CHAPTER 1
INTRODUCTION

Over the last several decades, scaling of device dimensions as described by Moore’s law [1] has been the key driver for growth in the semiconductor industry. Looking ahead, silicon based technologies are expected to continue dominating electronic applications for some more time, but innovations no longer stem from simple geometrical scaling according to Moore’s law. The technology road map for the semiconductor industry ITRS envisages two different paths to play a key role namely “More Moore” and “More Than Moore” (MTM) [2–5]. More Moore involves extending the scaling down process with further innovation. However, MTM calls for a new paradigm involving novel materials, devices and systems for man–machine and man–environment interface facilitation. This involves wide range of new materials and devices there off, including nanocarbon (in all its facets), amorphous/nano/micro silicon, metal oxides, other novel nano materials and polymers [5–8]. Among them nanocarbons are expected to be one of the first nano materials which could be incorporated in the ICs beyond 2012 [1]. Figure 1.1(a) shows the projection as per ITRS road map, the expected growth direction in the semiconductor industry. Figure 1.1 (b) shows the systems based on one of the most important emerging area of semiconductor technology namely large area and Flexible microelectronics, which would involve a wide range of new materials and devices and the associated area of technological applications [5].

Based on the current studies it may be seen from figure 1.2 that the emerging electronic materials have mobilities ranging from $10^{-3}$ to $10^{2}$ cm$^2$V$^{-1}$s$^{-1}$ [5]. The MTM technologies could leverage all these materials and the associated devices for a wide range of man to machine, machine to machine, and machine to environment related applications. The nanocarbons could be of interest as they are expected to be more stable compared to some of the merging polymer, molecular organic and even metal oxide materials.
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FIGURE 1.1 (a) Possible technologies and devices beyond CMOS and Moore’s law suggested by ITRS [2] (b) Next generation of flexible electronics system [5].

FIGURE 1.2 Correlation between mobility of TFTs and switching speed.
These nano carbons in its various forms including nanodiamond, nano structured graphite, fullerenes, carbon nanotubes, hydrogenated diamond–like carbon, tetrahedral amorphous carbon, carbon nanocluster and others [9-13] are expected to play an important role. Figure 1.3 shows emerging forms of nanocarbon. Hence, the interest to study the room temperature grown nanocluster carbon films using the cathodic arc process. The current study is a preliminary report on the material properties indicating the feasibility of this material for electronic applications.

1.1 Emerging Nano Carbons and its diverse forms

Emerging nanocarbons in its wide range of allotropes with properties varying with sizes and spatial directions are being extensively studied. This may be classified into categories of different dimensionality, such as three dimensional (3D), two–dimensional (2D), one–dimensional (1D) and zero–dimensional (0D) (Figure 1.3). Diamond, a very hard, isotropic and electronically insulating material, is composed of a fully 3D tetrahedral sp³–hybridized C–C bonding configuration. Graphite, another example of 3D carbon, is a semi–metal with an insignificant overlap of bands (about 40 meV). The best representation of a 2D carbon system is characterized by graphene. Graphene is an ideal 2D system. 1D carbon is
characterized by cylindrical forms of carbon, such as single and multi-walled nanotubes. Carbon nanotubes can be either semiconductors or metals, depending on their geometric structure. In addition, fullerene, which has the shape of a soccer ball, is considered as a 0D carbon. Harold Kroto at the University of Sussex discovered carbon clusters containing C\textsubscript{60} or C\textsubscript{70} atoms in 1985 [13]. This sparked the interests of researchers in determining the properties of fullerenes and the accuracy of their predicted properties based on their shape and chemical bonds between each carbon atom. Multiwalled carbon nanotubes (MWCNTs) [14] were discovered by Sumio Iijima of NEC laboratory in Tsukuba in 1991 [14]. CNTs [15] are now found to have properties varying from metallic to semiconducting.

As far as structure is concerned, 0D fullerene and 1D carbon nanotube are regarded as being wrapped up from 2D graphene. In addition, 3D graphite can be stacked by 2D graphene. As such, 2D graphene is always regarded as a foundation for 0D, 1D and 3D graphitic carbon. However, graphene was presumed not to exist in free states. Recently, free–standing graphene has moved from “academic” material to reality, with demonstration of its growth using multiple ways [16]. The methods that are developed in getting 2D carbon fall into two categories: the bottom–up approach and the top–down approach and discussed in detail in references [17,18].

**Nanocrystalline graphite (NCG)**

Nanocrystalline graphite (NCG) is a film with crystalline (graphene) domains in random orientation. The film consists of graphite crystallites with thickness of 2–20 nm (it corresponds to 5–50 graphite atomic layers) and length of 1–3 μm. The crystallites are randomly distributed in the film and are separated from one another by 0.5–1 μm. The graphite atomic layers are preferably oriented along the substrate. SEM study of grown NCG films showed the structure predominantly consists of nano flakes normally oriented toward the substrate [19, 20]. Average height of the nano flakes is 1 μm and width is 0.5–1 μm. Raman
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spectrum of NCG film indicates the presence of D and G lines in Raman spectrum. This indicates that the nano flakes are formed by fragments of graphene planes (domains). These films have distinct peaks at 1350 cm\(^{-1}\) (D–peak), 1600 cm\(^{-1}\) (G–peak) and 2700 cm\(^{-1}\) (2D) peaks when characterized by Raman spectroscopy [21]. Their typical I(D)/I(G) ratios is typically two which indicates the presence of nanocrystalline graphite with disorder. All peaks have FHWM broadened due to disorder.

The NCG material is produced in form of thin films grown by plasma enhanced CVD non catalytic process either on a conductive or dielectric substrate in a dc glow discharge in mixture of hydrogen and methane on substrates placed on anode [22]. Also, there have been a few attempts to obtain NCG using high energy laser pulses [23], mechanical milling [24], ball milling for 8 hr [25] and thermal chemical vapor deposition (CVD) from methane/hydrogen precursors [26]. NCG films have found applications in high current field emission cathodes [22], Electrochemical Sensing [27], material for Electrochemical super capacitors [28] and for Gas Sensing Applications [29].

**Nanodiamond**

Nanodiamond films are synthetic poly / single crystalline thin film diamonds whose size range from a few hundreds of nanometers to two/three nanometers. It is the crystal size that is used to classify these materials into four categories namely ultra nano–crystalline diamond (UNCD) films, nano–crystalline diamond (NCD) films, micro–crystalline diamond (MCD) films and single crystalline diamond.

Nanodiamond films have been grown using Hot Filament CVD or conventional thermal CVD and increasingly later using a wide range of plasma CVD processes. Many gas phase carbon sources can be used, including methane, alcohol, acetylene, and carbon monoxide, while methane is most commonly used [30, 31].

In recent years nanodiamond films have caught the attention of many researchers because of their unique properties for example high hardness, excellent thermal conductivity, chemical inertness, and optical
transparency over a wide spectral range just to name but a few. In addition to this it has been discovered that synthetic diamonds can be doped to produce semiconducting materials with a wide band gap and this has opened another exciting chapter on the possible applications of this novel material. Unlike natural diamond which is produced through geological processes, nanodiamonds are very small and this makes it relatively easy to manipulate their properties because of the large surface area and reproducible synthesis. One further interesting thing about these particles is that their mechanical properties are comparable to natural diamond and these can be exploited at nano scale, to make miniaturized devices that can withstand harsh environments. Single crystal diamond which can be produced by microwave plasma chemical vapor deposition (MWCVD), is now replacing natural diamond in some cutting and abrasive tools [32]. The music industry is now using synthetic diamond for tweeters; the high frequency part of a loudspeaker and has improved the sound quality in one top manufacturer’s products [33]. Doped diamond is currently being investigated for possible application in Micro Electro Mechanical Systems (MEMS) based devices, while some functionalized nanodiamond films are being tried in medicine for drug delivery [34].

Many NCD or UNCD films have very low surface roughness compared to MCD, hence it is considered to be ideal for Nano Electro Mechanical Systems (NEMS). Polycrystalline diamond films with high band gap of 5.5 eV are being studied for its optoelectronics and dielectric properties [35]. Nanodiamond is ideal for high power switches, fast field effect transistors for electronic devices that can be used in harsh environments, e.g. high temperatures and high radiation. The optical transparency over a wide spectral range can be utilized in making diamond lasers, optical sensors and light emitting diodes (LED) [36].

**Fullerenes**

In the mid–1980, Richard E. Smalley, Robert F. Curl and Harold W. Kroto discovered the new family of carbon molecules as fullerene C_{60}[13]. They exist in the form of C_{28}, C_{32}, C_{80} etc. This allotrope of carbon was named after Richard Buckminster Fuller, who among other things
invented the geodesic dome. Various other sizes of fullerenes \( \text{C}_{60} \), \( \text{C}_{70} \), \( \text{C}_{80} \), \( \text{C}_{90} \) etc. are formed when carbon containing materials are burned with limited oxygen [13]. Their structures are composed of hexagons and pentagons [12]. They all have closed structure with the carbon in cages.

Each carbon has a bond between three others, and its hybridization is \( \text{sp}^2 \). The \( \text{C}_{60} \) molecules are arranged into a face centered–cubic (FCC) unit cell. The sides of this cubic cell measure 1.4 nm. Each \( \text{C}_{60} \) molecule has a diameter of 1 nm. The molecules are held together in the crystal by weak Van der Waals forces. In this space–filling model, each carbon atom is represented by a wedge. Buckminster fullerene is neither aromatic nor super aromatic, and its delocalization of electron density is poor. \( \text{C}_{60} \) behaves like alkenes, which have sufficient electrons, so it reacts with electron rich species. Fullerenes can take different forms such as a sphere, tube ellipsoid or ring.

Fullerenes are being considered for use in combat armor [12]. Researchers have found that water–soluble derivatives of fullerenes inhibit the HIV-1 protease (enzyme responsible for the development of the virus) and are therefore useful in fighting the HIV virus that leads to AIDS [37]. Super hard fullerenes can be used for mechanical application [38]. Fullerenes can be used for diodes, transistor [39] and photovoltaic devices [40].

**Carbon nanotubes (CNT)**

The next key nano carbon discovered a decade after fullerene was the carbon nanotubes, which has already been used in a large number of practical applications. Carbon nanotube has a unique structure of helical arrangement of carbon atoms in hexagonal arrays. The helicity (local symmetry), along with the diameter (which determines the size of the repeating structural unit) introduces significant changes in the electronic density of states, and hence provides a unique electronic character for the nanotubes. The other factor of importance that determines the uniqueness in the physical properties is topology, or the closed nature of individual nanotube shells. When individual layers are closed onto themselves, certain aspects of the anisotropic properties of graphite disappear, making
the structure remarkably different from graphite. The nanotubes, for the first time represent the ideal, most perfect and ordered carbon fiber, the structure of which is entirely known at the atomic level. These nanotubes consist of layers of graphite in the form of cylinders and often closed at both ends. They can exist as single and multi–walled nanotubes. Normally, their diameter is only a few nanometers and their length a millimeter. Multi–Walled Nano Tubes (MWNT), are collections of several concentric graphene cylinders and are larger structures compared to Single–Walled Nano Tubes (SWNTs) which are individual cylinders of 1–2 nm diameter.

CNT's have sufficient contractility to make them candidates to replace muscle tissue [41]. Multi–walled carbon nanotubes (MWNT coated with magnetite can generate strong magnetic fields). Recent advances show that MWNT decorated with magnetite nanoparticles can be oriented in a magnetic field [42] and enhance the electrical properties of the composite material in the direction of the field [43]. Nanotubes have been shown to be superconducting at low temperatures [44]. CNTs can act as antennas for radios and other electromagnetic devices [45]. Semiconducting CNTs have been used to fabricate field effect transistors (CNTFET) [46] and in interconnects [47].

Graphene–2D Carbon of High Perfection

Graphene is a two dimensional sp² hybridized forms of single layer carbon. Graphite is nothing but multilayers of Graphene sheets stacked one upon other to form the bulk material [48]. The distance between graphene planes is about 0.335 nm in graphite. Those graphene sheets are held together by Van der Waals forces. The weak interaction between the sheets allows them to slide easily across each other. This gives pencils their writing ability and graphite its lubricating properties. Bulk graphite has been studied for decades [48], but until recently there were no experiments on graphene. This was due to the difficulty in separating and isolating single layers of graphene for study.

The initial demonstration and the further development of process technologies to exfoliate and also grow graphene layers by Andre Geim
and his co–workers, has in recent time led to a huge surge in activity in the area of graphene [18]. Recently stamping methods has been developed, which uses graphite pillars to transfer graphene flakes [49] or electrostatic voltage assisted exfoliation, which uses electrostatic forces to controllably separate graphene from bulk crystals [50]. Another common top–down approach of graphene fabrication is to disperse graphene from solution. Graphite flakes have been sonicated in a solution. Long sonication time is needed to break the Van der Waals force in graphite [51]. Following this step, the graphene flakes are then dispersed onto a wafer. Atomic force microscopy (AFM) is used to locate individual sheets.

Chemical vapor deposition (CVD) is one of the most common bottom–up techniques to fabricate graphene. Large size graphene sheets have been fabricated in different groups by CVD and annealing growth. Typically epitaxial graphene forms on silicon carbide (SiC) surface by heating a SiC wafer [52]. The number of layers and the sheet sizes can be controlled easily [53]. However, the mobilities of epitaxial graphene are comparatively lower than those of exfoliated graphene [54]. Furthermore, isolating single sheets is difficult and additional lithography is required to pattern electrostatic gates on top of epitaxial graphene [55]. Transition–metal–catalyzed graphene growth was demonstrated to yield macroscopic single–crystalline graphene domains with very low defect density and outstanding thickness control [52]. It is still a challenge to find a way to transfer the graphene layers to an insulating surface. Those recent successful demonstrations of fabrication of large graphene by Chemical vapor deposition (CVD) or epitaxial hold out huge promise. Yet lot more needs to be done.

Typical areas of applications include Organic Thin Film Transistors (OTFT) [56], touchscreen [57], LEDs [58], solar cells [59], smart windows [60], graphene oxide for resistive switching [61]. Due to its high electronic quality, graphene has also attracted the interest of technologists who see it as a way of constructing ballistic transistors. Graphene exhibits a pronounced response to perpendicular external electric fields, allowing one to build FETs (field–effect transistors) [18].
1.2 Diamond–like carbon (DLC) and its manifestation

Diamond–like Carbon (DLC) films are one of the relatively earliest from of thin film carbon material. The properties of the DLC vary depending on the growth process and the nature of bonding. The film could have anything from near 90% of diamond like (tetrahedral–sp³) bonding to as small as 30 to 40 % sp³ bonding, and with additions of graphite like (sp²) bonding or even linear sp¹ bond (like in acetylene). Depending on the nature of the ratio of the sp³ / sp² bonding ration the properties of the film could vary between diamond, graphite and polymers/hydrocarbons [62]. The properties of DLC films as discussed above are determined by the bonding hybridization of carbon atoms and the relative concentration of the different bonds, i.e. sp², sp³ and sp¹ as well as hydrogen distribution among the different types of bonds. Figure 1.4 shows the ternary phase diagram of DLC in terms of sp², sp³ and H concentrations proposed by Robertson [63]. The exact position of the diamond–like material in the phase diagram is determined by the precursor and the deposition parameter [64]. The three corners represent diamond, graphite and the hydrocarbons, respectively. There is a region of high H contents, where films cannot form. The glassy carbon and evaporated a–C lies in the sp² corner. In the hydrogenated DLC films, some of the carbon atoms are terminated by hydrogen.

![FIGURE 1.4 Ternary phase diagram of DLC [28].](image-url)
The detailed chemical bonding and structure of DLC is not clearly understood. Different models have been put forward by different workers. Robertson [63] modeled the structure of DLC as a random network of covalently bonded carbon atoms in the different hybridization, with a substantial degree of medium range order on the 1 nm scale. Angus and Jansen [65] have described the structure of hydrogenated DLC by random covalent network (RCN) model. According to this model, the structure of a–C: H can be regarded as a three dimensional array of mostly six membered rings, which is able to contain 17–61 % of bound hydrogen.

DLC films can be mainly classified into two categories: hydrogenated (a–C: H) and non–hydrogenated (a–C). Hydrogenated DLC films may contain up to 20–50% hydrogen and are quite different from the hydrogen–free DLC films [66]. The hydrogen content of a–C is less than 1%. Both hydrogenated and hydrogen–free diamond–like carbons are metastable materials deposited using a variety of deposition methods under the influence of energetic particle bombardment [67]. The Plasma enhanced CVD (PECVD) method is the most frequently used technique to deposit diamond films, polycrystalline diamond films and diamond–like carbon films. These films typically have hydrogen in them. Certain applications call for hydrogen free films or reduced/controlled hydrogen incorporation. DLC films have been synthesized by processes like cathodic arc [68], filtered cathode arc [69], using an ion beam assisted deposition [70], mass selected ion beam (MSIB) [71] and laser ablation [72].

DLC films have found application in Thin–film Transistor (TFT) [73], Anti–fuse [74], and low dielectric constant film for ULSI [75], Field emission display [76], driving electrochemical applications [77], bio compatible coatings like coating hip joints, heart valves and stents [78].

1.3 Nanocluster carbon thin films

From the above discussions, it may be seen that by varying the type of carbon bonding namely sp³, sp² and sp¹ a wide variety of nanocarbons like nanodiamond, nano structured graphite, fullerenes, CNT, graphene, amorphous carbon, tetrahedral amorphous carbon (ta–C) and DLC could
be grown. These nanocarbons have been mostly grown using processes like Hot Filament Chemical Vapor Deposition HFCVD [79] microwave plasma chemical vapor deposition [80] plasma assisted RF/DC discharge [20], pulsed laser ablation [81], mass selected ion beam (MSIB) [82], electron cyclotron wave resonance (ECWR) [83]. Most of these processes are not easily compatible with conventional semiconductor processing technology and also typically they use high temperature. However, particularly for large area and flexible microelectronics applications, there is need of a fabrication process at room and low temperature process, large area deposition, high deposition rates, and capability of growth on inexpensive substrates. Arc based deposition process (cathodic arc) either at low or room temperature offer unique opportunity to grow nanocarbon for large area applications.

Cathodic arc process offers the unique opportunity of growing any form of carbon films varying from diamond–like film to graphite–like film and various intermediate stage materials such as tetrahedral amorphous carbon (ta–C), diamond–like carbon (DLC), nanotubes, and even nanocluster carbon thin films. Smooth carbon films with inclusions of fullerene, nanoparticles, and nanotubes grown using the arc process have also been reported [84]. The earliest reports of growth of nano cluster carbon and coral–like structured nano carbon material using cathodic arc process appeared in early mid–90s [85]. Typically, nanocluster carbon thin films are mixed phased material containing both sp² and sp³ bonded carbons with varying clusters dimensions (5 nm to 200 nm). Systematic study of controlled growth of clusters for field emission applications under varying process parameters and observation of resonant tunneling behavior in the multilayered device based on nanocluster carbon thin films [86] have been reported at room temperature by B.S.Satyanarayana [9,87].

1.4 Objective of this work

It is understood from the discussion in section 1.3 on nanocluster carbon thin films that most of the materials properties and compatibility
to microelectronic application has not been fully established. To establish the feasibility of the nanocluster carbon thin films for electronic and optoelectronic application, similar to those demonstrated by a–Si: H and other emerging electronic materials and its use in large area and flexible microelectronics, it is necessary to study the morphological, structural, electrical and optical properties of room temperature grown nanocluster carbon thin films.

Hence with aim to understand and establish the feasibility of this material for diverse applications, following work have been proposed

(a) Study of the morphological and compositional properties of nanocluster carbon films grown at room temperature using cathodic arc process
(b) Study of electronic transport behavior of nanocluster carbon films grown and establish a correlation between the two.
(c) Simulate a thin film transistor using the nanocluster carbon film as the channel material.

1.5 Organization of the thesis

This thesis is structured as follows:

Chapter 1: Provide a brief review on the various forms of nanocarbon and their applications including nano graphite, nanodiamond, DLC, carbon nanotubes, fullerenes and graphene and the motivation to work on nanocluster carbon. Subsequently, define the objective of this work and present an outline of the thesis.

Chapter 2: Briefly analyzes the various transport mechanisms like space–charge–limited–current conduction (SCLC), Poole–Frenkel (PF) effect, ballistic transport, bulk–limited transport, hopping transport and injection limited transport observed in various structured and disordered carbon films.

Chapter 3: Describes various morphological, compositional, electrical and optical characterization techniques used to characterize the nanocluster carbon films. Also discuss the experimental facility that has been created to carry out the various electrical and electronic characterization measurements.
Chapter 4: Discussed in this chapter is a correlation between the morphological, compositional and optical properties of the nanocluster carbon grown under varying process parameters, to that of the cluster dimensions, sp² and sp³ bonding or the associated diamond like and graphite like properties. The process parameters of the cathodic arc considered include arc current, throw distance, ion energy and ambience or growth environment such as the partial pressures of gases like nitrogen, hydrogen and helium during the deposition.

Chapter 5: A detailed study of the electrical and electronic properties of the nanocluster carbon films are reported in this chapter. This includes study of temperature dependent electrical conductivity to first establish the nature of the material and then the nature of electronic transport. Next the defect densities are estimated using techniques like Space–Charge–Limited–Current (SCLC) and Capacitance–Voltage (CV) measurements. Also reported is the optoelectronic properties and dielectric constants measured. Then discussed in the end, is a possible transport mechanism in this novel nanocluster carbon material and the corresponding correlation with the morphological, compositional, electronic and optical properties of the films grown under varying deposition parameters.

Chapter 6: Presented in this chapter is a study of the influence of high energy electron irradiation on nanocluster carbon thin films using a variable energy Microton source. It is observed that the surface morphology and the electrical properties of the films are influenced by the radiation.

Chapter 7: Deliberated in this chapter is the possibility of use of the nanocluster carbon thin film as an electronic device. Based on the estimated material parameters, the nanocluster carbon thin films is used as the channel material in a Thin Film Transistor, and its Deals with two dimensional analysis and numerical simulations carried out using the SILVACO TCAD software to extract the device parameters.

Chapter 8: Presented in this chapter is the key conclusions drawn from this work on the possible feasibility of use of this room temperature grown nanocluster carbon thin film as an electronic material.