CHAPTER 1

Introduction

1 INTRODUCTION

1.1 From Carbon to Carbon Nitride: A Progression in Research

The interest in carbon based thin films started as early as 1970 with the production of the first insulating carbon films (Aisenberg and Chabot 1970). These films were obtained using an ion beam deposition technique and were classified as hydrogenated amorphous carbon (a-C:H) films. Later the same researchers introduced diamond–like–carbon (DLC) (Aisenberg and Chabot 1971; Chu and Li 2006) films which became the first milestone in the study of carbon films. Though DLC films are predominantly amorphous, they show similar properties to those of natural diamond. Even up to now, DLC is one of the most actively researched carbon-based thin films. The continual interest in a-C:H and DLC is derived from their potential in commercial applications. In the progression in the research on a-C:H and DLC, studies on other structures have been reported such as the polymeric-like and tetrahedral carbon (ta-C). The interest in ta-C and hydrogenated ta-C may have begun much later in 1984 with the report by Hiraki et al (Hiraki et al. 1984). This film being of lower H content is an extension to the studies of hard coatings of DLC.

The discovery of polymeric-like carbon films is relatively difficult to pinpoint. There have been many studies done on carbon polymer compounds particularly by chemists (Kipling et al. 1964a, 1964b) which date back even earlier then the work on DLC. Some of the earliest polymeric films were obtained by means of film evaporation (Luff and White 1970; Presland and White 1969). However these polymeric films were focused mostly on anisotropic conducting hydrocarbon films such as polyacetylene which is not exactly related to this work. Thus it is necessary to properly segregate and define the polymeric carbon films of interest in this work. With regards to this, these polymeric-like carbon films are part of the a-C:H family and are made up of sp^2 bonded clusters embedded in amorphous sp^3 matrix. They are softer compared to DLC and ta-C which is due to a relatively high H content in the films. These H atoms forms the terminating CH_n group and thus with the increase of H content, the connectivity of sp^3-C decreases and lowers the film hardness (Motta and Pereyra 2004). Accordingly, these films are polymeric-like but are normally categorised as polymeric hydrogenated carbon films (p-C:H). Determination of the earliest studies carried out on p-C:H films is challenging since earlier works on a-C:H would categorise these films, be they DLC, or polymeric, into a general identification of a-C:H.

The earlier work on a-C:H focused mainly on the fabrication of hard films (in other words DLC and ta-C(:H)) and thus, the softer polymeric films may have been avoided purposefully until later in the research progression of a-C:H films. Examples of the earlier work on p-C:H are those of Biederman (Biederman 1981). Throughout the years more studies were carried out on p-C:H films with emphasis on their photoluminescence properties (Bourée et al. 1998; Godet and Berberan-Santos 2001; Zhang et al. 1999b) in relation to their prospective application in optoelectronic devices. Currently, p-C:H is still actively studied particularly in relations to other carbon structures (Ikenaga et al. ; Kim et al.). However some unanswered questions including the origin of photoluminescence (PL) emission and characteristics for p-C:H remains unresolved.

The second milestone in the study of carbon films started with discovery of carbon nanostructures. This begun by the discovery of buckminster-fullerene C_{60} by Kroto et al in 1985 (Kroto et al. 1985). This initiated the study of nanostructured carbon films which lead to the discovery of free-standing carbon nanotubes (CNTs) by Ijima in 1991 (Iijima 1991). In the early 1990s a lot of focus and effort were put into studying CNTs. However as the years pass, other nanostructures were discovered and opened new avenues and possibilities both in research and applications. These nanostructures includes nanofibers (Ajayan et al. 1994), nanocones (Ge and Sattler 1994), nanotips (Binh et al. 1996), nanowalls (Wu and Yang 2002) and nanosheets (Chen et al. 2003a).

Initially CNTs were formed using arc-discharges similar to the synthesis of C_{60} (Iijima 1991). As the research progressed, a number of different deposition techniques were employed in the fabrication of the carbon nanostructures. Among these, the most well known is the catalytic-plasma enhanced chemical vapour deposition (c-PECVD) initiated by Chen et al. (Chen et al. 1997) in 1997 in the fabrication of nanofibers. This is followed by the large scale synthesis of free-standing aligned CNTs by Ren et al (Ren et al. 1998) using a hot filament (HF)-PECVD. Vertically aligned carbon nanostructures are of great interest since these arrangements allow more control on the dimension, patterning and positioning, even of individual fiber (Melechko et al. 2005). Owing to this, the ability to form vertically aligned CNT has yet again further extended the research interest and applicability of CNTs (Brown et al. 2011; Liu et al. 2010; Melechko et al. 2005; Nozaki et al. 2007) particularly in applications such as field emission displays (Ahmed et al. 2007; Chang et al. 2003; Zhong et al. 2001), nanoelectronics (Du et al. 2011), sensors (Li et al. 2008; Wang and Lin 2008) and scanning probe tips (Melechko et al. 2005).

The third milestone occurred only recently with the discovery of graphene by Novoselov et al. in 2004 (Novoselov et al. 2004). Even in this short time span, graphene has received great interest since it can provide an excellent base both for condensed physics and material science studies (Craciun et al. 2011; Falkovsky 2008a; Liao and Duan 2010; Wu et al. 2010; Zhao et al. 2011a). Its fascinating properties such as high electron mobility with atomic thickness, high surface area, chemical tolerance and broad electrochemical window one of the most promising material candidate for future nanoelectronics (Wang et al. 2011a; Wei et al. 2009).

Over this period effort to enhance the carbon films by introducing various dopant such as boron and nitrogen, were taken. In particular, nitrogen doping through the incorporation of N atoms into the carbon network resulting in the formation of carbon nitride CN_x films of various N content, has been of great interest. According to Muhl and Mendez (Muhl and Méndez 1999), the first deliberate attempt to produce carbon nitride was probably by Cuomo et al. in 1979 (Cuomo et al. 1979) which proposed a planar polymeric structure of the material. However, it was the work of Liu and Cohen in 1989 (Liu and Cohen 1989) that initialled the surge in the interest in CN_x. This theoretical work proposed a variation of CN_x structure, namely the β-C_3N_4 which possesses properties similar or superior to those of diamond. Numerous works and efforts have been invested into the reproducible production of crystalline C_3N_4, though the synthesis of crystalline CN_x has proved to be most elusive and most attempts produced amorphous a-C:N alloy with varied N concentration (Cappelli et al. 2011a). Indeed, in most reports the nitrogen incorporation into these materials are much lower than the concentration of 57 at.% required for C_3N_4 (Riascos et al. 2006).

However, even these a-C:N films show characteristics interesting enough to further encourage research on CN_x films (Ding et al. 2008). Work on nitrogen incorporation into a-C films have been reported since as early as 1989 and 1991(Amir and Kalish 1991; Kaufman et al. 1989). Following that, efforts to incorporate N into various carbon structures were undertaken. Early examples of these are N incorporation into fullerene (Pradeep et al. 1991) and nanotubes (Yi and Bernholc 1993).

N has also been incorporated into graphene. This was reported only recently with various works emerging in 2009 (Li et al. 2009b; Li et al. 2009c; Wang et al. 2009; Wei et al. 2009), and prior to that, this study was limited to results obtained from simulations such as those by Huang et al. (Huang et al. 2007a) and Kim et al. (Kim et al. 2008). Another remarkable discovery in the studies of N incorporation is the formation of new and unique structures which are induced by the formation of various carbon and nitrogen bonds. Some of these structures include the CN_x nanobells which were realized in 1999 (Ma et al. 1999) and recently, nanorods in 2002 (Liu et al. 2002). These are the milestones in the research in carbon and the progression in the enhancement of their characteristics by N incorporation or doping. The summary of these findings are shown in Figure 1.4.

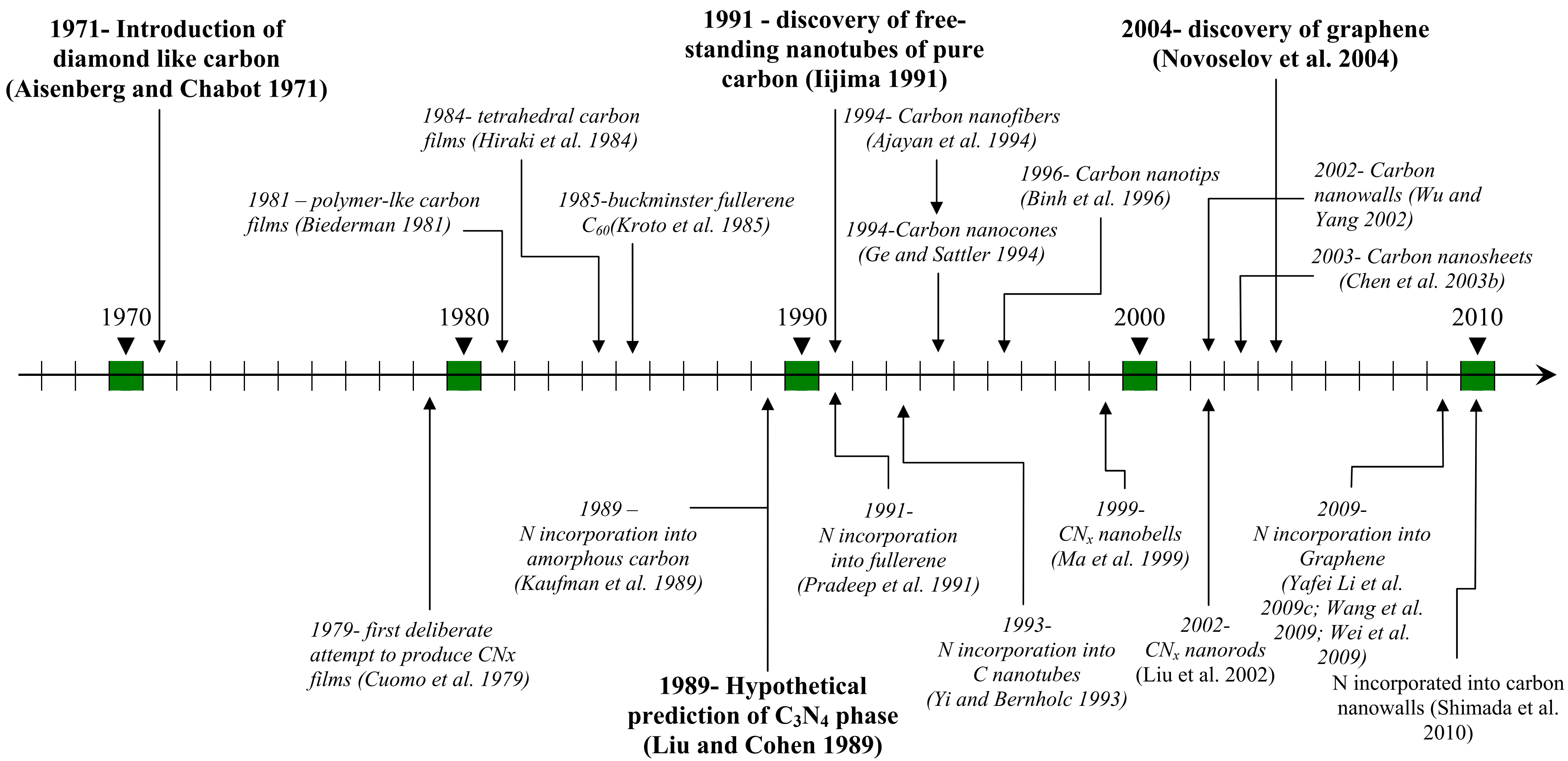

Figure 1.1: Diagram representation of the timeline in the research of carbon and carbon nitride thin films with critical milestones shown in bold letters followed by some other relevant findings. This information is accurate to the knowledge of the author.

1.2 Nitrogen Incorporation into Carbon Films: Advantages and Applications

The advancements in research into carbon thin solid and nanostructured films have revealed various outstanding properties which make these films suitable for numerous potential applications. As example, a-C(:H) films, including DLC and ta-C(:H), are commonly studied towards their use as hard protective coatings owing to their high mechanical strength and hardness, good chemical inertness, high optical transparency, exceptional friction and wear performance and good biocompatible behaviour (Randeniya et al. 2010; Tang et al. 2011; Wang et al. 2011c; Zou et al. 2010). Moreover, the potential of carbon nanostructures in various applications have been extraordinary. Apart from their potential in nanodevices (Yu et al. 2011), field emission devices (Hojati-Talemi and Simon 2011; Wang et al. 2011b; Yu and Zheng 2010), gas sensors (Wu et al. 2010), other researchers have shown functionality of these materials as biosensors (Feng et al. 2011; Wang et al. 2010b) and in energy (hydrogen) storage (Brownson et al. 2011; Comisso et al. 2010; Gotzias et al. 2011).

The applicability of these nanostructures is further enhanced by the ease in producing vertically aligned structures which enhances both the properties and functionality of the materials (Melechko et al. 2005). Among the most popular application of C nanostructured films are as an electron field emitter (FE) where they are regarded as the most efficient electron emitters among various materials (Varshney et al. 2010). Studies on FE has been extended to CNTs (Noh et al. 2010; Varshney et al. 2010), nanotips (Yeong et al. 2006), nanorods (Sasaoka and Nishimura 2011), nanowalls (Banerjee et al. 2011; Hojati-Talemi and Simon 2011; Teii and Nakashima

2010), nanosheets (Wang et al. 2006a; Zhu et al. 2011), nanoflakes (Shih et al. 2010) and graphene (Lahiri et al. 2011; Wang et al. 2011b; Xiao et al. 2010).

Over the years a lot of efforts have been put into incorporating N into these C structures. One of the reasons for the preference in using N as the dopant is the size similarity with C atoms (Ayala et al. 2010) which allows N to be intrinsically incorporated into the C network. N contains one additional electron as compared to C, which upon direct substitution of C atoms in the network transforms the normally p-type carbon films into an n-type material. The percentage of nitrogen incorporation in carbon films can change their electrical response from conductive to highly resistive (Alibart et al. 2008a), suiting CN_x films for applications in very large and ultra scale integrated circuits (Aono and Nitta 2002). N incorporation is also reported to reduce the internal stress in C films which increases the adhesion of the film onto substrates (Muhl and Méndez 1999) which is one of the critical problems in the functionality of carbon films.

Similarly in a number of studies, N incorporation has resulted in significant changes in the carbon films' PL properties. PL in carbon thin films is of considerable scientific and technological importance, as it provides valuable information on the nature of the electronic states and mechanisms of carrier recombination and also shows the possible application of these films as electroluminescence (EL) devices (Fanchini et al. 2003). PL properties of C films have high tolerance to defects (Tóth et al. 2003; Tóth et al. 2006) and white electroluminescence has been observed (Kim and Wager 1988). The PL intensities of CN_x films as well as the efficiency are significantly enhanced by N incorporation (Lejeune et al. 2004; Plass et al. 2001). Also, PL intensities increase with increase in N content in the films (Mutsukura and Akita 2000; Mutsukura 2001) although the peak position may remain the same (Zhang et al. 1999b).

The PL emission in these CN_x films occurs from carrier recombination in the films though there are different views as to the origin of the recombination centers. Some researchers correlate these centers to the presence of sp^2 clustering in the films (Plass et al. 2001; Robertson 1996b) and C≡N bond content in the material (Daigo and Mutsukura 2004; Mutsukura and Akita 2000; Mutsukura 2001), while others show the relationship between defects, pores and hydroxyl (OH) inclusions (Fanchini et al. 2003). Until now, the origin of these recombination centers is still debated. Nonetheless the enhancement due to N incorporation is such that bright EL emission at room temperature is achievable (Zhang et al. 1999b).

Of late significant breakthroughs in the incorporation of N into nanostructured C films have been achieved. Depending on the substitutional configuration, N incorporation into these nanostructures could lead to a metallic or n- or p- type semiconducting behaviour (Ayala et al. 2010). Numerous work have also been carried out on field electron emission (FE) on N doped C nanostructures including nanowalls (Shimada et al. 2010), nanotubes (Ghosh et al. 2010; Jiang et al. 2006; Lee et al. 2008; Srivastava et al. 2006), bamboo-shaped nanotubes (Ghosh et al. 2008), nanofibers (Kimura et al.) and graphene nanoribbons (Yu and Zheng 2010). N incorporation in these devices allows the tailoring of the FE property (Ghosh et al. 2010) and has the advantage of lowering the voltage threshold requirement for the field emission (Shimada et al. 2010).

Other researchers have also reported the use of N doped nanostructures in various fields such as those of CN_x nanosheets for lithium storage (Wang et al. 2011a) and N doped graphene for biosensors (Wang et al. 2010a; Wang et al. 2010b) and fuel cells (Kim et al. 2008; Zhang et al. 2010b). Some of the most recent work on N doped nanostructures is in the field of oxygen reduction carried out mainly using N doped nanotubes (Rao et al. 2010) and graphene (Geng et al. 2011; Imran Jafri et al. 2010; Lee et al. 2010; Qu et al. 2010). In all these applications, N incorporation gives the flexibility and the ability to modify the properties of these CN_x nanostructures particularly in terms of their structural and chemical bonding to tune them for various application and devices.

1.3 Aspects, Motivation and Objectives for This Study

In the initial phase of this study, it was crucial to decide on two different aspect of the work. The first was the deposition method to be employed in the production of the CN_x films. The second involved the type of CN_x structure together with the objective and direction of these studies on the structure.

For the first aspect, the criteria were governed by the fact that the deposition system was to be home built. This was both to minimize financial cost and give a deposition system which could be easily modified to achieve the optimum conditions for the fabrication of these films. From the various deposition systems reviewed from literature, radio frequency plasma enhanced chemical deposition (rf PECVD) was found to fit these criteria well. Furthermore this system was relatively easy to design and operate, and have the potential of producing various types of carbon nitride structures. Methane and nitrogen gases were used as gas sources for the film depositions. These two gases are commonly used in other studies and were deemed to be relatively safe and easily obtained.

For the second aspect, two different types of carbon structures were chosen for the study which include polymeric like and nanostructured CN_x films. These are significantly different from each other and thus different approaches were taken to study each of them. The polymeric films were found to be of interest since most studies in CN_x films have been devoted to harder films such as N doped DLC and ta-C:N. The number of published work on polymeric CN_x:H are also a lot fewer than those of other structures. Thus there are many aspects of polymeric CN_x films which were not yet fully studied. One of them is the PL properties, especially the origin of the recombination centers in these films. In this work efforts were taken to study the PL properties of the polymeric CN_x films particularly in correlation to the structural and bonding characteristics of the films.

The study of the nanostructured CN_x films was motivated by the interest in finding new, simpler ways to produce nanostructured films. The aim was to fabricate these nanostructures at low temperatures which could open the way for future deposition to be carried out on temperature sensitive substrates. Also, fabrication of nanostructured CN_x films directly on the substrates without the need of templates or metal catalyst was desired. This would eliminate the necessity of removing the catalyst and/or template. The study of these nanostructured films focused on optimizing the deposition parameter to obtain highly vertical aligned nanostructures fabricated using rf PECVD. To the best of the author's knowledge, the resulting films obtained from the deposition condition employed here, have not been studied by other researchers. This in turn means that the growth mechanism may well be different from those expected for catalytic or template-assist deposition. Thus effort to formulate the growth mechanism of these structures was taken. This presents novel work as a part of the fulfilment of this PhD thesis.

1.4 Outline of Thesis

Following this first chapter providing the introduction to this thesis, Chapter 2 presents the literature survey related to the work done. This contains a simple review which could be broken up into two major parts. The first part contains a brief discussion of the different types of deposition methods commonly employed in the fabrication of CN_x films. For each method, examples of deposition setups from various references are also shown. It was from these examples and review that rf PECVD was chosen and the setup was designed. The second part discusses briefly the theoretical aspects of some of the characterization tools used in this work. These include optical characterization, Raman scattering measurements, Fourier transform infrared analysis and photoluminescence characteristics. Some observations and analyses from recent publications by other researchers are also presented.

Chapter 3 presents the experimental and analytical methods employed in the study of these films. This chapter is divided into three main parts. The first part describes the deposition procedures, which also includes a description of the home-built radio frequency PECVD, the procedure for substrate cleaning and the actual deposition process. The second part gives a short overview of the procedure of the thermal annealing. The final part consists of the different measurements employed to characterize the samples. Since most of the analytical apparatuses used are quite common, description of the instruments and measurement procedures are either purposely left out or simplified. Instead emphasis is given to the calculation and analytical methods used to interpret the data.

The experimental results and discussion were divided into three sequential chapters that is Chapter 4, 5 and 6. This began with Chapter 4 entitled “from polymeric to nanostructured carbon nitride thin films: a study of electrode distance”, and reveals the transformation of film structure from polymeric to nanostructured film. This occurred solely from the changes in the electrode distance whereby other deposition parameters were kept constant. Comparatively thorough studies of these films were conducted to compare their optical, structural, morphological, composition and photolumiscence. In the subsequent chapters two separate studies are reported for each structure.

Chapter 5 presents the studies done on the p-CN_x:H films deposited as a function of radio frequency (rf) power and nitrogen-to-methane gas flow-rate ratio. The focus on this chapter is the optimization of PL characteristics of the films and the study of recombination centers for PL emission in these films. The study on the effect of rf power was carried out first whereby an rf power was selected to produce the highest PL intensities in the films. Subsequently this power was fixed in the ensuing study of the effects of varying the nitrogen-to-methane gas flow-rate ratio. Similarly, the film deposited at the optimized ratio (and rf power) was selected to be annealed.

Chapter 6 presents the study on the nanostructured CN_x:H films. While the study on p-CN_x:H focused on the PL characteristics which looks toward the future application of these films, a more fundamental approach was taken for the nanostructured films. Here the focus was on the study of the effects of rf power and nitrogen-to-methane gas flow-rate ratio on the growth of these structures. The third parameter involves the study on the effect of deposition duration which enables a systematic analysis on the growth progression of these nanostructures. This chapter was concluded with a proposed growth mechanism for these structures.

This thesis is concluded with Chapter 7 which presents the summaries of Chapters 4,5 and 6, and a general conclusion on the findings. Also, suggestions for future works are offered.