Development of a novel filtered cathodic vacuum arc deposition system for carbon metal nanocluster thin films

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**DEVELOPMENT OF A NOVEL FILTERED
CATHODIC VACUUM ARC DEPOSITION SYSTEM
FOR CARBON METAL NANOCLUSTER THIN FILMS**

XU NAIYUN

School of Electrical & Electronic Engineering

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in partial fulfillment of the requirement for the degree of

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Dedicated to my parents, my wife

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Summary

Carbon metal nanocluster (C:Me) films have been used to protect the metal nanoclusters from oxidation and enhance its properties, in the same time the incorporation of metal nanoclusters within the carbon thin film is also able to reduce the high compressive stress of the carbon film, improve its mechanical, electrical properties. However, the conventional deposition methods to synthesize C:Me nanoclusters film still have difficulties in controlling the density of metal nanoclusters, and the metal content, etc. Hence, a better deposition method is desired to meet these requirements.

In this thesis, a novel Y-shaped magnetic filters and anti-Helmholtz focusing coil is specially designed and implemented on the filtered cathodic vacuum arc (FCVA) deposition system. By using the Y-bend FCVA deposition system, two streams of plasma can be generated simultaneously, which is able to deposit C:Me nanocluster film. The ways to control the microstructure and property have been explored, such as magnetic trap generated by the anti-Helmholtz focusing coil which can be used to control the metal cluster density, arc current and growth temperature which can affect the film microstructure. Other than the deposition parameters, influence of post treatment such as thermal and laser annealing has also been studied. In addition, the electrical, tribological properties and applications of carbon based thin film have also been investigated.

Firstly, the effect of magnetic trap generated by the anti-Helmholtz coil on the metal cluster density has been investigated. To do this, the input current of the anti-Helmholtz coil has been raised from 0 to 10 A. The as-deposited C:Me nanocluster film have been studied using energy dispersive X-Ray spectroscopy (EDX) and scanning

electron microscope (SEM). It is found that the density of the metal cluster strongly depends on the strength of the magnetic trap generated by the anti-Helmholtz coil—the stronger the traps, the higher metal cluster density is able to be achieved.

In order to control the metal content of the C:Me nanocluster film, C:Me nanocluster films have been deposited by varying the arc current of metal source (0 A, 100 A, 110 A, 120 A, 130 A and 140 A) at room temperature. It is found that by varying the arc current of metal source. The metal content within the film can be controlled, the metal content is found to increase from 1.8 at% to 10.9 at % when the arc current of metal source raises from 100 A to 140 A. In addition, it is also noticed that the increase in Ni plasma density, the C:Ni film becomes more graphite-like, by visible Raman spectroscopy. Furthermore, High resolution transmission electron microscopy (HRTEM) shows the formation of (002) sp^2 clusters when high Ni plasma density is applied during deposition, as well as the Ni nanoclusters are found to be embedded within the nanostructured carbon. I-V characteristics shows non-contact related transport mechanism for C:Ni films, and the resistivity is shown at least a six orders drop with the incorporation of Ni and formation of conducting sp^2 clusters.

The effect of growth temperature on the microstructure and properties of C:Me nanocluster film have been studied. Pure C film, C:Ni and C:Ti nanocluster films have been deposited at various growth temperature (room temperature, 200°C, 400°C and 600°C). X-Ray Photoelectron spectroscopy (XPS) shows that both the incorporation of metal nanoclusters and increase in growth temperature can promote the formation of sp^2 bonded carbon, however not all metals can form carbide with carbon atoms (in this work, only Ti is found to be able to form C-Ti carbide). Raman results shows that with the

presence of metal nanoclusters, the graphitic microstructure can form at lower temperature (200°C comparing to 400°C for pure C film), which is also confirmed by the HRTEM results. C:Ni nanocluster films display better electrical performance comparing to pure C film, while C:Ti nanocluster films exhibit superior tribological performance.

Post treatment such as thermal and laser annealing has been performed on pure C film and C:Me nanocluster film. To study the effect of thermal annealing, pure C film, C:Ni and C:Ti nanocluster films have been annealed at different temperatures. Among the different types of carbon based thin films in this experimental work, C:Ni nanocluster film is shown to be the most active film subjecting to the change in annealing temperature, which can be shown by the Raman results. SEM, Raman and HRTEM results also reveal the formation of silicon oxide nanowires (SiONWs) and carbon black after the annealing of C:Ni nanocluster film at 1000°C. Localized transformation of carbon using laser annealing has also been reported in this thesis. Results show the possible factors that affect the microstructure and property change during laser annealing, such as initial film property— sp^3 content of the film, the film stress, and laser energy density. HRTEM shows the enhancement in formation of graphite-like sp^2 cluster as the laser energy density increases, while for C:Ni nanocluster film curved carbon fringes enclosing the Ni nanoparticle are observed after annealing using high laser energy density.

Lastly, this thesis reports on the growth of carbon nanotubes (CNTs) on C:Me nanocluster films such as C:Co nanocluster, which can be used as carbon hybrid system. The C:Co nanocluster film deposited using a 500°C growth temperature shows electrical conducting behavior, which can be used to eliminate the use of insulating barrier layer used in conventional CNTs growth.

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Chapter 1: Introduction

1.1 Motivations

In modern electronics, due to the continuous down scaling in device dimension and the augment in complexity and functionality of various device applications, well established bulk materials have become the show-stopper for further development. Even for the case of copper (Cu), one of the most popular materials for conventional interconnects, it is mentioned in the International Technology Roadmap for Semiconductors (ITRS) 2011 that it has become a bottleneck for the further scaling down in the interconnect geometry, due to the significant effects of its surface and grain boundary scattering [1]. On the other hand, nanomaterials, such as nanoclusters, a material with size lesser than 10nm in its diameter, have gained traction due to its many unique properties. In the past decade, metallic nanoclusters have attracted a lot of attentions. For example, gold (Au) nanoclusters are believed to be a suitable candidate for the next generation of high density non-volatile memory, owing to the advantage in ease of scaling [2]. Besides, metallic nanoclusters exhibit potential in many applied fields due to their excellent ferromagnetism property [3], photoluminescence [4, 5], quantum behavior [6], single-molecule optoelectronics [7] and high activity and selectivity behavior [8]. However, due to their large surface to volume ratio, most of those metallic nanoclusters will be easily oxidized, agglomerated and corroded in atmospheric environment [9, 10]. Hence, to utilize metallic nanoclusters in practical applications,

encapsulation of these metallic nanoclusters with materials which are more stable in atmospheric environment is necessary.

Oxide based materials are commonly used for nanoclusters encapsulation, such as silicon dioxide (SiO_2) and hafnium oxide (HfO_2), because of their thermal stability and mechanical support. However, oxide based encapsulating nanoclusters materials are limited for memory applications due to their insulating nature. On the other hand, carbon encapsulated metallic nanocluster (C:Me) system has attracted more attention due to its higher chemical and thermal stability [11-13], cheaper, easier for fabrication and lighter in weight. Moreover, unlike oxide based material, the C encapsulating layer can be easily de-encapsulated when it is required, by hydrogen or oxygen plasma treatment [14].

Carbon, the smallest atom of group 14 on the periodic table is known as one of the few elements since antiquity and the basic building block for everything on the earth. Owing to three different possible hybridizations— sp^1 , sp^2 and sp^3 hybridized orbitals, C can exist in many natural forms. Among those, the two best known carbon allotropes are diamond and graphite, which consists of only sp^3 or sp^2 hybridized orbitals respectively. Unlike diamond and graphite, which only consists of single type of carbon orbitals, amorphous carbon (a-C) contains a mixture of all three types of carbon hybridization. In past decades, many research works have been done on a-C, regarding to its synthesis, properties and applications. Dependent on its hybridization configurations, a-C is able to exhibit a large variety of different intrinsic properties [15-21].

For instance, diamond-like carbon (DLC), a type of a-C with high fraction of sp^3 hybridized orbitals, has high hardness and elastic modulus, excellent wear resistance, low

coefficient of friction, chemical inertness, large band gap, transparency in the IR and visible region, high electrical resistivity, high dielectric strength and excellent thermal conductivity [17]. Attributing to these unique properties, DLC films have been adopted in many industrial applications, such as protective coatings for hard disk media, heat sink material, tribological applications and protective coatings for optical devices [17, 18, 22-26].

In contrast to DLC films, graphite-like carbon (GLC) film is another type of a-C with a majority of the carbon hybridization in sp^2 orbitals. The high content of sp^2 allows the GLC film to exhibit a better electrical performance as compared with DLC [27]. Besides, although it has been widely known that the superior mechanical properties of carbon film are governed by the high content of sp^3 [17, 18, 28], recently, GLC is also shown to have excellent mechanical and tribological performance [29-31]. It is believed that the superior mechanical properties of GLC is contributed by the cross-linking between the graphite-like planes in amorphous network [32]. The improved hard GLC coating could overcome the high compressive stress issue related to DLC film, which is the main restriction to its poor adhesion property [30-32].

Lately, nanocrystalline graphite (NCG), another type of GLC film that consists of nanometer sized sp^2 clusters within the film, has been discovered [33-37]. While typical GLC is only defined by the content of sp^2 hybridization and not restricted by the orientation of sp^2 clusters, as a result of the biaxial stress presented within the NCG films, their basal planes are oriented perpendicular to the direction of the highest stress component during film growth. Figure 1-1, shows Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED) of the typical NCG film [38]. Due

to the basal planes orientation, NCG film has demonstrated excellent through-film electrical and thermal conductivity [39-41], which makes it a promising candidate for future electrical and thermal applications.

Figure 1-1 Cross section HRTEM image of NCG film deposited using FCVA technique [38]

Hence, with different types of carbon encapsulated layer, C:Me nanocluster films are suggested to have various interesting properties as well. Despite retaining the original properties such as ferromagnetism, biological labeling, catalysis and trace of tumors [42-45], C:Me nanocluster films are also able to exhibit better performance comparing to pure C film. For example, the most common advantages of C:Me nanocluster film over pure C film is overcoming the high compressive stress issue, which can improve the film adhesion [46, 47]. In addition, other mechanical properties of carbon based thin film also can be improved with the presence of metal nanoclusters within the film, such as high hardness, low friction coefficient, high thermal stability and high electrical conductivity

[48-51]. However, to realize all these, the synthesis of the C:Me nanocluster film must be come to the first.

Typically, there are several approaches to produce C:Me nanoclusters film, such as by having electrical arcing discharged between metal - graphite junction[12, 52, 53], detonation[11, 54], pulsed laser deposition (PLD) [55], mass selected ion beam deposition (MSIBD) [56], unbalanced magnetron sputter [57, 58], high temperature treatment of mixture of carbon based material and metal precursors [59], pyrolysis of organometallic compound [60] and chemical vapor deposition (CVD) [61-63]. Although large quantity of C:Me nanocluster films have been successfully synthesized through these methods, there are drawbacks including a slow deposition rate, contamination of unwanted macroparticles, and the need of high Radio Frequency (RF) power and temperature which may hinder the applications of metastable nanoparticles, and metals with low melting point. Besides, the control of the thin film composition is limited because the content of the target is usually prefixed. In addition, the actual metal content in the C:Me film could be different from the C:Me target, due to the difference in melting points of the two elements that affects the ionized rate of the element, and would also significantly affect the consistency in the quality of the as-deposited film [55].

Furthermore, despite the increase in interest for C:Me nanocluster thin film and the rich configurations and properties of C thin film, there is still a lack of understanding of the correlation between various type of carbon microstructure encapsulation and the properties of the C:Me nanocluster film. It is therefore worthwhile to study the various in-situ and ex-situ formation and transformation of the carbon encapsulation layer, as well as their properties, and hence extend the range of applications of C:Me thin films.

1.2 Objectives

The main objective of the PhD project is to design a novel C:Me deposition system based on filtered cathodic vacuum arc (FCVA) technique that is capable of controlling the size, density and content of the metal nanoclusters, and to infuse Me nanoclusters into the continuous carbon thin film. Furthermore, the formation and transformation of the carbon encapsulation layer, the material properties of the deposited films, and their potential applications will also be studied. The details are listed as follows:

- To design and develop a new FCVA deposition system that could deposit two separate elements simultaneously and capable of producing C:Me nanoclusters thin film. In addition, how to deduce an approach to control the size distribution and the density of the nanoclusters will be also discussed.
- To characterize the deposition system by studying the composition of the C and Me content of the deposited film through various deposition parameters, such as arc current.
- To examine the possibility of controlling the microstructural properties of carbon encapsulation layer with in-situ and ex-situ approaches and to study the correlation of the whole film material properties.
- To explore the possible applications of C:Me nanocluster film.

1.3 Major Contributions of the Thesis

This thesis includes the design and development of the Y-bend FCVA deposition system, deposition of different kinds of C:Me nanocluster films, and the study of their material properties with various characterization methods. Major contributions of the thesis can be summarized as below:

- An innovative deposition system that is based on FCVA technology and capable of controlling the size distribution and clusters density is developed and patented. The system consists of a customized Y-bend magnetic filter that connects to two separate plasma target sources and a magnetic confinement setup that could enhance the intermixing of the 2 plasma beams. The Y-bend magnetic filter is to provide guiding for the plasma beams and focus into one while the magnetic confinement increases the density of the plasma, so as to increase their interaction. Properties of the deposited film could be controlled with various deposition parameters, such as the arc current, Y-bend filtering current and the strength of the magnetic confinement.
- C:Me nanocluster films such as C:Zn, C:Ni, C:Ti, C:Co nanocluster films have been successfully synthesized with the FCVA nanocluster system. The way to control the metal content and metal nanocluster density by changing the deposition parameters has been investigated. The metal cluster density can be controlled by varying the input current of the anti-Helmholtz focusing coil, which is shown by scanning electron microscope (SEM). By changing the arc current of the source, the metal content can be controlled, and the microstructure of carbon is also able to be tailored. Visible Raman spectroscopy shows the effect of increasing in metal content on the film

microstructure, the electrical measurement shows an improvement of electrical conductivity by incorporating more metal into the C:Me nanocluster film, and the formation of conducting graphite-like sp^2 clusters.

- C:Me nanocluster film with metal nanoclusters encapsulated with different forms of C substructures has been achieved. With fixing of deposition parameters such as arc current and focus current, only deposition temperature varies, the microstructure of the carbon can be influenced. The effect of deposition temperature on the C:Me film composition is studied using X-ray photoelectron spectroscopy (XPS), and the microstructure of the C:Me can be delineated by visible Raman spectroscopy. The detailed microstructure of the film can be shown using high resolution transmission electron microscopy (HRTEM). In addition, the electrical properties and tribological properties such as electrical resistivity and coefficient of friction are also measured and compared with those films without metal nanoclusters incorporated.
- The microstructural change of carbon film during post treatment with the presence of different metal nanoclusters has been studied. The conventional treatment such as thermal annealing was firstly performed on different carbon based thin film, the film transformation is shown by visible Raman spectroscopy and SEM. Despite thermal annealing, a localized microstructural transformation of C:Ni nanocluster film has been achieved using pulsed laser annealing. C film with different content of initial sp^3 content is used as reference samples to study the effect of laser annealing on C:Ni nanocluster film. The microstructural changes of the both C and C:Ni films before and

after laser annealing is shown by HRTEM, XPS and visible Raman spectroscopy. The change in electrical resistivity upon laser annealing with different laser energy densities is also shown by electrical measurement.

- Some possible applications of using C:Me nanocluster film have been demonstrated. CNTs are grown on C:Co nanocluster films with different electrical conductivity. With the presence of electrical conducting graphite-like sp^2 clusters and Co nanoclusters, the highly conducting C:Co nanocluster film can eliminate the use of barrier layer for CNTs growth using conventional Ni, Co and Fe catalyst. Raman result also shows a lower defect level for CNTs growth on C:Co nanocluster film with graphite-like sp^2 clusters.

1.4 Organization of the Thesis

The thesis is organized into the following chapters:

- Chapter 1 states the motivations, objectives and major contributions of the thesis.
- Chapter 2 provides the literature review of nanoclusters, especially on metallic nanocluster synthesis. This chapter also reviews on various carbon based materials, such as the different hybridization of C and deposition mechanism of a-C film. Current synthesis methods for C:Me film and as well as the characterization techniques used in this thesis are also discussed.

- Chapter 3 discusses the design and implementation of the Y-bend FCVA deposition system, which is able to synthesize C:Me film consisting of different types of nanoclusters without using a complex mixing target. Using Zn as an example, the feasibility of control the nanocluster distribution using the system has been shown.
- Chapter 4 demonstrates the synthesis of C:Me nanocluster film (C:Ni) with different Ni content and microstructure by simply controlling the arc current of Ni source.
- Chapter 5 investigates the effect of growth temperature on the composition, microstructure and properties of C:Me nanocluster film (C:Ni and C:Ti).
- Chapter 6 reports the post treatment, such as thermal and laser annealing effect on pure C films and C:Ni nanocluster films, on the aspect of their microstructure and electrical property evolution.
- Chapter 7 shows some possible applications by using C:Me nanocluster films. In this chapter, C:Co nanocluster films with different initial sp^2/sp^3 ratio were used as the catalyst layer for CNT growth.
- Chapter 8 gives the conclusion and recommendations for future work.

Chapter 2: Literature Review

2.1 Introduction

Carbon, the main composition of C:Me nanocluster film will be focused in this thesis, and the basic fundamentals of carbon such as carbon hybridizations, and deposition mechanism of carbon will be reviewed. In addition, as metal nanocluster is the main nanocluster type discussed in this thesis, a review on metal nanocluster especially its synthesis method will be discussed. As the most important phase for material study is its synthesis method, therefore in this thesis, the common methods for C:Me nanocluster film deposition will be compared, in term of mechanism, advantages and disadvantages. Last but not least, the characterization tools which are used to analyze the structures and properties the films will be introduced.

2.2 Carbon

As mentioned in previous chapter, carbon is one of the most versatile on earth which can have many forms of carbon based material. This is mainly due to its complex hybridizations. The electronic structure of carbon, is known as $1s^2$, $2s^2$ and $2p^2$, where only the four electrons from the valence shell— $2s^2$ and $2p^2$ contribute to the formation of chemical bonding [64]. Figure 2-1 a and b show formation of different carbon orbitals, example of related carbon based chemical respectively. In Figure 2-1 a, the lowest energy

state—ground state of carbon can be shown in (i). Based on the ground state electron configuration, there are two valence electrons in the 2s sub-shell and another two in the 2p sub-shell, while the two electrons in the inner 1s shell are not available for bond formation. This hybridization process starts with the excitation of one 2s electron into the empty 2p orbital, and based on the intermixing of the 2s electron with 2p electrons, there are three different types of hybridization formed. When the 2s electron mixes with all three 2p electrons, shown in (ii), four sp^3 hybrids form. sp^2 and sp^1 hybrids form when the 2s electron only mixes with two and one 2p electron respectively, which can be shown in (iii) and (iv). Ethane, ethane and ethyne are the most common chemical contains sp^3 , sp^2 and sp^1 bonded carbon, which are shown in Figure 2-1 b. Different orbitals participate in the formation of hybridization, as shown in Figure 2-2 below. In sp^3 hybridization, all four 2p electrons are involved in forming hybridization, with four σ bonds forming. For sp^2 and sp^1 hybridization, only three or two 2p electrons participate in hybridization, resulting the formation of additional π bonds which affect the material properties significantly, such as electrical conductivity, field emission and thermal conductivity [17].

Figure 2-1 (a) Formation of different carbon orbital, and (b) example of carbon based chemical contains sp^3 , sp^2 and sp^1 [17]

Figure 2-2 Carbon Hybridizations [17]

Due to this variety of possible bonding configuration, carbon has many allotropes, for example, the most common ones—diamond and graphite, which consist only sp^3 or sp^2 bonded carbon, some carbon nanostructure—graphene (single layer of graphite), carbon nanotubes and fullerenes (graphene sheets rolled over themselves forming cylinders or spheres, respectively), and another type—amorphous carbon (a-C), which is a mixture of sp^3 and sp^2 bonded carbon (very little amount of sp^1 bonded carbon), will be focused in this thesis.

2.3 Deposition Mechanism of a-C Thin Film

As mentioned in previous chapter, the properties of a-C film have closed relation with the amount of sp^3 and sp^2 bonding. Hence it is crucial to understand the formation mechanism of sp^3 and sp^2 bonding during the a-C film growth. The widely accepted mechanism is known as the subplantation model proposed by Lifshitz et al [65-67] and modified by Robertson [68]. They believe that subplantation of impinging ions is the crucial factor for stabilization of sp^3 hybridization. Based on this model, as shown in

Figure 2-3, the incident beam contains the impinging ion reaches the target substrate (in this thesis, the substrate used is Silicon substrate). The penetration profile depends on the mass and energy of the impinging ions as well as substrate properties. As illustrated in Figure 2-3, within the incident beam, a fraction “ ϕ ” are energetic ions (with energy higher than 32eV) [17]. The ions has lower energy will stick on the surface with its lowest energy state— sp^2 state. Next step is the stoppage of the impinging ions due to three main energy loss mechanisms, namely atomic displacement, phonon excitation and electron excitation, and only a fraction “ f ” of these energetic ions are able to penetrate the surface. Furthermore, a fraction of interstitials below the surface “ n ” determines the relaxing fraction—“ $n\beta$ ”. Since the deposition is accompanied by subplantation, during the early stages of the growth, the surface is just composed of the substrate atoms. However, the surface is gradually evolved by mixing of substrate and impinging ions and eventually a uniform phase consisting of depositing ions is formed.

Figure 2-3 Schematic diagram of subplantation process [17]

Using depth profile Auger spectroscopy Lifshitz et al. proves the presence of subplantation in PVD growth of carbon films. Supported by Moller’s modeling work [69], they then claimed that sp^2 and sp^3 sites would be displaced into interstitial sites and then

returned back to sp^2 or sp^3 sites. The sp^3 percentage will increase if there is a preferential displacement of sp^2 sites. Lifshitz used the displacement threshold of 25 and 80 eV for sp^2 and sp^3 bonded carbon proposed by Kelly [70] and Clark [71] respectively. However, more recent direct measurements of displacement thresholds show similar values for displacement of sp^2 and sp^3 bonded atoms (~ 35 eV) [72-74]. Robertson then proposed that subplantation results in local increase in density which stabilizes sp^3 bonding [75, 76].

Based on this model, a low energy carbon ion cannot penetrate the substrate or the growing film and will stick to the surface at its lowest possible energy configuration—the sp^2 sites; however, if the ion energy is higher than the required penetration energy, the ion penetrates into the subsurface and increases the density locally. Density increase results in stabilization of sp^3 hybridization. If the ion energy is further increased, the ion penetrates deeper into the surface. However, the excess energy is transferred to the neighboring atoms as thermal energy and results in relaxation of sp^3 sites to lower energy sp^2 hybridization through formation of high temperature thermal spikes.

Figure 2-4 Sp^3 fraction as the function of C ion energy [17]

In summary, according to subplantation theory, as shown in Figure 2-4 above, low energy ions result in the formation of high sp^2 content a-C films. Increase in ion energy (~ 100 eV), results in stabilization of sp^3 hybridization through local increase in density. Further increase in ion energy on the other hand, results in relaxation of sp^3 sites and hence increases the sp^2 content of the a-C film.

2.4 Metal Nanoclusters

In the field of modern nanotechnology, size is one of the main elements to classify materials. For example, comparing to bulk form, a particle is defined as a small object which can behave as a whole unit in terms of its transport and properties. Based on its size, it can be further assorted into different types. For example, those in the size range between 10000 and 2500 nm, they are defined as coarse particles. In the size range between 2500 and 100 nm, they are known as fine particles, and ultrafine particles also known as nanoparticles are in the size range between 1 and 100 nm. Nanoclusters are nanoparticles with the size between 1 and 10 nm. As they are considered as species intermediate in size between molecules and bulk matter, they can demonstrate different properties in contrast of their molecular and bulk form. As mentioned in chapter 1, nanoclusters exhibit many unique and outstanding properties, however before being able to utilize these nanoclusters, the synthesis must be considered. According to literatures, there are a few techniques to synthesize nanoclusters: attrition and pyrolysis, and thermal plasma.

Attrition and pyrolysis—In attrition, macro and micro scaled particles are placed in a ball mill to reduce their size. The milled particles are then recovered to nanoclusters using air classification, which is a process to separate lighter particles from heavier particles through vertically directing a stream of gas or liquid. In pyrolysis, a vaporous precursor in either liquid or gas form is forced through a venting port at high pressure and burned. The resulting product in solid form is air classified to recover oxide particles from by-product gases. Pyrolysis regularly leads the aggregation and agglomeration of nanoclusters rather than single primary clusters [77].

Unlike attrition and pyrolysis, which forms nanoclusters through mechanical approaches, another approach—thermal plasma forms nanoclusters through vaporizing the target material by supplying sufficient energy. The temperature up to 10,000 K can be generated by the thermal plasma, hence the target material can be evaporated from their solid form. Nanoclusters then can be synthesized by cooling down when they leave from the thermal plasma zone. Direct current—DC arc plasma and radio frequency—RF induction plasma are the common thermal plasma approaches to produce nanoclusters. In the DC arc plasma reactors, the energy used for evaporating the target material, and causing the reaction to happen is supplied by a DC electric arc generated between anode and cathode. In RF induction plasma approaches, energy used to generate the plasma is realized by the induction coil-induced electromagnetic field. The plasma gas does not come in contact with electrodes, so that possible sources of contamination can be eliminated, and other than it, a wide range of gases, such as inert, reducing, oxidizing and other corrosive atmospheres can be operated in this approach. The working frequency can be in the range of 200 kHz and 40 MHz. The power level is in the range of 30–50 kW for

laboratory use, while it can be up to 1 MW for large-scaled industrial use. The synthesis of different nanoclusters, such as various ceramic nanoclusters like oxide-based, carbours/carbides and nitrides of Ti and Si have been demonstrated using RF plasma method [78-81].

It can be noticed that mechanical approaches such as attrition and pyrolysis introduce large number of contaminations, thermal plasma is able to reduce the contamination level, however high frequency, high power source is required to make the reaction happen. In addition, all these methods can only generate pure nanoclusters without any encapsulations such as carbon encapsulated layers, which are able to protect nanoclusters, and enhance their performance. Hence other methods which can produce encapsulated nanoclusters such as C:Me nanocluster film are required.

2.5 Methods of C:Me Nanocluster Films Deposition

2.5.1 Sputtering

Sputtering is the most common physical vapor deposition process to deposit carbon based thin film in the industry [17]. Usually DC or RF assisted Ar⁺ ions are used to bombard the graphite target. To enhance the low sputter yield of graphite, magnetron sputtering is commonly used to increase the deposition rate. Permanent magnets are placed behind the graphite target, to create a magnetic trap will form in front of the target where the Ar⁺ ions will be trapped into. Some C atoms will be knocked out from the target, and since they are uncharged, they can leave through the trap and reach the substrate to form the C thin film.

To deposit C:Me nanocluster film using sputtering technique, as shown in Figure 2-5 below, the Co-sputtering system can be used [82-84], in which the Ar⁺ ions bombard the graphite and metal target together, and the C and Me atom will be generated at the same time and reach the substrate together, forming the C:Me nanocluster film. The film properties such as the compositional properties can be controlled by adjusting the RF power connected to each target, and the gas pressure of the deposition chamber. However, due to the neutrality of the C and Me atom generated during bombardment process, there is lack of control for the intermixing of the C and Me atoms, hence the density of the Me cluster within the film is very difficult to control, and the energy of the C and Me species is also independent on the substrate condition such as biasing [17].

Figure 2-5 Schematic diagram of a typical Co-sputtering system [85]

2.5.2 Pulsed Laser Deposition

Pulsed laser deposition (PLD) is another form of physical vapor deposition for thin film synthesis. It uses a laser beam (such as ArF) which is able to provide a very short and intense energy pulse, which hit the target material to cause the material vaporizing. The vaporized material will form the intense plasma plume and reach the substrate to form the

thin film. During the travel of plasma plume to the substrate, the mean ion energy of the deposition species is proportional to the laser fluence used to strike the target material, so that the film properties can be controlled by the laser fluence [86]. Due to the high ionization of the target material, the charged deposition species can be influenced by substrate conditions such as biasing.

Figure 2-6 below is the schematic for a typical PLD system. Many papers have shown by replacing the pure target with a C/Me mixture target, the C:Me nanocluster films can be synthesized [55, 87-89]. However, the lack of magnetic filtering system makes the particles unavoidable. In addition, the intermixing of the C and Me plasma cannot be controlled, the cluster density within the C:Me nanocluster film is also not controllable.

Figure 2-6 Schematic diagram of a typical pulsed laser deposition system [90]

2.5.3 Filtered Cathodic Vacuum Arc

Vacuum cathodic Arc deposition process is designed to deposit thin films for various applications, both in laboratory and industry, since 1960s [91]. The process starts with the generation of arc in a high vacuum, by contacting the target material placed on

the cathode using a small graphite striker, which is connected to the anode. The power supply used to generate the arc is low voltage, high current. When the striker contacts the target material forming the close loop, a high current density with the value up to 10^6 - 10^8 A/cm² [17] can be generated. This small contacting area has a very high localized temperature with the effect of the high current density. The target material will be ionized and form the macroparticles and the desired plasma with a high ion density of up to 10^{13} cm⁻³ [17] for film synthesis. However, macroparticles limit the production of high quality films, and to eliminate this issue, the magnetic filter is introduced into the technique [92]. The toroidal current passing around the magnetic filter generates a magnetic field, which only allow charged ions to pass through the filter and reach the substrate [93]. Figure 2-7 below shows the schematic of a typical FCVA deposition system.

Figure 2-7 Schematic diagram of FCVA deposition system [17]

Compared to other PVD deposition methods, the ability to produce highly ionized plasma is one of the outstanding advantages of FCVA technique. In addition, the ion energy of the plasma can also be controlled by changing the substrate bias. Unlike sputtering, which is only able to produce neutral atoms during deposition, the highly

ionized C^+ and Me^{n+} species generated during FCVA process are influenced by the focusing magnetic field before reaching the substrate.

Currently, the most common method to synthesize C:Me nanocluster films by FCVA technique is realized using C/Me targets. Its drawback is the difficulty in controlling the metal content, which is due to the different melting points, sputter yields and other factors governed by the material nature of carbon and different kinds of metal. Lin et al. has shown that the actual metal content within the film is not equivalent to the target composition [94]. Moreover, the utilization of carbon and metal within the mix target is also not the same, hence for each different deposition, the metal content will vary. Othon R. Monteiro [95] has invented a dual source structure to generate two plasmas at the same time, as shown in Figure 2-8 below. Various types of C:Me nanocluster films have been shown to be achievable using this method [51, 96-98], however, all current designs do not consist of the plasma focusing system, hence the control of cluster density is still not available.

Figure 2-8 Schematic representation of dual source plasma deposition technique [95]

2.6 Characterization Methods for C:Me Films

2.6.1 Energy Dispersive X-Ray Spectroscopy

Energy dispersive X-Ray spectroscopy (EDX) is a common analytical technique to analyze the elemental or chemical detail of thin film materials, which can reveal the film composition quantitatively [99]. The main components governing the ability to measure the film composition are:

1. The excitation source, which can be an electron beam (used in scanning electron microscope—SEM), or X-Ray Beam (used in X-Ray fluorescence—XRF).
2. The X-Ray detector. The most common material used for the EDX detector crystal is silicon doped with lithium, which can be considered as “intrinsic” semiconductor because of its higher purity level [100], and the Si(Li) crystal is encapsulated within a cooler consisting of liquid nitrogen, which can cool the detector to cryogenic temperatures during the EDX scan.
3. The pulse processor is used to measure the electronic signals to determine each X-Ray’s energy collected by the detector.
4. The analyzer shows the X-Ray data, and performs the necessary interpretations of the data.

The working principle of EDX is based on the interaction of the impinging source which can create the X-Ray excitation and the sample. Before scanning by the excitation source of the EDX spectrometer, the material atom has ground state electrons at discrete energy levels. When a high energy electron beam (depends on the material under investigation) first scans the sample, the electron beam excites the inner shell (lower

energy level E_1) electrons within the sample and eject them from their initial location, which results in electron holes. The electron from an outer shell which has the higher energy level (E_2) will then recombine with hole in the inner shell, at the same time emitting the energy in form of X-Ray ($E = E_2 - E_1$). The energy emitted is then detected by the EDX detector and the signal will be processed by the pulse processor. Finally the analyzer displays the EDX spectrum which is unique for certain elements. The illustration of the EDX detecting procedure is shown in Figure 2-9 below.

Figure 2-9 The working principle of Energy dispersive X-Ray spectroscopy

2.6.2 X-Ray Photoelectron Spectroscopy

Unlike EDX spectroscopy which is only able to detect the type of element and the quantity, X-Ray Photoelectron spectroscopy (XPS) can be used to determine the chemical composition and bonding details of the thin film [101], especially for C:Me nanocluster film, which may consist of more than one type of element. By using XPS analysis, the content of sp^2 and sp^3 bonded carbon, the existing form of the metal nanoclusters within the film can be determined[102].

Instead of using an electron beam as the excitation source, XPS uses a monochromatic X-Ray source, which can be magnesium (Mg) K_α radiation ($h\nu = 1253.6$

eV), or aluminum (Al) K_{α} radiation ($h\nu = 1486.6$ eV). When the photon or electron of the X-Ray source with energy of $h\nu$ focuses on the thin film sample, only the electron at the inner level (core-level) will response to the X-Ray energy, because the core electrons have a higher probability to match the energies of (Al) K_{α} or (Mg) K_{α} . This process is illustrated in Figure 2-10. The electron ejected by the X-Ray energy is defined as photoelectron, with a kinetic energy of K.E, and the binding energy B.E which is the difference in energy between the ionized and neutral atoms, based on the conservation of energy, can be expressed in Equation 2.1:

$$B.E = h\nu - K.E \quad 2.1$$

Figure 2-10 The working principle of X-Ray Photoelectron spectroscopy

Figure 2-11 Schematic of X-Ray Photoelectron spectroscopy system

Figure 2-11 is the schematic of a typical XPS working setup, which includes the focused beam of X-Ray source, electron collection lens, electron analyzer and electron detector. It is observed that the photoelectrons emitted from the material atoms by the excitation of X-Ray energy are collected by the electron collection lens. The K.E of the collected photoelectrons will then be measured by the electron energy analyzer. The total count of photoelectrons emitted from different material is detected by the electron detector, and reflected in the XPS spectrum, which is a plot of total count of electrons versus the B.E of the electrons detected. Based on the XPS peaks, the corresponding element within the material surface can be determined. These characteristic spectral peaks correspond to the electron configuration of the electrons within the atoms, for example, amorphous carbon which contains sp^2 and sp^3 bonded carbon, and thus its sp^2 and sp^3 ratio can be determined based on the XPS spectrum.

The analysis of the samples in this thesis was carried out using a VG ESCA 220i-XL Imaging XPS last calibrated in March 2012. Monochromatic Al $K\alpha$ X-Ray ($h\nu=1486.6$ eV) is employed for analysis with a photoelectron take-off angle of 90° respect to surface plane. The analysis area is approximately $700\ \mu\text{m}$ in diameter while the maximum analysis depth lay in the range of 4-8nm. Survey spectra were acquired for elemental identification while high resolution spectra were acquired for chemical state identification and surface composition calculation. The elemental composition of the thin film can be calculated use the Equation 2.2 below:

$$Y = \frac{\frac{A}{S}}{\sum_{i=1}^N (\frac{A}{S})} \quad 2.2$$

where Y is the composition of the element, A is the area of the overall area under the element in its spectrum, and S is the sensitivity factor.

Charge compensation was performed by means of low energy electron flooding and further correction was made based on C1s in graphite at 284.5 eV using the manufacturer's standard software. For chemical state analysis, a spectral deconvolution was performed by a curve fitting procedure based on Lorentzians broadened by a Gaussian using the manufacturer's standard software. The error of binding energy is estimated to be within ± 0.2 eV.

2.6.3 Raman Spectroscopy

2.6.3.1 Introduction on Raman Spectroscopy

Raman spectroscopy is one the most common characterization tools to identify materials, especially to determine the bonding structure of materials. It is quick and non-destructive, and relies on the ultra-violet (UV), visible or near infra-red laser as the excitation source. When the incident light—monochromatic light which is from the laser source impinges on the material under test, three different types of scattering between the light photon and the molecule of the material take place, namely Rayleigh scattering, Stokes Raman scattering and anti-Stokes scattering. Among these three type of scattering, only Stokes Raman scattering contributes to the signal useful for Raman spectroscopy [103]. It is based on inelastic scattering of photons by molecules of the material, which is also generally known as Raman scattering. When the incident photon interacts with the molecule in Raman active mode, the molecule becomes excited from the basic vibrational state into a virtual state by the laser photon, and it relaxes into a vibrational excited state,

which is known as Stokes Raman scattering. Based on the nature of inelastic scattering process, there is an exchange of energy between the scattered photon and the scattering molecule. The Raman effect is able to probe the vibrational energy of molecules and then can identify the structure.

Figure 2-12 Possible excitation process during a Raman process

The excitation process is illustrated in Figure 2-12. The thickness of the excitation lines indicates the signal strength of the scattering, whereas the Rayleigh scattering is shown to have the strongest signal. To minimize the Rayleigh scattering signal, filters (notch, tunable type), laser stop apertures and triple spectrometric systems can be applied [103].

2.6.3.2 Raman Spectroscopy for Amorphous Carbon

The two common types of Raman techniques to identify amorphous carbon film are visible and UV Raman spectroscopy. Due to the higher photon energy of UV mode, both σ and π states can be excited. As mentioned in the previous section, σ state indicates sp^3 bonded carbon and π state indicates sp^2 bonded carbon, hence UV Raman spectroscopy is able to detect both sp^2 and sp^3 bonded carbon directly. In contrast, in

Visible Raman, due to the lower energy of visible photons, only π states can be excited by the photon, hence generally visible Raman spectroscopy is 50-230 times more sensitive to sp^2 bonded carbon [104]. However, by using several interpretation techniques of Raman spectrum collected by visible Raman spectroscopy, the sp^3 fraction can also be known. In this thesis, due to the availability of equipment, only visible Raman spectroscopy will be focused.

For amorphous carbon, which is disordered form of carbon, there are two possible vibration modes which are defined as “G” and “D” mode [105-107], are shown in Figure 2-13 below. Figure 2-13 a indicates the G mode vibration. For the Raman peak caused by the G mode vibration, it has E_{2g} symmetry which involves the in-plane bond-stretching motions of pairs of sp^2 bonded carbon atoms. For this mode, sixfold rings are not required, hence it can be any type of sp^2 bonds—chain or ring-like. The G peak of amorphous carbon normally lies between $1500\sim 1630\text{ cm}^{-1}$. Unlike G mode, D mode is due to a breathing mode of A_{1g} symmetry shown in Figure 2-13 b, which involves phonons near the K zone boundary. It is only caused by sixfold aromatic ring-like sp^2 bonded carbon—NCG carbon, which does not appear in perfect single crystal graphite.

Figure 2-13 Vibration of sp^2 bonded carbon, (a) G mode and (b) D mode [17]

Although visible Raman spectroscopy is only sensitive to sp^2 bonded carbon, the sp^2/sp^3 fraction of amorphous carbon can be still derived using the information collected from the visible Raman spectrum, such as the intensity ratio of D peak and G peak—I(D)/I(G) ratio, and G peak position. For example, Tunistra and Koenig (TK) [107] has shown the relationship between the graphite-like sp^2 cluster and the I(D)/I(G) ratio, Equation 2.3 below shows the sp^2 cluster size (L_a) can be calculated by knowing the I(D)/I(G) ratio:

$$\frac{I_D}{I_G} = \frac{C(\lambda)}{L_a} \quad 2.3$$

where $C(\lambda)$ is a constant which is depended on the wavenumber of laser used in the Raman system, for example $C(515.5 \text{ nm}) \approx 44 \text{ \AA}$ [104].

In the visible Raman spectrum of amorphous carbon, there are a few factors which determine the shape of the spectrum—the clustering of the sp^2 phase, presence of chain or ring-like sp^2 bonded carbon, bond disorder and the sp^2/sp^3 ratio. Figure 2-14 below is the schematic showing how these factors can influence the shape of Raman spectrum.

Figure 2-14 Schematic diagram of influences on the Raman spectrum [17]

Figure 2-15 Three-stage model of Raman features [17]

To determine the microstructure of amorphous carbon, A.C Ferrari and J. Robertson has come out a three-stage model based on the study of various carbon films (from ta-C to nanocrystalline graphite) [108], which is used to indicate the amorphization of amorphous carbon. The three-stage mode is shown in Figure 2-15. It reflects the

relationship between the sp^3 fraction, phase of carbon film and the Raman features—G peak position and $I(D)/I(G)$ ratio.

Stage 1: Graphite—Nanocrystalline (NC) graphite:

In this stage, the main changes during evolution of the Raman spectrum are:

1. The G peak position moves up from $\sim 1581\text{ cm}^{-1}$ to $\sim 1600\text{ cm}^{-1}$
2. D peak starts to appear. As mentioned previously, D mode vibration is forbidden in graphite. The $I(D)/I(G)$ ratio increases as the graphite-like sp^2 cluster size decreases, hence in this stage, the change in intensity of the D peak follows the TK Equation.
3. There is no G peak dispersion. The main change in microstructure in this stage is pure graphite (single crystal) transforming into nanocrystalline graphite. Within the film, there is still all sp^2 bonded carbon. The increase of G peak position is because of the G peak merging with the second order D' peak, which is located at about 1620 cm^{-1} . The single line fit to G + D' peak results the increase of G peak position.

Stage 2: Nanocrystalline (NC) graphite—Amorphous carbon (a-C):

In this stage, the main changes during evolution of the Raman spectrum are:

1. The G peak position moves down from ~ 1600 to $\sim 1510\text{ cm}^{-1}$.
2. The $I(D)/I(G)$ ratio decreases from its maximum to zero value.
3. The size of graphite-like sp^2 cluster is proportional to the $I(D)/I(G)$ ratio, hence the TK Equation is no longer applicable.

In this stage, the disorder of the carbon will be further enhanced. At the end of this stage, the material is almost completely amorphous sp^2 carbon, without any nanocrystalline structure. The maximum sp^3 content in the end of this stage is only 20 % [109]. The decrease in $I(D)/I(G)$ ratio is due to the drop of D peak intensity caused by the decrease in ordered sp^2 rings. However the G peak is only influenced by the bond-stretching of sp^2 pairs (either chain or ring-like sp^2 bonded carbon), hence with a constant sp^2 content, the G peak intensity is not affected, so the $I(D)/I(G)$ decreases with the increase of amorphization degree. To describe the sp^2 cluster properties using Raman features, A. C Ferrari and J. Robertson [104] has developed another Equation. They conjectured that in this stage, the $I(D)/I(G)$ ratio is proportional to the number of the ordered sp^2 rings, and so is the graphite-like sp^2 cluster size, which can be shown in Equation 2.4 below:

$$\frac{I_D}{I_G} = C'(\lambda)L_a^2 \quad 2.4$$

where $C'(\lambda)$ they used is $C'(514 \text{ nm}) \approx 55 \text{ \AA}$.

Figure 2-16 below shows that L_a with value of about $20 \text{ \AA}$ is the boundary to determine the use of TK Equation or the Equation proposed by A.C Ferrari and J. Robertson.

Figure 2-16 The correlation between $I(D)/I(G)$ and sp^2 cluster size [17]

Stage 3: Amorphous carbon (a-C)—Tetrahedral carbon (ta-C):

In this stage, the main changes of the carbon film are the significant increase of sp^3 content, from ~10-20% to ~85%, and the transformation of sp^2 bonds from rings to chains. The remaining sp^2 bonded carbons are embedded within an amorphous sp^3 matrix [110, 111]. The main change in carbon microstructure is reflected by a few changes in Raman spectrum:

1. The G peak position moves up from ~1510 to 1570 cm^{-1} .
2. The $I(D)/I(G)$ ratio has a very small value which is approximately zero.
3. The G peak becomes more dispersive.

First of all, the up-shift of G peak position is caused by the structural change of sp^2 bonded carbons, changing their form from aromatic rings into olefinic groups, which have higher vibrational frequencies. In addition, the D peak disappears in this stage, which is caused by the decrease in the ring-like sp^2 bonded carbon.

2.6.3.3 Fitting of Amorphous Carbon Raman Spectrum

To know the detailed Raman features such as G peak position and I(D)/I(G) ratio, Raman curve fitting must be performed after collecting the Raman spectrum. So far there are many different ways to fit the two possible peaks (G peak and D peak) in the Raman spectrum, such as using two Gaussian or two Lorentzian line shapes. But the more accurate way was proposed by S. Praver, which is to use a Breit-Wigner-Fano (BWF) line shape for G peak, while a Lorentzian line shape is used for D peak [112], and the function of these two line shape can be shown in Equation 2.5 and 2.6 below:

$$I(\omega) = \frac{I_0[1 + \frac{2(\omega - \omega_0)^2}{Q\Gamma}]^2}{1 + [\frac{2(\omega - \omega_0)}{\Gamma}]^2} \quad \text{BWF} \quad 2.5$$

$$I(\omega) = \frac{\Gamma}{\Gamma^2 + \pi(\omega - \omega_0)^2} \quad \text{Lorentzian} \quad 2.6$$

where I_0 is the intensity of the G peak, ω_0 is the peak position for either G and D peak, Γ is the full width half maximum (FWHM) of the peak, and Q is the inverse of the BWF coupling coefficient [112].

Normally for amorphous carbon with high sp^3 content, the Raman spectrum can be fitted using a single BWF line shape. When sp^2 content and ring-like sp^2 bonded carbon increases, and the spectrum can no longer be fitted by only BWF line shape, the Lorentzian line shape is required.

2.6.4 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) is the most powerful tool to study the morphology, microstructure and local chemistry of materials such as metals, ceramic, and

other nanomaterials. TEM is used to study the detailed microstructure by providing high resolution and high magnification images. Its other functions such as diffraction pattern or electron energy loss (EELS) analysis provides information on crystal structure, orientation of the crystalline structure, and chemical compositions of phases, precipitates.

The first TEM was built in 1931 by Max Knoll and Ernst Ruska [113], while the first commercial TEM (Metropolitan Vickers EM1) was then built in 1939. The most significant development in TEM history is the thinning of the metal specimen down to electron transparency by Heidenreich [114]. Nowadays, TEM analysis is able to obtain the high resolution images up to 5000000x magnifications, and the best resolution achieved so far is 0.5 Å.

Figure 2-17 Schematic diagram of typical TEM system

The basic working principle of TEM is the interaction of an electron beam with the material atoms as passes through the ultra-thin material specimen. Figure 2-17 above shows the schematic of the typical TEM. To form the TEM images, the first components

required the electron beam source, which generates electron beam with energy in the range of 10 KeV to 300 KeV (depending on the acceleration voltage applied), and the higher the energy, the better the resolution is. The diverging electron beams then passes through the 1st and 2nd condense lens. The condense lens is constructed by circular electro-magnets generates the precise circular magnetic field. The magnetic field acts as an optical lens to focus the electrons. The condense lens aperture is a thin disk with a small circular through-hole (in range of 2 ~ 100 μm), which is used to filter away those undesired electrons, and only let the necessary electron beam hit the specimen. The electron beam passes through the condense lens aperture, reaches the specimen. The scattering of electrons and specimen then takes place, and the objective lens will form an image of the electron density distribution at the exit surface of the specimen based on the electron optical principles. A diffraction pattern forms in the back focal plane of the objective lens, and the recombination of the diffracted beams forms an image in the image plane of the objective lens. The selected area aperture examines the periodic diffraction of electrons by ordered arrangements of atoms in the specimen. The diffraction and projection lens then magnify either the diffraction pattern or the image, displaying it on the fluorescent screen. The signal of electrons is converted into visible light signal, and viewed from the view window. The resulting images can be recorded on photographic film or with a CCD camera linked to a computer.

Chapter 3: Design and Development of Y-bend FCVA Deposition System

3.1 Introduction

As introduced in previous chapters, FCVA deposition technique can be used to synthesize C:Me film, however C/Me target is required to produce the composite plasma. This may affect the composition of the as-deposited film, due to the different melting points between carbon and specified metal. To overcome this issue, in this thesis, a specially designed FCVA deposition system has been designed and implemented. This system can simultaneously generate two streams of plasma, control the density and intermixing of the nanocluster film. Hence the composition of the film and the density of the metal nanoclusters can be manipulated.

3.2 Design and Implementation of Y-bend FCVA Deposition System

To generate two streams of plasma simultaneously, it is necessary to have two independent arc sources, which are connected to the magnetic filters separately. Hence for this Y-bend FCVA deposition system, the compulsory parts include two sources, two arc current supplies, a specially designed Y-bend magnetic filter, deposition chamber, vacuum pumps. In the following section, the Y-bend magnetic filter will be introduced.

3.2.1 Y-Bend Magnetic Filter

As mentioned in chapter 2, the purpose of using a magnetic filter is to remove those unwanted macroparticles, at the same time maintain the relatively high deposition rate. Hence, our group has invented a patented off-plane double bend (OPDB), with a set of baffles being installed inside to serve as a mechanical filter. The 3-D view of the OPDB filter is shown in Figure 3-1, in the Y-bend FCVA deposition system, one side of the filter is connected to the source, while another side is connected to the deposition chamber.

Figure 3-1 3-D view of the off-plane double bend (OPDB)

In our new design, two sources and two connection ports for source are required. In addition, the two streams of plasma must intermix before reaching the substrate, hence two OPDB filters are required to build the new filter, in order to guide the two streams of plasma and provide the space for intermixing. The two bends are joined together and then connected to the deposition chamber. The schematic of the specially designed filter is illustrated in Figure 3-2. The filter consists of three main parts: A—OPDB filter 1, B—OPDB filter 2 and zone C—the focus coil which are indicated in the schematic. Both the carbon and metal source is connected to independent arc supply. When the suitable arc current is applied, an arc generates and plasma forms after the striker hit the target

material. The ion energy of the two independent plasmas can be controlled by adjusting the DC electrical current of the respective arc source. Due to the charged-nature of the plasma, the magnetic field generated by the OPDB filter 1 and OPDB filter 2 produces a steering force (Lorentz force), acting perpendicularly to the momentum of the charged particle and hence, providing a spirally guided motion for the plasma to travel towards the deposition chamber. The density of these plasma beams can be controlled by tuning the strength of the magnetic field at the Y-bend filter and the arc current of the source. For C:Me nanocluster film deposition, due to the different masses and charges of carbon and metal ion, the required strength of the magnetic field for guiding the ions will be different, by using this Y-bend filter, the two ion plasma can be guided and controlled independently.

Figure 3-2 3-D view of the Y-shaped filter consists of two OPDB filters

The two streams of plasma passing through the OPDB filter 1 and OPDB filter 2 will then enter zone C, engaging their 1st stage of the interaction. Zone C is compulsory since both of the two impinging plasma streams are positively charged, which tend to repel each other. With the effect of this focus coil, they can be confined and intermixed by the magnetic field generated by the focus coil. The strength of the magnetic field can be controlled by the current supplied to the copper wire. Figure 3-3 illustrates the confinement of ions through the focus coil.

Figure 3-3 Confinement of ions through first focus coil

3.2.2 Deposition Vacuum Chamber

The grounded deposition chamber is connected to the exit of the focus coil. To provide the vacuum environment, the chamber is connected to a turbo pump which is back up by a rotary pump. The pressure of the chamber can be pumped down to 1×10^{-7} Torr, however during the deposition the pressure increases due to the presence of deposition ions, but it can be still maintained at 10^{-5} Torr range. The substrate holder placed in this system is connected to the heater. For this system, a Model 101303 temperature controller from HeatWave Labs, Inc. is used, the temperature can be heated up to 1000°C.

3.2.3 Anti-Helmholtz Focus Coil

To further control the density and distribution of the metal nanoclusters, an anti-Helmholtz focus coil is implemented in this deposition system. The 2nd stage of interaction between the two plasmas is established at the magnetic confinement created by the anti-Helmholtz coil within the deposition chamber. The purpose of the magnetic confinement is to condense the density of the intermixed plasma and therefore, increases the probability of the interaction, as illustrated at Figure 3-4 below.

Figure 3-4 Schematic of the intermixing of 2 plasmas through the anti-Helmholtz coil

An anti-Helmholtz coil consists of two electromagnet coils, which are arranged in an anti-parallel configuration. Analogous with permanent magnet, the magnetic field from the two coils are at opposition direction and a net field of zero is created at the center of the coils (magnetic trap), as shown in Figure 3-5.

Figure 3-5 Schematic of the magnetic confinement and the similarity between permanent magnet and electromagnet

To further demonstrate the effect of the anti-Helmholtz coil, the simulation work has been done to show the formation of the magnetic trap by applying suitable current to the coils. The evolution of the resultant magnetic field of the anti-Helmholtz coil with the variation of the current is illustrated in Figure 3-6 below. The electrical current (DC) at electromagnetic coil (upper) is set at 10A, whereas, the current at electromagnetic coil (bottom) is increased from 2.5A, 5A, 7.5A and 10A, corresponds to Figure 3-6 a-d. Obviously no magnetic trap forms when the current applied at the bottom coil is much smaller than the upper one (shown in Figure 3-6 a). Figure 3-6 b-c show that the trap starts to form as the current applied to the bottom coil increases. Distinctively, a zero field (magnetic trap) forms at the center of the coils (shown in Figure 3-6 d) as the strength of the two opposing magnetic fields matches and counteracts with one another.

Figure 3-6 Simulation of the formation of the magnetic trap

Except the condition for the formation of the magnetic trap, it is also necessary to know factors to influence the magnetic trap, hence film properties of the nanocluster film can be controlled. Therefore after implementing the anti-Helmholtz coil, with all magnetic components such as magnetic permeability, and the number of turns of the coil forming by the copper wire being fixing, the only parameter which can be adjusted is the current applied at the two coils. Experimental work has been performed to show how the current affected the trap, resulting in difference on the plasma trapped by the anti-Helmholtz coil. Figure 3-7 a-c show the plasma condition with different current applied at the anti-Helmholtz coil captured by camera. Figure 3-7 a shows the plasma captured when no current is applied at the anti-Helmholtz coil, which is used as the reference to reflect the effect of the magnetic trap generated by the anti-Helmholtz coil. Figure 3-7 b and Figure

3-7 c are captured when 5A and 10A current is applied at the anti-Helmholtz coil, respectively. Due to the formation of the magnetic trap, the plasma previously guided towards the trap was confined and hence, the plasma density increased, as compared to the plasma in Figure 3-7 a. This condensation in plasma density would therefore reduce the mean scattering path of the plasma and enhance the intermixing between the two. Moreover, it is observed that the plasma in Figure 3-7 c is even denser than the one shown in Figure 3-7 b. Hence it indicates that with larger current being applied, the effect of the trap is more pronouncing, the two plasma streams will have more intermixing.

Figure 3-7 Experimental realization of the magnetic trap, (a) without current—no trap, (b) with 5A current and (c) with 10A current

3.3 Operation of Y-bend FCVA Deposition System

All C:Me nanocluster films discussed in the thesis were deposited using the Y-bend FCVA deposition system illustrated in Figure 3-8 a. In addition, Figure 3-8 b-c displays the Y-bend filters and the Y-bend FCVA deposition system. The operation of the deposition system includes:

Figure 3-8 (a) Schematic of the Y-Bend FCVA deposition system, (b) photo of the Y-bend filter and (c) photo of the Y-bend deposition FCVA system

1. Pumping the chamber to the required vacuum level for deposition—not higher than 5×10^{-6} Torr. This is achieved by the rotary pump and the turbo-molecular pump.
2. Adjusting the strength of the magnetic field for the two OPDB filters, the first focus coil, and the anti-Helmholtz coil. Since the amount of the current for the two OPDB filters required to generate the magnetic field with optimized filtering efficiency for different material is different, which depends on the mass and charge of the ion. Hence all of these electromagnetic coils are connected to corresponding DC current supply, so that the strength of magnetic field can be adjusted independently.
3. Generating the carbon and metal plasma by striking the target. To generate and sustain plasma from the material target placed within the source, it is necessary to maintain an electrical arcing across the target material. The current required is material dependent, such as the ionization energy, which relates to the melting point of the material. The graphite target for generating carbon plasma normally requires a 60A current, while for metal, the current required is higher, for example 70A for Zn, and 130A for Ti. Therefore it is necessary to connect the two sources to individual arc current supply.
4. The two streams of plasma are filtered by the two OPDB filters of the system. With macroparticles being filtered away by the filters, only carbon and metal ions are guided into the first focus coil. The two diverging ion beams can be covered and intermixed by the magnetic field generated by the focus coil.

The intermixing of the two beams can be adjusted by controlling the electrical current applied on the focus coil.

5. The converging beams enter into the deposition chamber, before landing on the substrate and forming the C:Me nanocluster film, firstly they will be condensed and intermixed again by the anti-Helmholtz coil. The placement of the anti-Helmholtz coil is crucial, to realize the its effect, the substrate must be placed within the anti-Helmholtz coil and near to the edge of the magnetic trap. In our design, the substrate holder is stationary which is fixed on the deposition chamber, and anti-Helmholtz coil can be moved along the substrate holder, so that the position of the substrate with respect to the magnetic trap can be adjusted. When the condensed ion plasmas reach on the substrate, the C:Me nanocluster film will form, and the microstructure and properties can be also controlled by the heater and bias.

3.4 Deposition of Density Controllable C:Me Nanocluster Films

To test the feasibility of C:Me nanocluster film synthesis, especially the effect of the anti-Helmholtz coil, Zn was firstly selected to be the metal nanocluster material. The reason of selecting Zn is because of its low melting point, which makes it easier for the generation of Zn plasma.

3.4.1 Experimental

To test the effect of the anti-Helmholtz coil, the only parameter varied in this experiment is the strength of the magnetic field generated by it. The (100) N-type silicon wafer was used as substrate, and before depositions, the wafer was firstly cleaned using acetone, followed by ultrasonic isopropanol (IPA) to remove the surface particles. The target used for generating C and Zn plasma is 99.999% graphite and 99.99% zinc, respectively. Table 3-1 below shows the deposition parameters for all as-deposited films, and all the depositions were carried out at room temperature, without any biasing.

	Arc current (A)	Duct current – OPDB (A)	Focus current (A)	Anti-Helmholtz coil current (A)
Film 1	$I_C = 60$ $I_{Zn} = 70$	$I_C = 8$ $I_{Zn} = 6.5$	$I_f = 2.5$	$I_1 = 0$ $I_2 = 0$
Film 2	$I_C = 60$ $I_{Zn} = 70$	$I_C = 8$ $I_{Zn} = 6.5$	$I_f = 2.5$	$I_1 = 5$ $I_2 = 5$
Film 3	$I_C = 60$ $I_{Zn} = 70$	$I_C = 8$ $I_{Zn} = 6.5$	$I_f = 2.5$	$I_1 = 10$ $I_2 = 10$

Table 3-1 Deposition conditions for C:Zn nanocluster films

3.4.2 Results and Discussion

The thickness of each film was 100nm approximately measured by Tencor Surface profiler meter. The SEM images of these films are shown in Figure 3-9 a-c respectively. Clearly, an increment of the nanocluster density (brighter spots) can be observed as the strength of the magnetic field increased.

Figure 3-9 SEM images of the as-deposited C:Zn nanocluster film with magnetic trap set at (a) 0A, (b) 5A and (c) 10A current

To verify the film composition of these as-deposited C:Zn films, the Zn content was measured by energy dispersive X-ray (EDX) spectroscopy. The scan area for each film was 5 μm by 5 μm , and to increase the accuracy of the measurement, 5 different areas were scanned. Figure 3-10 below shows the Zn content as a function of the current applied on the anti-Helmholtz coil. The Zn content increases as the increasing of the current applied, which reflects the effect the magnetic trap generated by the anti-Helmholtz coil. When there is no magnetic trap existing, the two streams of plasma only intermix within the first focus coil, and then immediately reach on the substrate and form the film. However with the influence of the magnetic trap, the C and Zn ions are also condensed and intermixed before forming the film, hence the Zn cluster density increases

comparing to the film deposited without the presence of magnetic trap. As shown in Figure 3-10, the condensing effect of the magnetic trap enhances as the current applied on the anti-Helmholtz coil increases, hence it explains that the increase in Zn content as the current increases from 5 A to 10 A, which is because of the stronger condensing and intermixing effect between C and Zn ions.

Figure 3-10 Zn content as a function of anti-Helmholtz coil current

3.5 Conclusions

In this chapter we have shown the design and implementation of a novel Y-bend FCVA deposition system, which can deposit C:Me nanocluster films. The Y-shape filter which consisted of two OPDB filters was able to filter away macroparticles in two different plasmas, and to guide the desired ions through the magnetic filter. The first focus coil was able to converge the two diverged ion plasma streams, and the resultant plasma stream containing both C and Me ions then entered the magnetic trap generated by the

anti-Helmholtz coil. The C and Me ions can be condensed in different degree according to the strength of the magnetic trap. In addition, the system also had its substrate connected to the heater, which was able to control the microstructure and properties of the C:Me film.

C:Zn films have been successfully deposited using the system. The SEM images and EDX results showed the effect of the magnetic trap generated by the anti-Helmholtz coil. The Zn cluster density was shown to be controllable by changing the current applied on the anti-Helmholtz coil, the higher the current, the denser the Zn cluster density can be achieved.

Chapter 4: The Effect of Ion Density for the Deposition of C:Me Nanocluster Films

4.1 Introduction

The formation of NCG is mainly attributed to the presence of a driving force and the activation energy. For the former, it has been shown previously that the presence of biaxial compressive stress, which is induced by the bombardment of high energy ion species during the film growth, is essential for the phase transition and it is found to be in optimum at an ion energy of $\sim 100\text{eV}$ [17]. Since the biaxial internal stress is in the growth plane, in the vicinity of the transition stress, basal planes will be formed with their orientation perpendicular to the growth direction where the total free energy of the system will be at its lowest. As for the activation of the phase transition, thermal energy is found to have an important role. It has been verified in both theoretically and experimentally that by supplying sufficient substrate annealing during the process of film deposition ($>240^\circ\text{C}$), nanocrystals with preferred orientation could be formed [36]. Besides, thermal activation energy can also be introduced as a form of high temperature spikes through the impinging of the depositing carbon ions. High temperature spikes can be used as a local annealing element and the density of temperature spikes is correlated with the density of depositing ions. With sufficient ion density, it has been demonstrated that graphite-like sp^2 clusters could be formed, even when the deposition is performed at room temperature [115].

While many have studied the incorporation of different metals into carbon thin film to enhance its various material performances [102, 116-118]. Limited work have considered of inducing a microstructural transition of the carbon film with metal infusion to extend its application horizon [119]. Hence, in this study, we have used nickel (Ni) as the metal source and graphite target for the carbon source. Since our main objective is to understand the effect of metal ion impingement on the microstructure of the carbon thin film, only the ion density of the Ni is varied and all the depositions are done at room temperature with no electrical bias applied at the substrate. To examine the elemental composition of the C:Ni thin film, EDX and XPS are used. The microstructural transition of the thin film is observed and analyzed with a HRTEM and visible Raman spectroscopy. Lastly, the implication on the electrical resistivity of the nanocluster film due to the transformation of its microstructure is studied with current-voltage (I-V) probing equipment.

4.2 Experimental

To examine the influence of arc current, pure a-C film and C:Ni nanocluster film using different arc current of Ni source were prepared using Y-bend FCVA deposition system. 99.999% pure graphite target and 99.99% nickel target were used for generating C and Ni plasma. N-type silicon wafers were used for substrate. For the deposition of C:Me thin film, the ion density of Ni was controlled by controlling the arc current of the metal source since for FCVA deposition, the ion density is correlated to its arc current

[120]. C:Ni nanocluster films were deposited at different Ni ion density (arc current of Ni source from 100 A to 140 A, at step of 10 A), with a general film thickness of ~100nm. For the purpose of comparison, a pure C film was deposited at the same deposition condition, without the Ni source.

The content of Ni for the nanocluster film was measured using EDX operated at 18 KeV. The film composition was obtained from a VG ESCA 220i-XL Monochromatic Al K α X-Ray Imaging XPS. The bonding structure of the pure C and C:Ni films were investigated using WITEC CRM200 Raman spectrometer system at an excitation wavelength of 532 nm. The detail microstructure of C:Ni film were examined using JEM 2010 TEM. For the electrical measurement, the I-V characteristic of the films were measured using a cascade 200 nm probe station with a Hewllet Packard 4365A precision semiconductor parameter analyzer with a voltage step of 0.1 V.

4.3 Results and Discussion

4.3.1 Ni Content Measurement using EDX Spectrometer

Figure 4-1 a-c show the EDX spectra of the C:Ni nanocluster film deposited using 100 A, 120 A and 140 A arc current of Ni source. The higher intensity of the Ni signal detected indicates the higher amount of Ni elements within the film. This suggested that the arc current of Ni source was able to influence the ion density of Ni plasma. Figure 4-2 below shows the correlation of the arc current of the Ni plasma source with the ion density of Ni and the atomic percentage of Ni in the deposited C:Ni film. As mentioned before, the ion density of Ni is closely related with the arc current of the Ni source [120]

and this could also be verified from the observation of the increase of the Ni content as the arc current increases. In this experiment, the ion density was measured using a Langmuir probe [120], which was placed at the joint of the two bends. With switching off the arc current of carbon source, the ion density generated by different arc current of Ni source can then be estimated. For the film deposited at an arc current of 100 A, the ion density of Ni is found to be $\sim 16.4 \times 10^{11} \text{ cm}^{-3}$, and based on the atomic ratio of C and Ni provided by the EDX spectrum, the Ni content is estimated to be 1.8 at%. When the arc current increases to 140 A, the ion density of Ni increases to $19.7 \times 10^{11} \text{ cm}^{-3}$ and the Ni content reaches 10.9 at%. For all of our depositions, the arc current for carbon source remains unchanged and therefore, the ion density for C arriving onto the substrate for film formation remains as a constant. By increasing the arc current of Ni source, the ion density of Ni increases and hence, contributing to the amount of Ni for the film formation, as reflected on the elemental analysis measurement.

Figure 4-1 EDX spectra of C:Ni nanocluster film deposited using different arc current of Ni source: (a) 100 A, (b) 120 A and (c) 140 A

Figure 4-2 The Ni ion density and the content of Ni within the film as a function of arc current of Ni source

4.3.2 Film Composition Analysis using XPS

Figure 4-3 a-d show the C 1s core-level XPS spectra of pure C film, and C:Ni nanocluster film deposited with 100 A, 120 A and 140 A in arc current of Ni source, respectively. It can be observed that there are two major peaks all these spectra, which is graphite ($\text{sp}^2\text{—C=C}$ bond) and diamond ($\text{sp}^3\text{—C-C}$ bond) peaks, with their peak center locating at 284.5 eV and 285.5 eV. It can be also noticed that there are two weaker peaks in these spectra—the C-O and C=O peak, located at 287.6 eV and 288.8 eV, they are possibly detectable because the samples are placed in the atmosphere and oxidized. By knowing the relative intensity of sp^2 and sp^3 peaks, the sp^2 ratio of these deposited films can be estimated. Based on the spectra in Figure 4-3, it was noticeable that the sp^2 content of the film increased as the increase in arc current of Ni source used during the film deposition. The reason can be explained in the way that higher arc current of Ni source results higher Ni content. Based on the subplantation model of carbon base thin film

growth, during deposition, the impinging ions landed on the substrate will only have a part of them penetrate the surface, forming sp^3 sites, the rest will relax back to the surface in the thermal spike, forming the sp^2 layer, which is known as graphitization process. The thermal spike depends on the ion energy of the impinging ions. Comparing to carbon ions, metal ions can generated more thermal spikes, which can be contributed in graphitization process. As the Ni content increases, the overall thermal spikes generated during the film formation will also be higher, hence the graphitization process can be enhanced, resulting the high sp^2 content during the film deposition. Based on the XPS results, the detail of each peak can be determined, which is shown in Table 4-1. Thus the sp^2 content of the pure C film was only 30.5 %, for C:Ni nanocluster film deposited using 100 A and 140 A arc current of Ni source was 41.6 % and 55.8 %, respectively.

Film	C=C Peak (284.5 eV) intensity	C-C Peak (285.5 eV) intensity	sp^2 (C=C) %
Pure C	5211.5	11867.8	30.50%
C:Ni using 100 A arc current of Ni source	6568.85	9238.06	41.60%
C:Ni using 120 A arc current of Ni source	8534.29	10080.9	45.80%
C:Ni using 140 A arc current of Ni source	9363.56	7408.89	55.80%

Table 4-1 Peak information of XPS spectra for film deposited using different Ni arc currents

Figure 4-3 XPS core-level spectra at C 1s for (a) pure C, (b) C:Ni using 100 A arc current of Ni source, (c) C:Ni using 120 A arc current of Ni source and (d) C:Ni using 140 A arc current of Ni source

Figure 4-4 shows the Ni 2p core-level spectra of the CNi nanocluster film deposited using 140 A arc current of Ni source. The spectra can be deconvoluted into three main peaks for the Ni2p3 envelope, which are metallic Ni (Ni-Ni) peak, NiO (Ni-O) peak and Ni2p3 satellite peak with their center located at 852.8 eV, 854.5 eV and 860 eV. There was no Ni-C phase detected, which indicated there was no carbide forming between C and Ni atoms regardless the change in Ni content. Although bulk Ni is stable and not easily oxidized, however the Ni in its nanocluster form can be easily oxidized [121], which explains the presence of Ni-O phase.

Figure 4-4 XPS core-level spectra at Ni 2p of the C:Ni nanocluster film deposited using 140 A arc current of Ni source

4.3.3 Microstructural Analysis of C:Ni Nanocluster Films using Visible Raman Spectroscopy

Figure 4-5 comprises of the Raman spectroscopy results for C:Ni nanocluster films deposited with different ion density of Ni and a pure C film for reference. As introduced in chapter 2, there are two possible Raman peaks detectable for carbon based thin film, which are G and D peak. For the pure C film, only one peak is observed, centered at about 1540 cm^{-1} , which corresponds to the position of the G peak. For the fact that only a single G peak is observed reveals that the film is highly amorphous without any short-range ordering [104]. As the ion density for Ni increases, the evolution of the microstructure for the C:Ni film can be clearly seen. A shoulder that coincided with the position of the D peak, centered at 1370 cm^{-1} begins to emerge as the ion density of Ni increases beyond $17.5 \times 10^{11}\text{ cm}^{-3}$. The shoulder becomes more prominent as the ion density of Ni reaches $19.7 \times 10^{11}\text{ cm}^{-3}$, an indication for the formation of disordered graphitic microstructure with short-range ordering of graphitic planes [17].

Figure 4-5 Raman spectra of pure C film and C:Ni nanocluster films deposited using different arc current of Ni source

Figure 4-6 a and b show the G peak position and $I(D)/I(G)$ ratio as a function of arc current of Ni source. These two features were extracted by fitting the Raman spectra by a BWF line shape for G band, and a Lorentzian line shape for the D band. The understanding of the nature for G and D vibration modes and the association with the microstructure of disordered and amorphous carbon have been well interpreted and established with the three-stage model [104, 122]. For the pure C film (Ni at 0 at%), the G peak is positioned at 1554 cm^{-1} and the $I(D)/I(G)$ ratio is zero. With reference to the three-stage model, the film falls into the domain of stage 3, indicating a microstructure closer to the tetrahedral amorphous carbon (ta-C). For C:Ni nanocluster film deposited using 140 A arc current of Ni source had its G peak position located at 1550 cm^{-1} , and its $I(D)/I(G)$ ratio increased to 0.49.

Figure 4-6 Raman features (a) G peak position, FWHM of G peak and (b) I(D)/I(G) as a function of arc current of Ni source

For films deposited with low ion density of Ni (up to $17.5 \times 10^{11} \text{ cm}^{-3}$), the position of the G peak down-shifted to a lower wavenumber (from 1555 cm^{-1} to 1533 cm^{-1}) and the I(D)/I(G) ratio remains to be low. These observations indicate that a low impingement of Ni ion density would induce a phase transition of carbon film from the ta-C state towards a-C [104]. For carbon films co-deposited with a large ion density of Ni (beyond $17.5 \times 10^{11} \text{ cm}^{-3}$), the position of the G peak rebounds and up-shifts towards 1550 cm^{-1} , together with the emerging of the D peak, leading to an increase of the I(D)/I(G) ratio to 0.5. The upward movement of G peak position in this stage indicates the

clustering of the sp^2 bonded carbon, from chain-like bonded carbon into graphite-like sp^2 bonded carbon and the increase in the $I(D)/I(G)$ ratio reflects the growth in size of the graphite-like sp^2 clusters. These indications show that a large impingement of Ni ions would provide sufficient energy to transform the microstructure of the carbon film from ta-C to NCG state.

As mentioned earlier, the main attributes to the formation of NCG are mainly determined by the presence of biaxial stress and the activation energy. Besides substrate annealing, by providing sufficient thermal spike during the deposition process, which is dependent on the quantity and the amount of ion energy of the impinging ions of the carbon source, NCG could also be formed [115]. As explained by the subplantation model of carbon based thin film growth, during the deposition process, partial of the impinging ions landed on the substrate would penetrate the surface and leads to the formation of sp^3 sites, while other would undergo a relaxation process at the surface in a form of thermal spike, result in the formation of the sp^2 layer, known as the graphitization process. Here, the observation of the phase transition of the carbon microstructure structure is similar. As a result of the co-deposition of Ni, the Ni ions are impinging on the surface of the film together with the C ions, producing thermal spikes. By increasing the metal content of the film, i.e. increase the ion density of Ni, the thermal energy produced at the surface increases. With sufficient ion density, the amount of the thermal energy produced would be sufficient to lead to the graphitization process and the formation of NCG.

4.3.4 TEM Analysis on the C:Ni Nanocluster Film Microstructure

To confirm the Raman results, TEM analysis has been performed. Figure 4-7 a and b below show the cross sectional high resolution TEM image and Fast Fourier Transforms

–FFT pattern of the C:Ni nanocluster film deposited with the arc current for Ni at 100 A and 140 A, respectively. Due to the higher density of Ni (8.908 g/cm^3) as compared with C (diamond: 3.515 g/cm^3 , graphite: 2.261 g/cm^3), the darker region in the TEM image corresponds to Ni and the lighter region corresponds to C. For both of the samples, clusters of Ni atoms are observed and with a spread of diameter of about 3~5 nm. Figure 4- a shows the C:Ni film deposited with an arc current of 100A (ion density of $16.4 \times 10^{11} \text{ cm}^{-3}$), it can be seen clearly that the morphology of the carbon is still mostly in the amorphous phase, without any observable formation of basal planes, as confirmed by the FFT image at the inset a. Figure 4-7 b shows the C:Ni film co-deposited with Ni at an arc current of 140 A (ion density of $19.7 \times 10^{11} \text{ cm}^{-3}$), fringe-like structures are shown and the interplanar spacing between two neighbor planes (fringes) is estimated to be $3.88 \text{ \AA}$, similar with sp^2 nanocrystalline carbon. (002) diffraction pattern is also shown in the FFT pattern (inset b), indicating a graphite-like nanocrystalline structure. Clearly, deposition with a larger Ni ion density would lead to a microstructural transformation for the amorphous carbon matrix but on the other hand, the size of Ni clusters remains the same, regardless of the ion density of the Ni source.

Figure 4-7 Cross section HRTEM image and FFT pattern (inset) of C:Ni nanocluster film deposited using different arc current of Ni source: (a) 100 A and (b) 140 A

4.3.5 Electrical Properties of C:Ni Nanocluster Films

To understand the implication of the microstructural transformation towards the electrical behavior of the C:Ni nanocluster film, the result of the I-V characteristic of the pure C film and C:Ni nanocluster film deposited with different Ni content are plotted and shown in Figure 4-8. For the carbon-only film, the I-V characteristic is asymmetric at the point when voltage = 0 V, indicating that the transport mechanism for the film is contact related or bulk limited Poole-Frenkel type [123]. The electrical current is also measured to be in the range of 10^{-9} - 10^{-13} A. As the incorporation of Ni increases, it is noticeable that the I-V properties of C:Ni films become symmetric at the point when voltage = 0 V, suggesting a non-contact related transport mechanism [87]. The conduction current is also increased to the range of 1×10^{-3} A for C:Ni nanocluster film with 10 at% of Ni, close to 6 orders higher than that of the pure C film.

Figure 4-8 I-V characteristics of pure C film and C:Ni nanocluster films deposited using different arc current of Ni

source

Figure 4-9 shows the electrical resistivity of pure C film and C:Ni nanocluster film as a function of arc current of Ni source. The point where the microstructural transformation from a-C to NCG occurs is also labeled, with reference to the observation from the Raman spectroscopy. For the carbon-only film (Ni=0 at%), due to its ta-C phase, the electrical resistivity is found to be in the range of $10^9 \Omega\cdot\text{m}$, fairly close to the resistivity of diamond ($10^{12} \Omega\cdot\text{m}$). Similar with the observation from the others [124, 125], a large drop of electrical resistivity occurs as the content of Ni increases, even for low content of Ni (1.8 at%), the resistivity of the film drops four orders and into the range of $10^5 \Omega\cdot\text{m}$. The drop reduces as the content of Ni increases beyond 1.8 at% and up to 5 at% of Ni. As well adopted by many, the sudden transition from the insulator to conductor nature of the C:Ni nanocluster film is an evidence of the percolation threshold. When sufficient content of Ni is met (i.e. the percolation threshold), the presence of the conductive Ni clusters would provide conductive paths within the insulating amorphous carbon matrix and transit the film into conductive phase. It is noteworthy that as the

content of Ni increases beyond 5%, a second plunge in resistivity occurs and drops further into the $10^3 \Omega\text{-m}$ regime, diverged from the usual percolation phenomenon. The occurrence also coincided with the microstructure transition of the a-C matrix into NCG phase. These observations suggested that at this phase, the electrical conduction mechanism of the film is beyond the provision from the connected electrical channels created by the Ni clusters. The formation of graphite-like sp^2 clusters within the insulating sp^3 bonded carbon matrix have provided additional sites for electron hopping, in addition to the Ni nanoclusters [51, 87]. Hence, attribute to the further increase (i.e. six orders) of the electrical conductivity of the whole film.

Figure 4-9 Electrical resistivity of pure C film and C:Ni film as a function of Ni content

4.4 Conclusions

In this chapter, We have demonstrated the feasibility of controlling the microstructure of the C:Ni nanocluster film by controlling the ion density of the Ni source using Y-bend FCVA deposition system. By increasing the arc current of the Ni source, a higher density of Ni plasma can be produced and resulted in an increase of Ni content within the C:Ni nanocluster film. As shown from the TEM results, the increase of the ion density of Ni also induced a phase transition among its carbon matrix, from ta-C state into NCG state. The content of sp^2 was increased from 30% and up to 56% for pure C film and C:Ni nanocluster film deposited with an ion density of Ni at $19.8 \times 10^{11} \text{ cm}^{-3}$, respectively. The transition was also studied with Raman spectroscopy and the mechanism of the phase transition was due to increases in the localized thermal spikes created by the increase in impingement of the Ni ions. The transformation of the microstructure for the carbon matrix in C:Ni nanocluster film has led to a change of six orders of whole film electrical conductivity, beyond the contribution from the Ni sites as typically explained in percolation theory for composite materials.

Chapter 5 The Correlation of Growth Temperature and the Changes of Microstructure and Properties for C:Me Nanocluster Films

5.1 Introduction

As mentioned in chapter 4, the ion energy of the C species determines the formation of nanostructured carbon during deposition. Instead of tuning ion density, which can be either carbon ions or metal ions, growth temperature is another parameter which can strongly influence the microstructure of the carbon based thin film. [36]. With the build-in heater in the Y-bend FCVA deposition system, it is possible to examine the effect of carbon microstructure on the C:Me nanocluster film properties. As introduced in chapter 1, NCG is a kind of highly oriented nanostructured carbon, one of its superior properties is the high electrical conductivity. In previous chapter, it has been shown that C:Ni nanocluster film exhibits an increase in electrical conductivity with the presence of metal nanoclusters and graphite-like sp^2 clusters. However, if further increasing the metal content within the C:Me nanocluster film, the film would lose the nature of C film [126]. Hence to further enhance the electrical performance, the possible solution is to increase the number of graphite-like sp^2 clusters within the film. Many have shown that by increasing growth temperature during pure C film deposition using a FCVA system, the formation of graphite-like sp^2 clusters can be promoted [36, 37, 127]. Hence, in this chapter, C:Ni nanocluster films with similar Ni content will be deposited at different

growth temperature (from room temperature upto 600°C), and their composition, microstructure and electrical properties of will be investigated.

Other than focusing on the electrical properties of C:Me nanocluster film, other properties such as mechanical properties are also worthwhile to be explored. Many researchers have demonstrated that with incorporation of metal nanoclusters such as Ti, Cr and W [128-130], mechanical properties of the film can be improved comparing to pure C film, such as corrosion resistance, tribological performance. However, the focus is only on the type and content of the metal nanoclusters, but how the difference in carbon microstructure affects the properties of the C:Me nanocluster film is still lacking. Hence in this chapter, C:Ti nanocluster films by only changing the growth temperature will be fabricated, in addition, their microstructural details will be studied, as well as their tribological performance will be investigated.

5.2 Synthesis of C:Ni Nanocluster Film using Different Growth Temperature

5.2.1 Experimental

Similar to studying of the influence of the arc current of Ni source, N-type silicon wafer was used as the substrate. The same target materials were used for film deposition. The arc current of Ni source used was set to 120 A for all depositions. Films were grown at room temperature (25°C), 200°C, 400°C and 600°C, respectively. For the sake of comparison, another set of pure carbon film was also grown using the same growth

temperature. The characterization methods for film composition, microstructure and electrical properties involved EDX, XPS, Raman, TEM and I-V probing equipment.

5.2.2 Results and Discussion

5.2.2.1 Ni Content Measurement using EDX Spectrometer

Figure 5-1 shows the Ni content within the C:Ni nanocluster film as a function of growth temperature. It is observed that the Ni content does not change significantly with the growth temperature. As shown in chapter 4, the film deposited using 120 A arc current of Ni source had about 5 at% of its Ni content.

Figure 5-1 The content of Ni within the film as a function of growth temperature

It is noticeable that there is a fluctuation on the Ni content for these films, which is believed to be not caused by the change of the growth temperature, but due to the instability of the arc generated during deposition. The arc sustained to generate the plasma could be off randomly during the deposition, which requires a re-strike process to initiate the arc again. In addition, even if the arc is sustained throughout the entire deposition, the

plasma generated will be affected by some other factor such as the vacuum condition. These may cause the amount of Ni ions generated to vary in a small range, hence the fluctuation on the Ni content occurs. This issue cannot be avoided during FCVA deposition process.

5.2.2.2 Film Composition Analysis using XPS

Figure 5-2 a-d show the C 1s core-level XPS spectra of C:Ni nanocluster film deposited at room temperature, 200°C, 400°C and 600°C. Again, there are four peaks detected after deconvoluted the XPS spectra using Gaussian line shape, which are the C-C, C=C, C-O and C=O peak. It indicates that even the film is grown at 200°C, the majority of carbon exists in C=C bonding. The detail of the C-C and C=C peak is shown in Table 5-1. The sp^2 content can be calculated to be about 79.8 %. As the continuous increase in growth temperature to 400°C and 600°C, the sp^2 content of the film further increased to 82.1% and 85.7%. Recalled from chapter 4, even the Ni content increased from about 5 at% to 10 at%, the sp^2 content only increased from 45.8% to 55.8%. In the subplantation point view, increasing the growth temperature is able to supply more energy to the impinging ions, as comparing to the effect of incorporating metal such as Ni. Hence by applying substrate heating during deposition, the enhancement of sp^2 formation will be more significant. However, Ni-C bonding which is theoretically located at 283.3 eV is still missing, which indicates there was no carbide forming within the C:Ni nanocluster film, regardless of the growth temperature changing. G. Abrasonis et al. has pointed out that only when the growth temperature is about 300°C, the Ni_3C forms by surface diffusion process, other than this temperature, the Ni atoms are preferable existing in metallic Ni nanoclusters within carbon matrix [82, 131].

Film	C=C Peak (284.5 eV) intensity	C-C Peak (285.5 eV) intensity	sp ² (C=C) %
C:Ni deposited at RT	8534.29	10080.9	45.80%
C:Ni deposited at 200°C	10191.3	2579.75	79.8 %.
C:Ni deposited at 400°C	7597.91	1656.55	82.1%
C:Ni deposited at 600°C	12441.1	2075.94	85.7%

Table 5-1 Peak information of XPS spectra for film deposited at different temperatures

Figure 5-2 XPS core-level spectra at C 1s for C:Ni nanocluster film deposited at (a) RT, (b) 200°C, (c) 400°C and (d)

600°C

Figure 5-3 a and b show the Ni 2p core-level spectra of the C:Ni nanocluster film deposited at room temperature and 600°C, respectively. As discussed in chapter 4, a very small amount of the Ni nanocluster within the film could be oxidized by the oxygen in the ambient, after being taken out from the deposition chamber. However for the film deposited at 600°C, except for the Ni-Ni and Ni-O peak, another peak—Ni(OH)₂ peak is also detected, which shows the film was also able to absorb the –OH group due to the low film density because of the high sp² content.

Figure 5-3 XPS core-level spectra at Ni 2p for C:Ni nanocluster film deposited at (a) RT and (b) 600°C

5.2.2.3 Microstructural Analysis of C:Ni Nanocluster Films using Visible Raman Spectroscopy

To investigate the effect of Ni nanocluster on the film deposited at different growth temperature, the pure C film was used as the reference set for ease of comparison. Figure 5-4 a and b show the Raman spectra of the pure C and C:Ni nanocluster film deposited at different growth temperature.

Figure 5-4 Raman spectra of (a) pure C film and (b) C:Ni nanocluster films deposited at different growth temperature

Compared to the Raman spectra in chapter 4, which showed the effect of Ni content, clearly the effect of growth temperature was more significant. Unlike pure C film,

which only had its D peak appeared at 400°C, for C:Ni nanocluster film, even at 200°C, the D peak became visible. This suggests the C:Ni nanocluster film was no longer amorphous when it was deposited at 200°C, whereas the Ni nanoclusters were believed to be able to enhance the graphitization. In addition, it was noticeable that at 600°C growth temperature, the D band was more distinct and stronger in its density. Also the G peak position of C:Ni nanocluster film deposited at 600°C growth temperature was more close to 1600 cm⁻¹. Both of these two Raman behavior suggested the C:Ni nanocluster film at this growth condition had graphite-like structure, and consisted plenty of graphite-like sp² cluster in nanometer size range. To have a deep understanding of the Raman spectra, once again all these spectra were fitted using a BWF line shape and Lorentzian line shape for G band and D band respectively.

Figure 5-5 Raman features (a) G peak position and (b) I(D)/I(G) ratio of pure C film and C:Ni nanocluster film as a function of growth temperature

Figure 5-5 a and b above present the G peak position and I(D)/I(G) ratio for both pure C and C:Ni nanocluster film, deposited at different growth temperature. In Figure 5-5 a, it can be observed that for pure C film, the G peak drops first and then shift to a higher wavenumber with increase in the growth temperature. As shown in three-stage model, the pure C film deposited at room temperature was located at stage 3, and closer to the ta-C phase. As the increase of the growth temperature, the energy of impinging ions increased, which promotes the formation of sp² bonds, and causes the C film to shift downwards to

the a-C phase, however, the film was still amorphous state hence it was still in stage 3. At 400°C growth temperature and above, the C film moved to stage 2, with some graphite-like sp^2 clusters forming and the G peak shifted upwards. For C:Ni nanocluster film, the different phenomena was observed, the G peak position continuous shifted upwards as the increase in the growth temperature. As shown in chapter 4, even at room temperature, the C:Ni nanocluster film deposited using 120 A arc current of Ni source was in stage 2. As the increase of growth temperature, G peak only shifted within stage 2, and the continuous upwards shift of G peak indicated the film was approaching to the NCG phase. With further interpreting the Figure, it was worthwhile to notice that even at 200°C growth temperature, the G peak position of the C:Ni nanocluster film was at 1563 cm^{-1} , which was more closing to NCG phase, which suggested the existence of graphite-like sp^2 clusters within the film. The $I(D)/I(G)$ ratio in Figure 5-5 b indicates the size of the sp^2 cluster. It can be observed that the $I(D)/I(G)$ ratio of C:Ni nanocluster film was always higher than the value for pure C film. Moreover, even C:Ni nanocluster film deposited at lower growth temperature comparing to pure C film deposition (200°C lower), the $I(D)/I(G)$ ratio was still higher. This suggested that during the film formation, with the assistance of metal clusters such as Ni, lower temperature would be required to form the graphite-like sp^2 clusters, which is because of the Ni ions can induce additional thermal spikes to promote the C sp^2 bonds formation. It was noticeable that the $I(D)/I(G)$ ratio of C:Ni nanocluster film deposited at 200°C growth temperature was about 0.6, which denoted the formation of visible graphite-like sp^2 clusters.

The G peak position of C:Ni nanocluster film deposited at 600°C growth temperature was about 1594 cm^{-1} , according to the three-stage model, it was approaching

the right end of the stage 2, which indicated this film was almost in the phase of nanocrystalline graphite. However, it was also noticed that the increase rate of the $I(D)/I(G)$ ratio for C:Ni nanocluster film tended to be lower comparing to the pure C film, as 600°C. This is because when the sp^2 cluster size is below certain value, which is 2 nm suggested by A.C. Ferrari—regime 1, the relation between $I(D)/I(G)$ ratio and sp^2 cluster size will be proportional. However, once the sp^2 cluster size exceeds the 2 nm boundary, the relation between them will be following the Tuinstra Koenig Equation, which is inversely proportional—regime 2. This statement explains why the C:Ni nanocluster film slows down in increasing its $I(D)/I(G)$ ratio when growth temperature increased from 400°C to 600°C, which indicated its sp^2 cluster size has been reaching 2 nm.

5.2.2.4 TEM Analysis on C:Ni Nanocluster Films Deposited at Different Growth Temperatures

To have a better view on the change in microstructure as the growth temperature increasing, HRTEM analysis has been performed on the as-deposited C:Ni film, and C:Ni film grown at 200°C and 600°C. Figure 5-6 a and b below show the HRTEM (cross section view) image and FFT pattern (inset) of C:Ni nanocluster film deposited at room temperature and 200°C. and the inset in each Figure represents the FFT pattern of the carbon structure respectively. As discussed in the Raman analysis, there was no obvious D peak shown in the Raman spectrum of the film grown at room temperature, which suggested the film was amorphous. Here it was observed that the carbon structure was purely amorphous without any crystalline structure shown in the TEM image, and the FFT pattern (inset a) also showed a continuous diffused ring around the central beam, which

confirmed there was no special ordering was present. In addition, the Ni nanocluster was about 5 nm in diameter. While the HRTEM image of the film grown at 200°C showed the formation of graphite-like sp^2 clusters, which can be confirmed by the (002) FFT pattern shown in the inset b. This HRTEM image matched with Raman spectrum which displayed a significant D peak at 200°C growth temperature.

Figure 5-6 Cross section HRTEM image and FFT pattern (inset) of C:Ni nanocluster film deposited at different growth temperature (a) RT and (b) 200°C

Figure 5-7 (a) Cross sectional HRTEM image of C:Ni nanocluster film deposited at 600°C, (b) zoom in view of area A and (c) zoom in view of area B

As the growth temperature increased, the microstructure of the nanocluster film also changes, which has been suggested from the Raman results. The HRTEM image of the film grown at 600°C is shown in Figure 5-7. Figure 5-7 a shows the low magnification view for the image, it can be noticed that the size of the Ni nanocluster increased above 5 nm, which was due to the aggregation of small Ni nanocluster at high temperature. It can be observed the orientations of the graphite-like sp^2 clusters were not uniformly distributed, which can be separated into area A—surrounding Ni nanocluster, and area B—absence of Ni nanoclusters. Figure 5-7 b and Figure 5-7 c shows the high magnification HRTEM image for area A and area B respectively. It was noticeable that for area A, the graphite-like sp^2 clusters were surrounding the Ni nanocluster, while for area B, where Ni nanoclusters were absent, the sp^2 clusters were still perpendicular to the growth substrate. These phenomena showed at high growth temperature, 600°C in this experiment, the Ni nanoclusters affected the orientation of the graphite-like sp^2 clusters. The carbon structure surrounding the Ni nanocluster tended to form globular structure due to the surface mobility and growth rate of the carbon phase on the Ni crystalline phase changes at high growth temperature [132]. Whereas the area lacking of Ni nanocluster, the carbon growth was still following the growth mechanism of pure carbon film, due to the carbon species can obtain enough ion energy through thermal excitation at high growth temperature, hence form the prefer orientation that has the lowest internal stress [35, 36].

Figure 5-8 a and b show the FFT pattern for the carbon structure in area A and area B. The FFT pattern again consisted of two (002) arcs which further confirmed the presence of graphite-like sp^2 clusters, however the different arrangement of the two arcs in the two FFT pattern indicated that these sp^2 clusters are oriented in different direction.

In addition, it can be clearly observed that the arcs are more enhanced for area B comparing to area A, which can be explained in the way of stress minimization during film growth. When the film is growing, the carbon atoms tend to orient in the direction to minimize the internal film stress [133]. However, it is known that with metal clusters present, the film stress is able to be reduced [134, 135], hence the carbon atoms is not required to form high degree oriented structure to minimize the film stress.

Figure 5-8 Fast Fourier transform (FFT) diffraction pattern of carbon in the C:Ni nanocluster film deposited at 600° (a) area A and (b) area B

5.2.2.5 Electrical Properties of C:Ni Nanocluster Film Influenced by Growth Temperature

Figure 5-9 a and b present the I-V characteristics of the pure C film and C:Ni nanocluster films deposited using different growth temperature respectively. It can be observed that only the pure C film displays a asymmetric I-V property about voltage = 0 V, this indicated the transport mechanism for the pure C film was contact related or bulk limited Poole-Frenkel type [136]. Other than this, all the other pure C film grown with substrate heating and all C:Ni nanocluster film show the symmetric I-V properties about voltage = 0 V, which meant the transport mechanism was non-contact related type.

Figure 5-9 I-V characteristics of films deposited at different growth temperature (a) pure C film and (b) C:Ni nanocluster film

Poole-Frenkel effect happens when the trapping sites of the band gap are positively charged when they are empty and neutral when they are occupied by the carrier [137]. The electron can only hop from one site to another when it has enough energy to overcome the Coulomb force of the positively charged site behind. Obviously the conduction in this case strongly depended on the size and density of the conductive sites (in this case amount and cluster size of sp^2 bonded atoms, and Ni nanoclusters). The increase in growth temperature is the effective way to enhance the formation of sp^2

clusters, which creates sufficient conducting paths, hence Poole-Frenkel effect is no longer the transport limiting mechanism.

Figure 5-10 displays the electrical resistivity of pure C film and C:Ni nanocluster film as a function of the growth temperature. The resistivity for both kind of film drops as the increase of the growth temperature. It can be observed that as the growth temperature increasing from room temperature to 600°C, the resistivity decreased from $10^8 \Omega\cdot\text{m}$ to $10^2 \Omega\cdot\text{m}$ for pure C film, and $10^4 \Omega\cdot\text{m}$ to $10^1 \Omega\cdot\text{m}$ for C:Ni nanocluster film. It was clearly seen that the change in electrical resistivity was more dramatic for pure C film comparing to C:Ni nanocluster film. The reason is that at low growth temperature—room temperature, the pure C film is high in its sp^3 content and purely amorphous, the amount of conducting sites is very small. While comparing to pure C film, C:Ni nanocluster film has higher sp^2 content and also Ni nanoclusters can also behavior like conducting sites. As the increase in growth temperature, the conducting sp^2 clusters start to form within the film, which leads to the drop in resistivity. Comparing to pure C film, which can be considered as the insulating material, the C:Ni nanocluster film grown at room temperature has a much lower resistivity, hence its change rate in resistivity with respected to the growth temperature is much lower. However, it can be noticed that even at high growth temperature—600°C, the resistivity of C:Ni nanocluster is still lower than the pure C film, which is contributed by both conducting sp^2 clusters, and the Ni nanoclusters to provide more conductive sites.

In addition, comparing to the C:Ni nanocluster film with high Ni content in chapter 4, which has its electrical resistivity in $10^3 \Omega\cdot\text{m}$ range, the film grown at 600°C,

but lower Ni content exhibited lower electrical resistivity. Hence it suggests the carbon microstructure dominates the whole film electrical conductivity.

Figure 5-10 Electrical resistivity of pure C film and C:Ni film as a function of growth temperature

5.3 Synthesis of C:Ti Nanocluster Film using Different Growth Temperature

5.3.1 Experimental

To form Ti nanoclusters within the film, 99.99% titanium target was used instead of nickel targets. The deposition conditions were the same as the C:Ni nanocluster film deposition, except for using 130 A arc current to generate Ti plasma. For The thickness of pure C and C:Ti films used in this study were ~100 nm, measured with Tencor P10 surface profiler meter.

The film composition for C:Ti nanocluster films was measured by EDX and XPS. The bonding structure of the pure C and C:Ti films were investigated using visible Raman

spectroscopy. The detailed microstructure of C:Ti film deposited using highest growth temperature (600°C) was examined TEM.

The tribological behavior of the pure C and C:Ti films was characterized using a CSEM pin-on-disk tribometer. All the samples were mounted on an aluminum holder which is fixed on a rotary turntable. All the friction tests were carried out at a load of 2 N and an average sliding speed of 10 cm/s. The sliding frequency and radius of the sliding were 10 Hz and 2.5 mm. And the ball used in all tests was an Al₂O₃ ball with dimension of 6 mm, the total distance for each test is 100 m. All the tests were carried out in the air atmosphere, with temperature and humidity value of 22°C and 65% respectively. And the film surface after friction test was inspected using Olympus BX 60 optical microscope.

5.3.2 Results and Discussion

5.3.2.1 Ti Content Measurement using Energy X-Ray Spectroscopy

Figure 5-11 The content of Ti within the film as a function of arc current of growth temperature

Figure 5-11 above shows the Ti content within the C:Ti nanocluster film as a function of growth temperature. Same as shown in previous section, it was observed that

the Ti content did not change significantly with the growth temperature also. The film deposited using 130 A arc current of Ti source was measured to be about 5 at% of its Ti content, hence the effect of Ti content for different films can be neglected.

5.3.2.2 Film Composition Analysis using XPS

Figure 5-12 a-d show the C 1s core-level XPS spectra of C:Ti film deposited at room temperature, 200°C, 400°C and 600°C. Except for the spectrum of film grown at RT, there are five peaks detected after deconvoluted the XPS spectra using Gaussian line shape, which are the C-C, C=C, C-O, C=O and the C-Ti carbide peak. Figure 5-13 shows the percentage of sp^2 content and C-Ti content as the function of growth temperature. The percentage of sp^2 content within the C:Ti film can be calculated with knowing the amount of the C-C and C=C bonding, which are 32.1 %, 82.2%, 84.4% and 88.9% for the film grown at RT, 200°C, 400°C and 600°C accordingly. For the film grown at RT, there is no C-Ti carbide bonding detected, while for film grown at 200°C, 400°C and 600°C, the carbide percentage of carbide is measured to be 1.1%, 1.7% and 2.0% respectively. Since the content of Ti for all films is considered to be the same, the formation of the carbide is believed to relate to the growth temperature. As the increase in growth temperature, more Ti ions are able to react with C ions during film deposition, which results the increase in carbide content.

Figure 5-12 XPS core-level spectra at C 1s for C:Ti nanocluster film deposited at (a) RT, (b) 200°C, (c) 400°C and (d) 600°C

Figure 5-13 Sp² content and C-Ti content of the C:Ti nanocluster films as a function of growth temperature

5.3.2.3 Microstructural Analysis of C:Ti Nanocluster Films using Visible Raman Spectroscopy

Figure 5-14 a and b below represent the Raman spectra for pure C and C:Ti nanocluster film grown at different growth temperature.

Figure 5-14 Raman spectra of (a) pure C film and (b) C:Ti nanocluster films deposited at different growth temperature

The microstructural change of pure C film influenced by the growth temperature has been discussed in previous section. The C:Ti nanocluster film shows a comparable Raman spectrum as the pure C film when it was grown at room temperature. When the

substrate heating was applied during growth, the D band of C:Ti nanocluster film becomes more pronouncing comparing to pure C film, which suggests the higher degree in clustering of sp^2 bonded carbon existing within the film.

The Raman spectra were fitted and the Raman features are shown in Figure 5-15 a and b below.

Figure 5-15 Raman features (a) G peak position and (b) I(D)/I(G) ratio of pure C film and C:Ti nanocluster film as a function of growth temperature

Figure 5-15 a shows the G peak position of pure C and C:Ti nanocluster film grown at different growth temperature. Same as the C:Ni nanocluster film discussed in previous

section, the C:Ti nanocluster grown at room temperature was also located at stage 2 in the three-stage model. As the increase in growth temperature, G peak is only shifted within stage 2, and the continuous upwards shift of G peak indicates the film has transformed into the NCG phase. Same for the $I(D)/I(G)$ ratio shown in Figure 5-15 b, which also increases as the increase in growth temperature. However although the enhancement of graphitization did occur with the presence of Ti, it was noticeable that the enhancement was not as high as incorporation of Ni.

5.3.2.4 TEM Analysis on C:Ti Nanocluster Film

Figure 5-16 demonstrates the cross section HRTEM image and FFT pattern (inset) of the C:Ti nanocluster film grown at 600°C.

Figure 5-16 Cross section HRTEM image and FFT pattern (inset) of C:Ti nanocluster film deposited at different growth temperature 600°C

It can be observed that the Ti nanoclusters are in the diameter range of ~4 nm, and embedded within carbon matrix. It was noticeable that the carbon was in the form of graphite-like sp^2 cluster. In addition, the FFT pattern (inset) shows the diffraction pattern

of the carbon structure in the circle, which confirmed the graphitic microstructure forming within the film. In contrast of C:Ni nanocluster film, which would form larger Ni nanocluster at high growth temperature, the size of Ti nanocluster was still in the range of less than 5 nm, and the Ti nanoclusters were more compacted comparing to Ni nanoclusters. The reason is that the formation of C-Ti carbide bonding resists the aggregation and diffusion of Ti nanoclusters within the carbon matrix.

5.3.2.5 Tribological Properties of C:Ti Nanocluster Films Influenced by The Growth Temperature

Figure 5-17 shows the coefficient of friction with sliding distance for pure C films and C:Ti nanocluster films grown at different growth temperature. In Figure 5-17 a, it shows that for pure C film deposited at room temperature until 400°C, the coefficient of friction does not change much, and when the growth temperature increased to 600°C, the coefficient of friction increases significantly. This observation can be explained by the Raman results, which shows a minor change in Raman features as the growth temperature increasing from room temperature to 400°C, the significant change only occurs when the growth temperature increased to 600°C. The change in Raman is caused by the increase in sp^2 content, and it would lead the decrease in the film hardness, which might cause higher worn volume. The worn area on the film surface is very roughen hence it causes the significant increase in the coefficient of friction for pure C film [118]. Comparing to pure C film, the coefficient of friction for C:Ti nanocluster film does not change significantly as the growth temperature changed, which is shown in Figure 5-17 b. Although the increase in sp^2 content with the growth temperature increased, which is one the factor to cause the drop in film hardness, however, the formation of more C-Ti carbide could be

able to compromise the decrease in film hardness. Hence the worn area can be kept in the small volume, and with formation of self-lubricating graphite-like sp^2 clusters, the coefficient of friction even decreased, which is shown in Figure 5-18. Figure 5-19 displays the surface images after sliding for pure C and C:Ti nanocluster film grown at room temperature and 600°C, it is obvious that the C:Ti nanocluster film grown at 600°C had minimizing worn surface comparing to the rest.

Figure 5-17 Coefficient of friction as a function of sliding distance, (a) pure C films and (b) C:Ti nanocluster films

Figure 5-18 Coefficient of friction as a function of growth temperature

Figure 5-19 Optical image of film surface after sliding, (a) pure C film (RT), (b) pure C film (600°C), (c) C:Ti nanocluster film (RT) and (d) C:Ti nanocluster film (600°C)

5.3 Conclusions

In this chapter, the effect of the growth temperature on the microstructure, properties of C:Me nanocluster film has been investigated. First of all, C:Ni nanocluster films have been deposited at different growth temperature (RT, 200°C, 400°C and 600°C). Comparing to pure C film deposited at the same growth temperature, C:Ni nanocluster film was shown to form graphitic microstructure at lower temperature, and there was no evidence to show the formation of C-Ni carbide. The electrical resistivity exhibited lower electrical resistivity with the presence of Ni nanoclusters and graphite-like sp^2 clusters, and the resistivity value was in $10^1 \Omega\cdot m$ range, which was even lower than the film with higher Ni content but had less conductive sp^2 clusters. It suggested that carbon microstructure dominated the whole film electrical conductivity.

Except for C:Ni nanocluster film, C:Ti nanocluster films deposited at different growth temperature have also been studied. Unlike C:Ni nanocluster films, C-Ti carbide formation was detected, and its content was shown to increase as the increase in growth temperature. Although the increase in sp^2 content of the film affected the tribological performance, the C-Ti carbide was shown to be able to retain the smooth film surface during tribology test, hence the C:Ti nanocluster films were suggested to have a better tribological performance comparing to pure C film.

Chapter 6: Post Deposition: Microstructural Modification of C Based Thin Films

6.1 Introduction

To obtain carbon based thin films with different microstructure and properties, in-situ controlling the deposition parameters, such as ion density, substrate biasing, and growth temperature, as well as the post deposition treatment can be used. Thermal annealing is the most conventional method which has been widely used in reducing the film stress through transforming high sp^3 content carbon film to high sp^2 content carbon film. Previous works have shown the thermal stability of different pure C film during thermal annealing has close relation with the initial film properties, for example the sp^2/sp^3 ratio [138]. In addition, Zhang, et al has shown that during thermal annealing, metal containing C film is more sensitive to the annealing effect [135]. However, it is known that with other deposition condition unchanged, by incorporation of metal into C film, the sp^2 content becomes higher, hence for those previous already been done, the factor such initial sp^2/sp^3 ratio may affect the annealing behavior. Hence, in order to have a clear comparison, the pure C film and C:Me film require comparable value for initial sp^2/sp^3 ratio. In addition, the effect of metal type during post thermal annealing is also lack of investigation. Hence in this chapter, post thermal annealing has been performed on pure C film, C:Ti and C:Ni nanocluster film with comparable initial sp^2/sp^3 ratio, and about the same metal content besides the pure C film. The microstructural changes were

monitored using visible Raman spectroscopy, the changes in film surface were also inspected using SEM.

Other than thermal annealing, approaches to induce localized transformation, which is crucial for the fabrication of hybrid carbon matrix (i.e. composite carbon matrix with predetermine electrical behaviors at designated site) for electronic and RF applications are limited with scanning probe microscopy (SPM) approach [139] and laser annealing. SPM approach is restricted to small scale, and time consuming, hence it is less suitable for commercial production. On the other hand, laser patterning provides a more versatile approach, as the scale of the transformation could range from a typical laser spot size (3mm by 3mm for the 248nm KrF excimer laser) to approximately the diffraction limit. In addition, the ease of large scale patterning is due to the simple scanning of the carbon film with a focused laser source. Comparing to post thermal annealing, laser annealing has not been fully investigated yet. The current work done only shows the laser energy is able to influence the film structure and properties. However, other factor such as initial film properties (sp^2/sp^3 ratio), incorporation of metal has not been concerned so far. Hence in this chapter, the localized transformation of pure C films with different initial sp^3 content and C:Me (C:Ni) nanocluster film have been realized through performing pulsed laser annealing. To examine the microstructure and properties change after laser annealing, visible Raman spectroscopy, HRTEM and electrical characterization were carried out.

6.2 Post Thermal Annealing

6.2.1 Experimental

To minimize the variation of the initial properties of different films, in this experiment, based on the results in chapter 5, the as-deposited film used was C film (grown at 400°C), C:Ti and C:Ni nanocluster film (grown at 200°C), which were about to have the same amount of initial sp^2 content. A home-made tube furnace was used to perform the thermal annealing treatment for these three different types of carbon based thin films. The furnace pressure was kept at atmospheric pressure during growth with Ar (500 sccm) and H_2 (200 sccm) flow. Annealing temperature used in this experiment was 200°C, 400°C, 600°C, 800°C and 1000°C, the temperature was ramped up and then kept at the corresponding for 15 minutes, followed by cooling down.

6.2.2 Results and Discussion

As shown in Figure 6-1 a-c, the bonding composition is reflected by the high C 1s core-level XPS spectra for as-deposited C, C:Ti and C:Ni film. After the deconvolution of the spectra, the sp^2 content can be estimated to be 78.9%, 82.2% and 79.8% for C, C:Ti and C:Ni film respectively. As discussed in chapter 6, at 200°C growth temperature, Ni only exists in metallic form within the nanocluster film, while Ti is able to exist in C-Ti carbide form and metallic form.

Figure 6-1 XPS core-level spectra at C 1s for as-deposited film, (a) pure C film, (b) C:Ti nanocluster film and (c) C:Ni nanocluster film

6.2.2.1 Microstructural Evolution after Thermal Annealing

To study the behavior of different carbon based thin film during post annealing, visible Raman spectroscopy is proven to be one of the effective techniques to probe the sp^2 configuration, such as the estimated value of sp^2 content, and sp^2 clustering, which are the main phenomena during annealing of carbon based thin film. Figure 6-2 a-c show the Raman spectra for C, C:Ti and C:Ni films annealed at different temperature. Since the initial sp^2 content for these three types of as-deposited films was about the same, it is observed that the shape of Raman spectra for these three as-deposited films is similar.

Figure 6-2 Raman spectra of (a) pure C film, (b) C:Ti nanocluster film and (c) C:Ni nanocluster film before and after thermal annealed at different temperature

However for as-deposited C:Ti and C:Ni film the peak intensity for D band is a bit higher, which indicates for carbon based thin film with comparable sp^2 content, the existence of metal nanoclusters enhanced the clustering of sp^2 bonded carbon. Moreover, when these films were annealed at different temperature, they exhibit noticeable differences. From these spectra, it is noticed that at low temperature, 200°C in this experiment, the spectrum for all of these three types of film shows minor change. As annealing temperature increased to 400°C, there is still no obvious change shown in spectrum for C film, and D peak intensity for C:Ti film increases with a small amount of value, interestingly, it is shown that for C:Ni film, there is a significant increase in D peak

intensity. When the annealing temperature increased above 400°C, the D band appears in all these three films, however the D band for C:Ni film is observed to be more pronounced.

Figure 6-3 Raman features of different C based film as a function of annealing temperature, (a) G peak position and (b) I(D)/I(G) ratio

To have a better understanding on the change in Raman spectra during annealing, the G peak position and I(D)/I(G) ratio values were extracted after fitting all these Raman spectra, and is shown in Figure 6-3 a, b and c above. The curve fitting used was a BWF line shape for G peak, while a Lorentzian line shape for D peak, however for C:Ni annealed at 1000°C, the spectrum was not able to be fitted using these two line shape.

Pure C film:

It is observed that at low temperature, in this experiment, below 600°C, the G peak position and I(D)/I(G) ratio almost remain the same value (1565 to 1567 cm⁻¹) after annealing, which indicates the film is thermally stable in this temperature range, there is insignificant increase in the amount of sp² bonded carbon atoms, and neither for the sp² cluster formation. As annealing temperature increases beyond 400C, the G peak position shift towards to a higher position up to 1593 cm⁻¹. Based on the XPS results, the sp² content is about 80%, Kalish et al. has shown that for pure C film with sp² content higher than 30%, G peak position moves towards to higher wavenumbers with increasing in sp² content, and also the clustering of sp² clusters [138]. The increase in I(D)/I(G) ratio supports this interpretation, its increase from 0.5 to 1 as the ramping of annealing temperature denotes the increase in the number of graphite-like sp² bonded clusters in the film.

C:Ti film:

The evolution of G peak position and I(D)/I(G) ratio for C:Ti film almost follows the same trend as pure C film. However the G peak position increases from 1560 to 1572 cm⁻¹ after annealing at 400°C, and as annealing temperature increased, its G peak shifts to a higher wavenumber comparing to pure C film, which can reach 1596 cm⁻¹. Same for the I(D)/I(G) ratio, which increases from 0.6 to 1.1 after annealing at 1000°C.

C:Ni film:

Same as C:Ti film, when the C:Ni film annealed at 400C, the surge increase in G peak position is observed, and the increment is even larger comparing to C:Ti film, which

changes from 1560 to 1587 cm^{-1} . As the annealing temperature increased to 600°C and 800°C, its G peak position increases to 1595 and 1598 cm^{-1} , respectively. However, although the I(D)/I(G) ratio also increases, the increasing rate is relatively smaller comparing to pure C and C:Ti film. This can be explained using the T. K Equation, when the size of graphite-like sp^2 cluster reaches certain value (2 nm), the I(D)/I(G) ratio is inversely proportional to the sp^2 cluster size.

Interestingly, after the C:Ni film annealing at 1000°C, the Raman spectrum shows very distinct D and G band, which cannot be fitted as other films. Sadezky et al. and Hauptman et al [140, 141] has used Raman spectroscopy to identify carbon based material, and based on the results, the C:Ni film annealed at 1000°C in this experiment shows the same Raman spectrum as carbon black. The Raman spectrum can be fitted using two strong peaks—G and D1 peak, and two weak peaks—D3 and D4 peak. The G, D1 and D4 peak is fitted using a Gaussian line shape, while the D3 peak is fitted using a Lorentzian line shape, the deconvolution of the spectra is shown in Figure 6-4 Below. The G and D1 peak is same as the G and D peak for amorphous carbon, hence the high intensity of D1 peak indicates high degree or sp^2 clustering. In addition, D3 and D4 peak represents that there are some fragments or functional groups and polyene-like structure existing [141].

Figure 6-4 Fitting of Raman spectrum of C:Ni nanocluster film annealing at 1000°C

Since the initial sp^2 content is almost the same for these three different films based on the XPS result, the reason to cause the different behavior upon thermal annealing is believed to relate to the incorporation of metal. According to the analysis in chapter 5, the metal content for the C:Ti and C:Ni nanocluster film is also about the same. Hence the metal type is also a factor to affect the microstructure change during annealing. Comparing to pure C film, the change in sp^2 content and sp^2 clustering is more sensitive subject to thermal annealing when metal nanoclusters are incorporated into the film. Lin et al. has shown that metal can enhance the formation of graphitization [142]. However, it is noticeable that with Ni nanocluster film present, the significant change in Raman features occurs at low temperature is more pronounced. This phenomenon denotes Ni nanoclusters are able to lead the graphitization easier comparing to Ti nanoclusters. Based on the XPS results, it is found that C-Ti bonded structure forms within C:Ti nanocluster film, but the C-Ni bonded structure is invisible. The C-Ti structure is believed to be thermally stable, Zhang et al has shown that even the graphitization process happened during thermal annealing of C:Ti film, the C-Ti structure is able to contribute to resist the

reaction happen of C atoms with the oxygen in the furnace tube (since the tube is not in vacuum) [143]. Hence it is able to retain more original structure comparing to C:Ni nanocluster film during high temperature annealing. The amorphous carbon structure becomes more unstable with the present of Ni nanocluster, hence at 1000°C annealing, the C atoms in C:Ni nanocluster films is able to be catalyzed by Ni and decompose to form carbon black.

6.2.2.2 Surface Morphology after Thermal Annealing

The film surface morphology is also worth investigating when we consider the thermal stability upon thermal annealing. Figure 6-5 a and b shows the SEM image for as-deposited pure C film and annealed after 1000°C. It is obvious that the surface condition does not change significantly even after annealing at high temperature. Even though the sp^3 to sp^2 transformation and graphite-like sp^2 clusters formation occurred, the film was still considered as stable without any surface transformation.

Figure 6-5 SEM image of (a) as-deposited pure C film and (b) pure C film annealed at 1000°C

Figure 6-6 a-f show the SEM images for as-deposited C:Ti film and C:Ti annealed at different temperatures, respectively. It is observed that until 800°C, the surface

condition almost remains the same as the as-deposited film. However after 1000°C annealing, some nanoclusters are observed on the film surface.

Figure 6-6 SEM image of (a) as-deposited C:Ti nanocluster film and (b)-(f) C:Ti film annealed at 200, 400, 600, 800 and 1000°C

For the SEM images, the contrast is determined by the conductivity of the material, the more conducting the material, the higher contrast is reflected in the SEM image, and hence it indicates that the nanoclusters are Ti nanoclusters. The Ti nanoclusters are invisible for as-deposited C:Ti film is because that the cluster size is small, and covered by the amorphous carbon layer. When the film is annealed, the reaction between C, Ti and O take places, and the surface C layer will form carbon dioxide, which can be considered as an etching process. As annealing temperature increases, for this film, up to 1000°C, the surface C layer is etched to the level that Ti nanoclusters can be observed. However, it has been shown that at high temperature, Ti also reacts with O to form titanium oxide, which can be acted as a barrier layer to resist the O further diffusing into the film [143]. Another reason leads the Ti nanocluster visible is that at high temperature, the initial Ti nanoclusters with smaller size in the film tends to aggregate together and form nanoclusters with larger size, hence they can be observed in the SEM image.

Comparing to C:Ti film, different behavior can be observed for C:Ni film after thermal annealing, which are shown in Figure 6-7 a-f below. It shows that at 600°C, the Ni nanoclusters started to appear. This is because that the melting point of Ni is much lower than Ti, hence when the C:Ni film is annealed at a lower temperature, the Ni nanoclusters are able to aggregate together and form larger nanocluster. As the annealing temperature further increased to 800°C, it can be found that the Ni nanoclusters become even larger, but the density of the nanocluster tends to decrease. This can be explained in the way that more Ni nanoclusters aggregate together, and leave some areas of the film lack of Ni nanoclusters. As discussed in the previous paragraph, when the C:Ni film was

annealed after 1000°C, it lost its film state, and formed carbon black. It is interesting that some nanostructures are found in the SEM image.

Figure 6-7 SEM image of (a) as-deposited C:Ni nanocluster film and (b)-(f) C:Ni film annealed at 200, 400, 600, 800 and 1000°C

To identify this nanostructure, TEM and EDX analysis has been performed, which can be shown in Figure 6-8 below. The TEM image showed this nanostructure was nanowire structure, and inset A indicates that these nanowires are purely amorphous. In addition, the EDX spectrum shown in inset B denotes this nanowire consists of Si and O, hence it can be confirmed that these nanostructures are silicon oxide nanowires (SiONWs).

Figure 6-8 TEM image of SiONW, inset A--the FFT pattern of the SiONW (amorphous), and inset B--the EDX spectrum of the SiONW

For the formation of SiONWs, it involves a solid-liquid-solid (SLS) growth [144-151], In a typical SLS growth process, liquid droplets of NiSi_2 are formed when temperature reaches the eutectic point of NiSi_2 , 993°C [144]. Silicon atoms from the solid substrate will diffuse into the NiSi_2 droplet through the solid and liquid interface. When these droplets are saturated, silicon atoms will precipitate into the solid form of whiskers or nanowires. After the formation of SiNWs, the oxygen in the tube furnace will oxidize the SiNWs and form SiONWs. For pure C film, the catalyst metal is absent, there is no

way to form Me-Si droplets which lead the formation of nanowires. While for C:Ti film, the Ti-Si alloy has a much higher eutectic point which is 1330°C [152], hence the annealing temperature used in this experiment is not high enough to form the Ti-Si droplets either.

6.3 Localized Transformation of Pure C Films

After studying the thermal annealing effect on carbon based thin film, it can be noticed that high temperature is usually required to realize the transformation of carbon structure, although metal nanoclusters such as Ni are able to reduce the temperature involved, temperature of at least 400°C is still needed. In addition the ramping up and cooling down of the temperature and the annealing itself are time consuming. Comparing to thermal annealing, the advantages of laser annealing are obvious, which is to transform the carbon structure on selected areas, and very short process time, which is only in range of “ns” is required. In this part, firstly the laser annealing effect on pure C films will be investigated, in aspect of laser energy density, and the correlation between laser annealing and initial film properties

6.3.1 Experimental

The pure a-C films were prepared by FCVA on N-type Si wafer at room temperature. Before film deposition, The Si substrate was mounted on a substrate holder connected to a regulated DC supply from 0 V to -600V. The average energy of the arc generated C⁺ ions can be controlled by adjusting the DC supply voltage. In this work, C⁺

ions with ion energy of 100 eV, 300 eV and 500 eV were used to obtain the different a-C films, named as film 1, film 2 and film 3. The thickness of the film was measured to be 100 nm using Tencor P10 surface profiler meter, and no delamination was found.

The intrinsic stress of the as-deposited films was determined by measuring the Si substrate curvature before and after deposition of the a-C film, and using Stoney's Equation 6.1 [153] given by,

$$\sigma_s = \frac{E_s}{6(1-\nu_s)} \frac{t_s^2}{t_c} \left(\frac{1}{R} - \frac{1}{R_0} \right) \quad 6.1$$

Where E_s , ν_s , t_s and t_c are the Young's modulus, Poisson ratio, thickness of the Si substrate and the film respectively. R and R_0 are the curvature of the as-deposited film and the Si substrate respectively.

Laser annealing was performed using a 248 nm KrF excimer laser with pulse duration of 23 ns in ambient condition. The spatial energy distribution of the laser pulse has a uniform near flat-top energy profile [154]. The samples were annealed by a single pulse, with different laser energy densities. And the microstructure and electrical property evolution upon laser annealing was investigated using visible Raman spectroscopy, HRTEM and IV electrical probing.

6.3.2 Results and Discussion

6.3.2.1 Film Properties

Figure 6-9 shows the stress of the as-deposited C films deposited using different ion energies. J. Robertson et al. has shown that the film stress has closed relation with the

deposition ion energy [17]. The highest stress in this experiment is approximately 11 GPa, which belongs to the film deposited using 100 eV ion energy. The stress is reduced to approximately 7 GPa and 5 GPa as the ion energy increases to 300 eV and 500 eV.

Figure 6-9 Film stress of as-deposited films as a function of ion energy

To determine the sp^3 content of these three as-deposited C film, Both Raman and XPS analysis has been performed. Firstly Raman spectra of these three different as-deposited films were fitted to determine the sp^3 content using three-stage model [104]. All these three spectra can be fitted using a single BWF line shape, and the G peak was located at 1561 cm^{-1} , 1543 cm^{-1} and 1533 cm^{-1} respectively, the shift of G peak position can be shown in Figure 6-10 a below.

Figure 6-10 (a) Raman spectra of as-deposited C films, (b) XPS core-level spectra at C 1s for as-deposited films and (c) sp^3 content extracted by both Raman and XPS results

Based on this interpretation, the sp^3 content for these three as-deposited films is estimated to be 80%, 65% and 50%. While for XPS analysis, which is more straight forward and accurate, by deconvoluting these three XPS spectra shown in Figure 6-10 b, the sp^3 content can be calculated to be 65%, 50% and 40%. The sp^3 content as the function of ion energy is shown in Figure 6-10 c, although the sp^3 content values obtained using these two methods are different, however the trend of change in sp^3 content with the ion energy change is the same. The relation between sp^3 content and film stress has been

widely studied [17, 36], here both initial sp^3 content and film stress can help in understanding the behavior of bonding structure during laser annealing.

6.3.2.2 Microstructure Evolution upon Laser Annealing

The relationship between initial sp^3 content and graphite-like sp^2 cluster formation:

Figure 6-11 shows the Raman spectra of these three different kinds of C film before and after laser annealing using different laser energy densities. Based on the three-stage model, the as-deposited film prepared with 100eV ion energy is more tetrahedral like (ta-C), and the films deposited with 300 eV and 500 eV are lower in sp^3 content, hence closer to the a-C state. Figure 6-11 a is the Raman spectra of the high sp^3 film (film 1) before and after laser annealing, and it shows that the spectrum changes very little before the laser energy density of 350 mJ/cm^2 . Figure 6-11 b shows the Raman spectra of the intermediate sp^3 film (film 2) subjected to laser annealing, and it is obvious that the change occurs at the energy density of 250 mJ/cm^2 . Figure 6-11 c is the Raman spectra of the low sp^3 film (film 3), which shows the significant change observed at an even lower energy density level— 100 mJ/cm^2 . The major changes of the Raman spectra are the shift of G peak position, and the appearance of the D band. The G band relates to both breathing and stretching modes of sp^2 bonds, and the D band only reflects the existence of breathing mode of sp^2 bonds, which are normally in form of nm size graphite-like cluster [104, 155]. Our previous work has shown that laser annealing can transform sp^3 bonding into sp^2 bonding, and promote the formation of graphite-like clusters [39, 40]. The difference of change among films with different sp^3 content is suggested to be related to the thermal stability of the film. The high sp^3 film is reported be thermally stable up to 1270 K [138]. In this work, only when the laser energy density is beyond 350 mJ/cm^2 , the

D band appears for the film 1, which suggests the formation of graphite-like clusters. A lower laser energy is required for films which contain less sp^3 content.

Figure 6-11 Raman spectra of as-deposited film and films annealed using different laser energy density (a) film 1, (b) film 2 and (c) film 3

To have a further understanding of the evolution of bonding structure for films having different initial sp^3 contents, Raman spectra of films annealed using different laser energy were fitted and Raman features were extracted, Figure 6-12 a and b show the shift of G peak position and the changes of $I(D)/I(G)$. By using the three-stage model, the evolution of the bonding structures can be analyzed.

Figure 6-12 Raman features (a) G peak position and (b) I(D)/I(G) as a function of laser energy density

High sp^3 film:

The as-deposited film is closer to the ta-C state in the stage 3, the majority of sp^2 bonds that exist in the film are in olefinic form (chain-like). The G peak position only shows a minor change when laser energy density increases from 50 mJ/cm² to 250 mJ/cm². This is due to the insufficient laser energy to induce the transformation from sp^3 into sp^2 bonds, and so the film is still ta-C like. When laser energy increases to 300 mJ/cm², the G peak shifts down to 1542 cm⁻¹, this suggests that the annealed film is still in stage 3, but it is closer to the a-C side. The decrease of the G peak is due to the change of sp^2 configuration from olefinic to graphitic rings, which has lower vibrational frequencies

[104]. The $I(D)/I(G)$ remains at zero value until this energy level, indicating that the graphite-like clusters are very few and can be neglected. As the laser energy increases, the G peak shifts to higher wavenumbers. This is because the G peak indicates all sp^2 bonds, the increasing in its position shows some sp^3 bonds have converted into sp^2 bonds. Another reason is due to the formation of larger graphite-like sp^2 clusters, which has smaller nearest neighbor distance [138]. Furthermore the significant increase in $I(D)/I(G)$ indicates the formation of breathing mode graphite-like sp^2 clusters. For the 80% sp^3 film, the process of microstructure evolution upon laser annealing involves the conversation from ta-C to a-C, and then to NC-graphite. The energy density can be classified into two regimes for this film, regime 1—below 350 mJ/cm^2 , only a small amount of sp^3 bonds convert to sp^2 bonds, with few graphite-like sp^2 clusters forming, and regime 2—above 350 mJ/cm^2 , graphite-like sp^2 clusters form.

Intermediate sp^3 and low sp^3 film:

These two films have lower sp^3 content thereby placing them at the a-C side of stage 3. Unlike the film 1, the laser energy density required to form graphite-like sp^2 clusters is lower. For film 2, its regime 1 is below 250 mJ/cm^2 , $I(D)/I(G)$ increases significantly when laser energy increases beyond 250 mJ/cm^2 . The energy required to reach regime 2 for 50% sp^3 film is even lower, which is 100 mJ/cm^2 . The reason why lower energy is required for the film 3, is due to there is less sp^3 bonds needed to be converted into sp^2 bonds, and therefore the graphite-like sp^2 clusters can form easily.

The relationship between intrinsic stress and graphite-like sp^2 cluster formation:

The evolution of bonding structures of C film during thermal and laser annealing relates to the mechanism of stress relaxation of the C film [33, 37, 156]. The as-deposited film has very high intrinsic compressive stress, which can be varied by the deposition ion energy [156]. The intrinsic stress in the film is the cause of formation of high strain energy within the film. Laser annealing is a way to introduce the external energy to the build-in energy system of the film. The intrinsic internal stress can be relieved with the help of the introduced energy, by forming preferential graphite-like sp^2 clusters which has their basal planes perpendicular to the direction of the high stress component. The shifts of G peak and the change in $I(D)/I(G)$ reflect this statement; when laser energy applied is less than 350 mJ/cm^2 , for film 1 with high stress, there is no significant amount of graphite-like sp^2 cluster formed in the film, as the energy is not high enough to relieve the internal stress, and hence the film is still amorphous without a preferred structure. For film 2 and film 3, the initial internal stress is lower; therefore a lower energy is sufficient to relieve the stress, with formation of preferred graphite-like sp^2 clusters in the film. When the laser energy applied is beyond 350 mJ/cm^2 , the energy is high enough to relief the high stress within the film 1. However, the G peak position of film 1 shifts to an even higher wavenumber at higher laser energy densities (above 350 mJ/cm^2), compared with other films. Similarly, for $I(D)/I(G)$, film 1 has the relatively higher value compared to the film 2 and film 3. This can be caused by the stress relaxation level for films with different initial intrinsic internal stress. For film with higher initial stress, higher laser energy is required to induce the stress relaxation. With sufficient laser energy applying to anneal the film, more graphite-like sp^2 clusters with preferred orientation tend to form, and hence the internal

stress can be reduced. Similarly, compared to the film 3, film 2 also has the higher G peak position and $I(D)/I(G)$, when annealed at high laser energy densities.

To confirm the interpretation based on the Raman results, HRTEM was used to show the microstructural detail before and after laser annealing. Figure 6-13 a-c show the cross sectional HRTEM image and selected area diffraction pattern of the as-deposited film 1, and after it being annealed using a laser energy density of 350 mJ/cm^2 and 550 mJ/cm^2 , respectively. In Figure 6-13 a, the films are fully amorphous in structure and no considerable sp^2 clusters can be observed in the microstructure. This viewpoint is also confirmed by considering the diffraction patterns of the films which are shown as inset in the image, which does not show a continuous diffused ring around the central beam (blocked by the mechanical beam blocker). This indicates that there is no special ordering existing in the as-deposited film. This TEM image matches with the Raman results, the as-deposited film is purely amorphous and no graphite-like sp^2 clustering can be detected. In contrast, Figure 6-13 b shows some small sp^2 clusters start to appear after the film being annealed with a laser energy density of 350 mJ/cm^2 . These sp^2 clusters lead the unique pattern in the diffraction pattern, as shown in the inset, two dim arcs can be observed, this reflects the (002) graphitic microstructure within the annealed film. The Raman results have shown at the laser energy density level, the D band starts to become significant, which is the sign of graphite-like sp^2 clusters formation. However it can be noticed that the crystalline structure is not uniformly distributed throughout the film. As indicated in Raman analysis, as laser energy density used for annealing increasing, more sp^2 clusters will form. The HRTEM image shown in Figure 6-13 c shows the microstructural detail of the film annealed using 550 mJ/cm^2 laser. It shows the crystallinity increases as compared

to the film annealed using 350 mJ/cm^2 laser, and the structure is uniformly distributed throughout the film. Also the diffraction pattern shown in the inset is more obvious comparing to the one in Figure 6-13 b. The HRTEM and diffraction pattern are in good agreement with the Raman results, which confirms as the increasing of laser energy density enhance the formation of graphite-like sp^2 cluster

Figure 6-13 HRTEM image and SAD pattern (inset) of (a) the as-deposited film (film 1), (b) annealed film using laser energy density of 350 mJ/cm^2 and (c) annealed film using laser energy density of 550 mJ/cm^2

6.3.2.3 Electrical Properties Evolution upon Laser Annealing

Figure 6-14 shows the resistivity for film 1-3 pre and post laser annealing, in a logarithmic scale.

Figure 6-14 Electrical resistivity of films with different initial sp^3 content as a function of laser energy density

Film with higher sp^3 content exhibits higher electrical resistivity, because of the isolative effect of sp^3 bonding. The resistivity of the film changes as different laser energies are applied and sensitivity is closely related to the initial properties of the film. The film 1 will only have a large drop in resistivity at 350 mJ/cm^2 , and for film 2 and film 3 is at 250 mJ/cm^2 and 150 mJ/cm^2 respectively. This is because of the conversion of sp^3 to sp^2 bonding, and the formation of graphite-like sp^2 clusters. During laser annealing, some sp^3 bonds are converted into sp^2 bonds, so even at low laser energy level, the resistivity starts to reduce. When the laser energy density increases to a point whereby graphite-like sp^2 clusters start forming, resistivity drops dramatically. The lower sensitivity in resistivity change of the film 1 is because of a higher laser energy required to form graphite-like sp^2 clusters. The lower electrical resistivity also indicates there are more graphite-like sp^2 clusters within the film.

6.4 Localized Transformation of C:Me Nanocluster Films

In previous section, it has shown that the different behavior with the presence of metal nanoclusters during thermal annealing. However for laser annealing, there is no study has been performed on C:Me nanocluster films yet. It is worthwhile to know how the C and Me atoms response when they are under the irradiation of laser pulse. Hence in this section, the laser annealing effect on C:Me nanocluster film such C:Ni film will be investigated.

6.4.1 Experimental

The C:Ni thin films used in this experiment was same as the film grown at RT in chapter 5, the arc current of Ni source applied was set to be 120 A. The as-deposited C:Ni films were then subjected to laser irradiation at different laser energy densities. The laser used in this work was the same as the one used to anneal pure C film in previous section. All the samples were only exposed to a single pulse irradiation, with intensity various from 100 to 500 mJ/cm² in a step of 100 mJ/cm². The evolution of film microstructure and properties were studied using visible Raman, XPS, TEM and electrical IV probing.

6.4.2 Results and Discussion

6.4.2.1 Compositional Analysis

The film composition was measured by XPS analysis, the Ni content of the as-deposited C:Ni film was measured to be about 4.5 at%. Figure 6-15 a and b show the high C 1s core-level XPS spectra of as-deposited C:Ni film and the C:Ni film exposed with 500 mJ/cm² laser energy density. For the as-deposited C:Ni film, the content ratio of sp²

and sp^3 bonding was measured to be about 0.85, which is equivalent to 46% of sp^2 content. While for the C:Ni film annealed with 500 mJ/cm^2 laser energy density, the sp^2 content increases to 88%. Besides these two peaks, there are several other peaks detected after the deconvolution of the spectra. For the as-deposited film, C-O peak and C=O peak centered at 286.7 eV and 288.7 eV were detected and for the laser annealed film, one more C $\equiv$ O peak was detected at 290.8 eV. However, there is no C-Ni carbide peak observed for both samples. Figure 6-15 c and d show the Ni 2p core-level spectra of the C:Ni film before and after laser annealing. The spectra can be deconvoluted into three main peaks for the Ni2p3 envelope. For the as-deposited film, there are Ni metallic peak, NiO peak and Ni2p3 satellite peak centered at 852.8 eV, 854.5 eV and ~ 860 eV, respectively. For the laser annealed film, the three peaks are Ni metallic peak, Ni(OH)₂ peak and Ni2p3 satellite peak centered at 852.8 eV, 856 eV and ~ 860 eV. Based on the XPS data, one of the major changes observed due to the laser annealing process is the transformation of sp^3 bonds into sp^2 bonds, which is identical to pure C film [157]. Another change observed is the incorporation of oxygen into the film. The laser annealing process was carried out in the ambient condition, the heat induced by the laser can cause the oxidation of the C atoms, and the Ni also could also react with the water (-OH) group. The reason for the absence of Ni-C bonding when annealing at 500 mJ/cm^2 is related to the temperature of the film. As suggested by G. Abrasonis, the Ni₃C bonding is only favorable and dominant at $\sim 300^\circ\text{C}$ due to the surface diffusion. For higher temperature, the Ni₃C bonding is metastable and preferred to reform into metallic fcc Ni phase [158]. It has been shown that the surface temperature of the C film with thickness of 300 nm could reach above 400°C even when it is only exposed to 80 mJ/cm^2 of laser energy density

[136]. Therefore, in this work, the Ni atoms are found to be remained in their metallic phase and NiO or Ni(OH)₂ forms.

Figure 6-15 XPS core-level spectra at C 1s for (a) as-deposited C:Ni film and (b) C:Ni film annealed with 500 mJ/cm² laser energy density, and XPS core-level spectra at Ni 2p for (c) as-deposited C:Ni film and (d) C:Ni film annealed with 500 mJ/cm² laser energy density

6.4.2.2 Microstructural Analysis

The transformation of the microstructure for the C:Ni film corresponds to the laser annealing was investigated using visible Raman spectroscopy. Figure 6-16 shows the Raman spectra of the as-deposited C:Ni film and film exposed to different laser energy density. The as-deposited C:Ni film exhibit a strong G band, as a result from both of the breathing and stretching mode of sp² bonds and a weak D band, due to the present of small graphite-like clusters. As the laser annealing intensity increases, the intensity of the

D and G band increase concomitantly. Also, the evolution of the D band and the splitting between D and G band became more prominent as the laser intensity reaches 200 mJ/cm^2 . Although our previous work has already shown that the formation of graphite-like sp^2 clusters can be achieved by low laser energy density for a-C film with relative high sp^2 content [157], however, the C:Ni film exhibits a more pronounced D band formation at a lower laser intensity indicating that the present of Ni clusters did enhance the sp^2 cluster formation.

Figure 6-16 Raman spectra of as-deposited film and films annealed using different laser energy density

Figure 6-17 displays the Raman features as a function of laser energy density. Similar to pure C film with high low sp^3 content, the G peak shifted to a higher wavenumber while the $I(\text{D})/I(\text{G})$ ratio increased even at a low laser energy density level, which is 100 mJ/cm^2 in this experiment. It corresponds to the graphitization of the microstructure, and the formation of graphite-like sp^2 clusters.

Figure 6-17 Raman features as a function of laser energy density

Figure 6-18 a shows the HRTEM image of the as-deposited C:Ni thin film and the FFT pattern is shown in the inset. The darker regions correspond to Ni clusters while the lighter regions are consisted of C. The Ni clusters are observed to be 3~6nm in diameter and embedded within the carbon matrix, which are generally amorphous as there is no distinct graphitic plane observed in the TEM and diffraction spots from the FFT, in agreement with the microstructure of the typical carbon film obtained from the FCVA technique at room temperature [159]. Figure 6-18 b shows the TEM image and the inset shows the FFT of the C:Ni thin film after a single pulse laser exposure at 500 mJ/cm². Several curved carbon fringes can be observed in the TEM image and interesting, the contour of the carbon fringes follow the boundaries of the Ni surface and enclosing the Ni clusters. Although discontinued, these 2-3 layers of carbon shells are graphite-like, as indicated by the (002) diffraction arc observed at the FFT pattern. The interlayer spacing between these carbon shells is estimated to be about 0.34nm, which is corresponding to the (002) planes of the NCG [159]. These observations are different from one observed on a pure a-C thin film undergoes the same laser annealing process [39, 40, 157]. For the

latter, due to the present of biaxial stress, basal planes are usually formed and oriented themselves perpendicularly to the highest stress component (the growth substrate) when additional energy is supplied to the a-C structure. The formation of graphitic layers is to relax the high intrinsic stress and it is the preferred structure with minimum strain energy [40, 159].

Figure 6-18 HRTEM image and FFT pattern (inset) of (a) the as-deposited film and (b) C:Ni film annealed with 500 mJ/cm² laser energy density

Although it is widely known that transition metals, such as Ni, promotes graphitization through the "super-saturation" approach [82], this may not be applicable here as most of the graphitic shells are seems to be incomplete, the evident for the nickel carbide formation is missing and the elemental composition of Ni before and after the laser irradiation process is similar. The mechanism for the transformation from a-C to shell-like graphitic encapsulation structure should be identical to a typical a-C film where the formation of the graphitic planes is used as a form to relax the internal stress [159].

6.4.2.3 Electrical Properties Evolution upon Laser Annealing

The electrical resistivity of films as a function of the laser energy density is measured in the logarithmic scale and shown in Figure 6-19. It is clear that the resistivity decreases from about $10^5 \Omega/\text{m}$ to $10^1 \Omega/\text{m}$ as the laser energy increases to $500 \text{ mJ}/\text{cm}^2$. It is known that the electrical conductivity of C film is closely related to the graphite-like sp^2 clusters though electron hopping transport mechanism [87], as a result, conductivity increases as the amount and size of the sp^2 clusters increase [51]. Therefore, by simply applying a single laser pulse onto the C:Ni nanocluster film, it is possible to alter the electrical conductivity of the film in 5 orders through the transformation of carbon microstructure.

Figure 6-19 Electrical resistivity (in log scale) of C:Ni films as a function of laser energy density

6.5 Conclusions

In this chapter, first of all we have shown the thermal annealing effect on pure C and C:Me nanocluster films. It showed with presence of metal nanoclusters within the

film, it was easier for the graphitization process. The metal types were also suggested to affect the change in microstructure of films during annealing. As shown in previous chapter, the metal such as Ti which can form carbide at high growth temperature, the C:Ti nanocluster film is relatively stable comparing to C:Ni nanocluster film. In addition, when the C:Ni nanocluster film was annealed at 1000°C, both carbon black and silicon oxide nanowires (SONWs) formed.

Except for thermal annealing, a method to realize localized transformation of C based thin film—laser annealing, and its effect on change in microstructure and properties of C based thin film has been investigated. The effect of initial sp^3 content on bonding structure of pure carbon upon pulsed laser annealing was discussed firstly. The results demonstrated that the higher the sp^3 content, the more stable the film when it was subjected to the laser irradiation, hence a higher laser energy density was required to induce the transformation from sp^3 bonds to sp^2 bonds, and the formation of graphite-like sp^2 clusters. The laser annealing with sufficient laser energy promoted the formation of graphite-like sp^2 clusters, and resulted the decrease in electrical resistivity. In addition it also suggested that higher sp^3 film was more preferable to form a DLC/NCG hybrid film with large contrast in electrical conductivity for future carbon based electrical interconnect and RF applications.

The effect of laser annealing on tailoring microstructure and properties of C:Me nanocluster film has also been demonstrated in this chapter. Depends on the laser energy density, the laser annealing process transformed the carbon encapsulation matrix from a-C to graphitic shell-like structure and modified the electrical conductivity. After annealing using high laser energy, it showed the present of curved carbon fringes enclosing the Ni

nanoparticle. It also indicated that Ni only exists in metallic phase and no nickel carbide formation regardless the effect of laser annealing. The transformation mechanism was believed to be associated with the relief of the internal stress and the Ni nanoparticles were considered as a template for the formation of the graphitic layer. The C:Ni film exhibited a wide range of electrical resistivity (~5 orders), correlated with the energy density of the laser annealing, providing a possibility to enhance the electrical performance for carbon encapsulated metal nanoparticle material.

Chapter 7: Applications of C:Me Nanocluster Films—Growth of CNTs on Conducting C:Me Nanocluster Films

7.1 Introduction

Carbon nanotubes (CNTs) have attracted a lot of attention in the fields of nano-science and nano-technology because of their superior physical, electrical properties and thermal properties [160, 161]. A substantial amount of work has been done to promote them in the industry, and one of the requirements is growth of CNTs onto conductive metal or substrates [162, 163]. The conventional way of growing CNTs is a multi-step process, the first of which is to deposit a barrier layer, which can be insulating material such as silicon oxide (SiO_2), or conductive material such as titanium nitride [164]. Secondly it requires the deposition of a catalyst layer such as nickel (Ni), cobalt (Co) or iron (Fe). However, the effective electrical conductivity of the CNTs is higher when CNTs are grown directly on a conductive substrate [165]. An alternative approach to eliminate the use of barrier layer during growth is to deposit amorphous carbon a-C metal (C:Me) nanocluster film, such as C:Ni, C:Fe and C:Co as the catalyst layer.

Previous studies had shown that nanocluster film serving as catalyst layer results in better density control of CNTs [166, 167], and also better performance in CNTs field emitter array (FEA) applications [116, 135]. Other than serving as the catalyst layer of CNTs growth, another advantage of incorporation of metal within C film is to increase the

conductivity of the film. Takeno, et al. found that the electrical conductivity is proportional to the amount of metal incorporated into the C:Me nanocluster film [51, 168, 169]. However the focus was only on tuning the metal content of the film. The relationship between the CNTs growth and the intrinsic properties of C:Me nanocluster film, such as the sp^2/sp^3 ratio is not well-understood yet. Recent work has shown that by in-situ thermal annealing and ex-situ laser annealing, sp^2 rich high electrical conducting nanostructured C film can be synthesized [37, 39, 40, 127], which can then be adopted in future electronic applications. Hence the electrical properties of C:Me nanocluster film can be varied by only changing the sp^2/sp^3 ratio of the amorphous carbon.

In this chapter, C:Co nanocluster film has been adopted as the catalyst layer of CNTs growth. The feasibility of CNTs growth on conducting C:Co nanocluster film has been shown, by only varying the sp^2/sp^3 ratio of the film. It adequately shows that CNTs can be grown in a conducting catalyst layer without the use of a barrier layer.

7.2 Experimental

C:Co nanocluster films were deposited on N-type silicon wafer as described in the previous chapters, with using 99.99% cobalt target instead of nickel target. The substrate heating temperature was varied from room temperature to 500 °C to obtain the various sp^2/sp^3 ratios. The three C:Co nanocluster films were then cut into a dimension of 1 cm by 1 cm, and placed into a plasma enhanced chemical vapor deposition (PECVD) chamber where the CNT growth would be carried out. The CNT growth was performed at 600°C

with a plasma power of 85 W for 30mins. The ramp rate was set at maximum. The heater stage reached 600 °C in less than 10 sec, and the carbon feedstock gas (C_2H_2) was immediately introduced to reduce the influence of annealing on the samples. The pressure in the chamber during CNT growth was maintained at 4.5 Torr with a C_2H_2/NH_3 gas ratio of 1:5. The characterization tools used were visible Raman spectroscopy, SEM and IV electrical probing.

7.3 Results and Discussion

Figure 7-1 a shows the Raman spectra of C:Co nanocluster films deposited using different substrate temperatures. The main changes of the Raman spectra are the shift of G peak position and the increase in D peak density. The G band relates to both breathing and stretching mode of sp^2 bonds, and the D band only reflects the existence of the breathing mode of sp^2 bonds, which are normally in the form of nanometer size graphite-like clusters [17, 104]. The spectra of the C:Co nanocluster film at room temperature shows only one peak and a neighbor peak at around 1350 cm^{-1} started to emerge with increasing substrate temperature.

Figure 7-1 (a) Raman spectra of C:Co nanocluster film grown using different growth temperatures and (b) Raman features as a function of growth temperature

The microstructure subjected to different growth temperature is shown in Figure 7-1 b—the rightward shift of G peak position is due to the conversion of sp^3 bonding to sp^2 bonding [39, 82, 104]. Based on the three-stage model [104], the film grown under RT is estimated to be 30% in sp^2 content, and as the growth temperature increases, the sp^2 content in the film raises to more than 80%. Beside the rise in sp^2 content, the six-ring graphite-like sp^2 bonds also become dominant, which is shown by the increase in I(D)/I(G) ratio [104].

Figure 7-2 I-V characteristic of C:Co nanocluster films grown using different growth temperatures

The changes in the microstructure of C:Co nanocluster film influence the electrical properties of the film as represented by the I-V curve of these three films is shown in Figure 7-2 above. The film grown under RT has high resistance of $\sim 10^9 \Omega$, and the resistance reduces with the growth temperature. The film grown under 500°C has a much lower resistance of about $10^1 \Omega$. The reduction of resistance is attributed to the increase in sp^2 content, and the formation of more graphite-like sp^2 clusters, which has been reported in a previous study [39, 40, 127], and also the incorporation of Co nanoclusters.

Figure 7-3 a-c below show the CNTs grown on different C:Co nanocluster films. CNTs of the same length ($\sim 1 \mu\text{m}$) can be synthesized on all these three types of C:Co nanocluster films. However the density of CNTs does not have a significant change among these three kinds of C:Co nanocluster film. Zhang et al. has reported that the density of CNTs grown on C:Me nanocluster film has a strong relation with the content of metal [166]. In this work, it was demonstrated that the initial sp^2/sp^3 ratio does not affect the density of CNTs grown on the C:Co nanocluster film.

Figure 7-3 SEM images of CNTs grown on different C:Co nanocluster film: (a) RT, (b) 250°C, and (c) 500°C

The quality of the CNTs is characterized and shown in Figure 7-4 below. The two peaks detected in the spectra are D peak and G peak which fall in the range of $1370\sim1400\text{ cm}^{-1}$ and $1580\sim1600\text{ cm}^{-1}$. Unlike C film, D peak for CNTs represents defects, and G peak is an indication of crystalline graphite [170]. The inset lists the $I(D)/I(G)$ ratio of these CNTs. CNTs 3 has the lowest ratio which indicates the lowest defect level. Although the defect level is desired to be zero, it is difficult to be eliminated in the PECVD process [171].

Figure 7-4 Raman Spectra of CNTs grown on different C:Co nanocluster films and the I(D)/I(G) ratio (inset)

7.4 Conclusions

C:Co nanocluster films with same Co content but different initial sp^2/sp^3 ratio were deposited using Y-bend FCVA deposition system, with varying growth temperatures. The electrical resistance of C:CO nanocluster film grown at 500°C was shown to be reduced to approximately $10^1 \Omega$. CNTs can be successfully synthesized on C:Co nanocluster film regardless of the change of initial sp^2/sp^3 ratio of the film. There was no clear evidence to show the influence of initial sp^2/sp^3 ratio on the density of CNTs grown on C:Co nanocluster film, however the quality such as defect level, was shown to be dependent on the initial sp^2/sp^3 ratio of the C:Co nanocluster film, which can be reduced by using film with higher initial sp^2/sp^3 ratio. However the detailed reasons to affect the quality of CNTs grown on the nanocluster films are still need to be explored further.

Chapter 8: Conclusions and Recommendations for Future Research

8.1 Conclusions

In chapter 3 we have demonstrated the design and implementation of the Y-bend FCVA deposition system, which consists of two independent cathode sources, several focusing systems which controls the cluster density, and a substrate heater to tailor the film microstructure. We firstly tested the effect of focusing system on the cluster density, by using Zn target at the metal material. The results show that by changing the input current of the anti-Helmholtz coil, which adjusts the magnetic strength generated, the Zn cluster density can be controlled—the stronger the magnetic field, the more intermixing of the C and Zn ions, hence the film deposited has a higher density of Zn nanoclusters.

In chapter 4 the effect of arc current of metal source on the film microstructure and electrical properties has been investigated. It showed that the arc current of metal (Ni in this experiment) source was able to influence the ion density of the Ni plasma. By increasing the arc current, the Ni ion density was also increased, which results in the increase of the Ni content within the C:Ni nanocluster film. In addition, when the arc current further increases to 140 A, the graphite-like sp^2 clusters became visible, which can be reflected by the appearance of D peak in the Raman spectrum, and confirmed by the HRTEM images. The electrical measurement suggests that with the presence of Ni nanocluster within the film, the conduction mechanism is non-contact related transport type. The Ni nanoclusters are able to increase the electron hopping sites. In addition it

shows that those graphite-like sp^2 clusters formed when high arc current applied, and Ni nanoclusters, both of them contribute to the increase in electrical conductivity.

In chapter 5, we have further explored the feasibility to control the film structure using the newly designed Y-bend FCVA deposition system. The important deposition parameter focused is the growth temperature. Pure C, C:Ni and C:Ti nanocluster films have been deposited at different growth temperatures. The microstructural analysis has been performed using EDX, XPS, visible Raman and HRTEM. The results show that the growth temperature has greater effect than elemental composition (such as metal content) on the film structure. Compared to pure C film, with the presence of metal nanoclusters, the sp^2 clusters formation can be enhanced as the growth temperature. The XPS results also show that Ni does not form C-Ni carbide regardless of the growth temperature, while Ti is found to be able to form C-Ti carbide and the content increases as the growth temperature rises. The film property such as electrical property has also been investigated. Comparing to pure C film, C:Ni nanocluster film exhibits better electrical performance (low in resistivity), and C:Ti also shows a better tribological performance (low coefficient of friction for even high sp^2 content).

The annealing effect on C based thin films has been discussed in chapter 6. First of all the thermal annealing effect on pure C, C:Ti and C:Ni nanocluster film has been shown. It shows that Ni is more active during thermal annealing comparing to Ti, hence causes the graphitization process to occur at a lower annealing temperature—400°C here. However, as the annealing temperature is increased to 1000°C, it is found that SiONWs and carbon black could be able to synthesize. This involves a SLS growth between C:Ni nanocluster film and Si from substrate.

Another type of annealing process—laser annealing, which induces the localized transformation of carbon based material has also studied in chapter 6. First of all, the effect of laser annealing on pure C film has been investigated. The factors such as laser energy density and initial properties of the C film (initial sp^3 content) are focused on. Results show that for film with same initial properties, the microstructural transformation strongly depends on the laser energy density, a higher laser energy density leads more graphite-like sp^2 clusters to form within the film. For film with higher initial sp^3 content, higher laser energy density is required to induce the transformation in microstructure, hence the switching from electrical insulating to conducting. In contrast to the film with higher initial sp^3 content, the film with lower sp^3 content requires a lower laser energy density to form enough conductive graphite-like sp^2 clusters. However, it is found that due to the fact of annealing of carbon based thin film which related to the stress relaxation, film with higher initial sp^3 content tended to form more sp^2 cluster after high laser energy density annealing, which was able to minimize the higher stress of the as-deposited film. Thus, the film with higher initial sp^3 content was able to provide a large contrast in electrical conductivity for future carbon based electrical interconnect and RF applications.

The effect of laser annealing on C:Me nanocluster film has also been investigated in chapter 6, C:Ni nanocluster film was studied in this experimental work. Unlike the formation of fringe-like sp^2 clusters which are perpendicular to the growth substrate, the curved carbon fringes enclosing the Ni nanoparticle forms after annealing using high laser energy density. Similar to pure C film, the electrical resistivity also decreases as the laser energy density used.

In chapter 7, we showed the feasibility of growing CNTs on different types of C:Me nanocluster film. We showed that CNTs can be grown on C:Me nanocluster film such as C:Co nanocluster films, which have the same Co content, but different sp^2/sp^3 ratio. C:Co nanocluster film with high sp^2/sp^3 ratio is electrically conducting, and hence provides a possible solution to eliminate of the use of insulating barrier layer for conventional CNT growth.

8.2 Recommendations for Future Research

In chapter 3 we have implemented the new Y-bend FCVA deposition system, and also shown the possibility to control the metal cluster density by adjusting the magnetic trap generated by the anti-Helmholtz focusing coil. The film properties and detailed microstructure should be further investigated in the future.

As it was shown in chapter 4, the metal content and the film structure can be controlled by only changing the arc current of the metal source. It is worthwhile to know that how the composition and microstructure will be affected by changing the arc current of carbon source at the same time. In chapter 5, it was shown that the growth temperature can strongly affect the film microstructure through the TEM study, however the TEM analysis cannot be performed on all nanocluster films. In the future it is worth to do a more completed TEM study on all nanocluster films grown at different temperature, and also includes the electron energy loss spectroscopy (EELS) analysis.

In this work, we changed the film microstructure and properties by only controlling the magnetic trap, arc current of source, and growth temperature. However a more detailed systematical measurement on how the deposition parameter affects the film growth requires further investigation.

Last but not least, we need a further exploration on the applications of the C:Me nanocluster film, such as thermal, magnetic area. In addition, a more complete study on CNTs growth on C:Me nanocluster films, and the performance of the CNTs-C:Me nanocluster film system is required in the future work.

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Journal Publications

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8. **N. Xu**, S. H. Tsang, B. K. Tay, E. H. T. Teo, X. Wang, "Enhancement of Amorphous Carbon (a-C) Graphitization using Multi-Pulsed Laser Annealing," *Nanoscience and Nanotechnology Letters* (In press).

Conference Publications

1. **N. Xu**, E. H. T. Teo, X. Wang, A. Du, C. M. Ng, B. K. Tay, "Carbon metal composite film deposited using novel Filtered Cathodic Vacuum Arc technique," 61st Electronic Components and Technology Conference (ECTC), Florida, 2011. (Oral Presentation)
2. **N. Xu**, C. C. Yap, E. H. T. Teo, C. M. Ng, B. K. Tay, "Carbon nanotubes growth on cobalt-containing amorphous carbon films," MRS Spring Meeting, San Francisco, 2012 (Poster Presentation)
3. **N. Xu**, E. H. T. Teo, X. Wang, C. M. Ng, B. K. Tay, "The effect of pulse laser annealing on amorphous carbon films with different sp^3 fraction," International Conference on Diamond and Carbon Materials 2012, Granada, Spain. (Oral Presentation)
4. **N. Xu**, S. H. Tsang, E. H. T. Teo, C. M. Ng, and B. k. Tay, "Formation of thick textured carbon film using filtered cathodic vacuum arc technique," 5th IEEE International Nanoelectronics Conference 2013, Singapore. (Oral Presentation)
5. **N. Xu**, S. H. Tsang, E. H. T. Teo, C. M. Ng, and B. k. Tay, "Synthesis of nanostructured carbon:titanium thin film for tribology applications," International Conference on Diamond and Carbon Materials 2013, Riva del Garda, Italy. (Oral Presentation)

Patent

1. Tsang Siu Hon, **Xu Naiyun**, Teo Hang Tong Edwin, Tay Beng kang "Apparatus for the Generation of Nanocluster Films and Methods for Doing the Same", PCT Patent WO/2013/119182, (Publicaiton data: February 6, 2013), international publicaiton number: 2013/119182
2. **Xu Naiyun**, Tsang Siu Hon, Teo Hang Tong Edwin, Tay Beng kang "Y-bend Filtered Cathodic Vacuum Arc (FCVA) System", U.S Patent, (filing in progress)

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