities along with the existing digital functionalities. ITRS (International Technology Road map for Semiconductors) is very successful in road mapping the digital domain of the microelectronics that offers guidance to the microelectronic ecosystem, and also allows synchronizes the technological progress and the timely availability of manufacturing techniques [9, 10].

Thus the challenge of the microelectronic industry is extended further to the MtM technologies without losing the performance. As per ITRS, the nanostructured materials are expected building blocks of future nanoelectronic devices and biomedical systems, where self-aligned, highly ordered, self-generating, multifunctional, adaptive, self-repairing, biocompatible and biodegradable nanocarbons plays a major role [8-13].

Carbon as a material has shown more diversity compared to many of similar other materials. The carbon bonded differently and resulted in the evolution of materials like diamond, graphite, fullerenes, carbon nanotubes, diamond like carbon and tetrahedral amorphous carbon, carbon nanoclusters and others [10, 12-19]. The interesting characteristics, assured functionalities of nanocarbons motivated the researches to focus on the study of a series of nano carbons, and its characterization.

However, most of the semiconductor chips or transistors are created with silicon in microelectronics industry, where silicon material is acting as the heart of the electronic devices. But miniaturization or the scaling of silicon devices are associated with the Moore’s law ("The number of transistors incorporated in a chip will approximately double every 24 months") [10]. But the limitations in scaling the ICs lead into the need for significant new nanomaterials and device research. The microelectronics is turned towards a new era called nanoelectronics, where researchers focuses on alternate material, processing techniques or characterization techniques or finally alternate device if could substitute available silicon for
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the future electronics industry. Among the innovated nanostructures including nanocarbon, ZnO2 and many other composite types, the nanocarbon is the most attracted nano material [9, 10]. In the context of growing challenges integrated circuit technology based on CMOS scaling, a special emphasis will be made on hybrid semiconductor/nanodevice integration [9-11]. On the other side, when challenging flexible and stretchable electronics is thought, this may be unachievable with the conventional Si technology.

All such industry requirements are lead into new innovations in the material science as well process technology, resulted in the evolution of new nanomaterial’s like carbon nanotube, graphene etc. This nanomaterial’s are expected to the building block of future bottom up approach of and could support engineering of functional systems at the molecular level [10, 17-19].

The various forms of nanocarbons being studied may include: diamond like carbon (DLC) [20-23], tetrahedral amorphous carbon (t-aC) [24, 25], single-walled/multi-walled carbon nanotubes (SWNT/MWNT)[26-36], fullerences(C60)[37], graphene [38-48], nanodiamond [49], nanowalls, and nanocluster or nanostructured carbon [49]. Growing areas of technology were these nanocarbon find applications include Nanoelectronics, Vacuum nanoelectronics, Sensors, Biomedical applications, Novel energy sources, Interconnects in ICs, Novel light, strong and even conducting Composite materials and Flexible electronics [33, 50-59]. In case of biomedical applications of nanocarbon, it is considered as one of the magic nanomaterial. The nanocarbon in biomedical engineering is used as tribological coating (over surgical or for implants), tweezers / probe tips, sensors, miniaturized X-Ray source, bio-pharmaceutics (drug delivery and drug discovery), implantable devices (nanosensor, nanorobot, actuator, nanofluidic system) [54, 59].
However, the interesting characteristics, assured functionalities, and promising results of nanocarbons motivated researches to focus on the study of a series of nanocarbons, and its characterization.

1.2 MOTIVATION

Carbon in various form have been studied extensively. However, these studies do not seem to look at leveraging the properties in an integrated way. To make use of benefits of the varied form of the carbon, it is important to understand the morphological, dimensional, compositional, structural similarities or dissimilarities between them. Hence the motivations to study the varying form of carbon and to establish a correlation between morphological, dimensional, compositional, structural properties. Further, most of the nanocarbons are grown with higher temperature process. Generally, the nanocarbon process technology is not compatible with the conventional semiconductor technology. Hence, there is a need to look at compatible technology. In this context nanocluster carbon are looked at. These nanocarbons are grown at low temperature or at room temperature. It is always desirable to have a low temperature process as this enables deposition on substrates such as glass and plastic. There is a possibility to use this nanocluster carbon in the large area electronics, printed electronics, or in case of flexible/stretchable electronics. Thus, there is huge potential to study these mixed phase low temperature grown nanocluster carbon.

The nanocarbons in its diverse forms find applications in many domains including applications like high quality paints for military aircraft, highly conducting inter-connects, efficient energy systems, a huge variety of sensors, environment friendly purification systems (gas and water), storage systems and other vacuum nano-electronic applications like cold cathodes (field assisted electron emitters) for diverse gas sensing applications(using CNTs), field emission displays, electron beam lithography, electron and ion guns, multitude of
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sensors, electron microscopes and microprobes, low & medium power microwave sources, micro and pico satellite propulsion systems, high power devices and Tera Hz communication devices and also tribological applications. Nanomaterials in case of novel biomimetic microelectronic systems (BMES), allow bi-directional communication with tissue and by doing so enable implantable/portable microelectronic devices to treat presently incurable human diseases, such as blindness, paralysis, and memory loss.

The "More-than-Moore" approach allows for the non-digital functionalities to migrate from the system board-level into the package (SiP) or onto the chip (SoC). “More-than-Moore” may extend the use of the silicon-based technology developed in the microelectronics industry to provide new, non-digital functionalities along with the nanocarbons and may help in the design of MEMS or NEMS.

Biomimetic materials are developed with an inspiration from nature are composite materials or material structures for future. This variety makes carbon all the more, a very interesting material which can be further studied. Among the new nano materials that are evolving nanocarbon is expected to play a key role in the future. However, nanoscale materials dissolve in different ways, and take different characteristics from the way they would at normal size. To understand the influence of nanocarbon on environment or health essentially cytotoxicity test are also important. Nanocarbons are so small and extremely mobile, that they may pass easily into the bloodstream when inhaled or swallowed, and possibly when applied to the skin. Once they are inside the body, they may have access to most or all tissues.

One of the key motives of this study is to use this low temperature grown nanocluster carbon film for biomedical application and especially looking at invasive or noninvasive sensor or system. Once these materials are tested with biocompatibility, the proposed nanocarbons may be used along with the invasive- sensors or with the prosthetics or with the implants.
1.3 OBJECTIVE

To study wide variety of nanocarbons and to look at their morphology, dimension, structural and compositional properties along with the room temperature grown nanocluster carbon for consideration in the area of nanotechnology, flexible electronics, large area microelectronics, vacuum nanoelectronics and biomedical engineering.

Given below are the key objectives:

- Proposed to study wide range of nanocarbons, along with a low temperature grown nanocluster carbon (grown using cathodic arc system).
- To use SEM (Scanning Electron Microscope) data for studying the morphological and dimensional properties.
- To use Raman spectroscopy to understand the $sp^2$-$sp^3$ bonding (indirectly), a possible correlation to size and possible grouping of nanocarbons.
- To study and understand if there is correlation, between process conditions or growth conditions and a) Morphology, b) Dimension, c) Composition, d) Structure and e) Electrical and Electronic properties.
- Finally, to look at feasibility of usage of these nanocarbons for device or sensor based application.

1.4 SCOPE

Once characterized and reasonably understood, these nanocarbons may be useful in diverse domains such as: nanoelectronics, vacuum nanoelectronics, biomedical applications, nanosensors, Nano /Micro Electro Mechanical System (NEMS & MEMS) and novel biomimetic microelectronic systems (BMES).
The room temperature grown nanocluster carbon, when fully characterized, could be an attractive material for application in the areas of Nano-electronics, Vacuum nano-electronics, large area microelectronics (macro-electronics) and Sensor technology. Nanocluster carbon presents an opportunity to evolve beyond the stated high temperature processes and also be compatible with the existing semiconductor technology. There exists an interesting option to grow nanocluster carbon deposited at low temperatures on substrates such as glass and plastic through the use of ion assisted deposition processes like cathodic arc, Pulsed laser assisted deposition, Mass separated ion beam technique etc. This mixed phase low temperature grown nano-cluster carbon has not been systematically characterized, so exploring the nature and characteristics of nanocluster carbon is challenging.

1.5 ORGANIZATION

The thesis titled “Characterisation of nanocarbon thin films” has organized with the following chapters. The first chapter of the thesis has a brief introduction to carbon as a material for nanotechnology, its importance, motivation to molecular level engineering and its applications are discussed. Chapter two is an overview on series of nanocarbon includes fullerene, carbon nanotubes, grapheme, amorphous carbon, nanocluster carbon, and nanodiamond. These series may have 1-dimensional, 2-dimensional and 3-dimensional nanocarbons having different morphology, composition and dimension. The discussion provides a comprehensive understanding of nanocarbons, its process technologies. The principles of Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and Raman Spectroscopy are also reported. The chapter three focuses on the discussions of morphological study and dimension analysis of various nanocarbons. Chapter four is on Raman spectra of various nanocarbons. Discussed Raman response as unique signature and discussed possible correlations of Raman spectra with various process parameters. Also
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reported principle component analysis (PCA) based classification of nanocarbons including three classes of carbon. The chapter five discusses the electrical/ electronic characterization, discovering the nature of nanocluster carbon as semiconductor. The chapter also discusses feasible applications of low temperature grown nanocarbon for field assisted electron emission. The final chapter provides the thesis conclusion.