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Multifunctional nanocomposite co-containing diamondlike carbon thin films

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MULTIFUNCTIONAL NANOCOMPOSITE CO-CONTAINING DIAMONDLIKE CARBON THIN FILMS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Interdepartmental Program in Engineering Science

by

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December 2004
DEDICATION

This dissertation is dedicated to my sister and my son for their support and love throughout all my days in the USA.
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ABSTRACT

Metal-containing, hydrogenated carbon films (Me-a-C:H) is a special class of nanocomposite films of particular interest since they can be multifunctional through the synergistic interaction of their individual components. Thus, nanocomposite thin films possess high potential in a wide field of engineering applications, especially in small scale devices. A series of multifunctional nanocomposite Co-a-C:H thin films have been synthesized by a hybrid chemical vapor deposition (CVD) and physical vapor deposition (PVD) process to uncover the relationship between synthesis, microstructure and properties. The effects of deposition parameters on the microstructural evolution and properties have been systematically studied.

The results showed that the microstructure can be controlled through proper adjustment of the processing parameters, to produce Co in the shape of: nano particles, elongated particles, wormlike columns, self-assembled multilayers, self-assembled nano columns embedded in an amorphous a-C:H matrix. Self-assembly of Co nano columns in a-C:H is discovered. As-deposited Co-a-C:H thin films are composed of defect rich ε-Co encapsulated in a-C:H matrix. Regarding the properties, raising C content (reducing Co content) in the films improves their hardness and corrosion resistance and decreases friction and wear rate. All the Co-a-C:H films exhibit a low surface roughness. Nano columnar Co-a-C:H films show size-dependent magnetic behavior, such as superparamagnetic and perpendicular magnetism. Annealing studies reveal that the phase transitions of Co in Co-a-C:H film follow the sequence of Co-a-C:H film \( \xrightarrow{300^\circ C} \) ε-Co + \( \delta^\prime\)-Co\(_2\)C \( \xrightarrow{343^\circ C} \) hcp-Co + \( \delta^\prime\)-Co\(_2\)C \( \xrightarrow{407^\circ C} \) hcp-Co + graphite \( \xrightarrow{459^\circ C} \) fcc-Co + graphite. A mechanism and a zone diagram are presented to
describe the microstructural evolution of Co-$\alpha$-C:H films. Knowledge gained from this research allows the design and synthesis of nanocomposite Co-$\alpha$-C:H films and other multifunctional systems of interest for new applications in the field of nanotechnology.
CHAPTER 1. INTRODUCTION AND MOTIVATION

Thin film devices and circuit assemblies are growing rapidly for the need in commercial, military and space development from reliable, high performance, low cost, compact and versatile consumer appliances to superior, lightweight, low-power and rugged communication, control and detection systems. Magnetic, superconducting, dielectric, acoustic and optical thin films provide functions in micro-volume devices and circuit architectures in high-density integrated systems. Furthermore, it has been observed that materials exhibit enhanced/unique properties when their critical dimension is in the nano regime (<50 nm). Therefore, our interest on nanocomposite Co-containing amorphous hydrogenated carbon (Co-a-C:H) thin films emerged to pursue multifunction and nano effects. Moreover, initial studies on Co-C films provide us with such information\(^1\)\(^-\)\(^4\) as their potential application in high density magnetic recording media,\(^1\) their anti oxidation merit and other unique structures and properties. The idea to replace C by a-C:H (or diamondlike carbon, DLC) comes from the reality that DLC is superior to C in terms of mechanical properties and wear resistance without the loss of excellent anti-corrosion properties.

The last few years in our laboratory, we have studied DLC and metal-containing DLC films (Me-DLC, Me: Si, Cr, Ti) in an effort to increase the thermal stability of DLC films.\(^5\)\(^,\)\(^6\) It has been shown that above 350°C, DLC films graphitize (the diamondlike sp\(^3\) domains transform into graphite-like domains with sp\(^2\) C bonding) and thus, lose their otherwise excellent tribological properties (coefficient of friction < 0.1 and wear rate \(~1\times10^{-7}\)mm\(^3\)/Nm).\(^7\) During the course of the above program, we were able to synthesize Cr and Cr carbide nanocrystals (3-5 nm) embedded in a DLC matrix.\(^6\) The films were
found to exhibit improved thermal stability and mechanical properties through a nanodispersion hardening mechanism, while maintaining the tribological properties of DLC. Thus, the idea evolved that replacing the Cr nanocrystals with another element such as Co, in addition to the aforementioned properties, the films can also be magnetic and thus “multifunctional”. Successful design and synthesis of such films may address for example, the ever-increasing space limitations facing the magnetic recording media industry. A layer of less than 2 nm thick DLC film is required at present for low friction and wear resistance preventing the head of coming closer to the underlying magnetic films.8 In these films, the DLC can also play the dual role of reducing the media noise and preventing surface oxidation. Also, DLC is inert and shows good anti-corrosion properties in humidity and acidic environments.9-11 Furthermore, DLC is superior to carbon in terms of tribological and mechanical properties.12-20 Me-DLC can overcome the drawbacks of DLC in adhesion,21-25 surface energy,26 electrical conductivity27 without losing the good mechanical and tribological properties.28 In addition, multifunctional Co-DLC films have the potential to overcome such limitations and provide a promising solution for applications in small-scale devices and systems (micro-, nano-electronics, MEMS, NEMS, sensors, etc.)

Until now, research related to Co-DLC is very limited. There are two previous reports in the literature by Laurent et al. relevant to Co-DLC films.29,30 They synthesized metal (Co) clusters in polymerized hydrocarbon and studied the magnetic behavior of the films. There are a few more studies on Co-DLC films in the literature but no detailed analysis of processing effects, microstructural characteristics and other properties besides preliminary results and reported surface energy measurements.31-34 Thus, the motivation
behind the present study was to investigate systematically the microstructural evolution of nanocomposite Co-DLC films and develop a fundamental understanding of their synthesis-structure-property relationship.
CHAPTER 2. OBJECTIVES

Multifunctional Co-\textit{a}-C:H films possess significant potential in responding to current and future technological needs relating to small-scale materials and devices and the field of nanotechnology. The objective of the present study is to gain a basic understanding of the synthesis-structure-property relationship in these films with particular emphasis on the nano scale effects on properties. The Co-\textit{a}-C:H system can be considered as a model system and development of fundamental understanding in this system will allow design and development of future systems of interest.
CHAPTER 3. REVIEW OF LITERATURE

3.1 Magnetic Thin Films

3.1.1 Background

Magnetism has been a human curiosity for nearly three thousand years. For a long time, macroscopic magnetism had been the focus, such as compass needles, geomagnetic field, and electromagnets. Atomic scale magnetic phenomena were discovered in the early part of the last century. It was not realized that solid state magnetism is largely a nanostructure phenomenon until recent decades. One of the natural examples is the biomagnetic phenomenon. Magnetic nano particles have been found in the brain of bees, pigeons and tuna serving as field sensor for migration. Magnetic Fe$_3$O$_4$ nano particle precipitation was also found in bacteria, mollusks and insects.$^{35}$

A smaller and smaller size or length is at the root of progress in new magnetic materials. Recently, the interest has moved from the micro to nano scale. Nano-structure describes those materials that have a majority of grain diameters in the range of ~1 to 50 nm. Typical geometries of interest in nano magnetism were divided into 5 categories: particles and clusters, thin films and multilayers, particle arrays and functional components, nano wires, nano composites and other bulk materials.$^{35}$

Magnetic materials are traditionally classified by their magnetic coercivity or hardness. The term historically comes from iron. The addition of carbon to iron increases both the mechanical hardness and the coercivity. And the hardness is adopted to classify magnetic materials into three distinct sets. In descending order, they are hardmagnets (permanent magnets), recording media and soft magnets. Materials with low coercivity are called soft; those with high coercivity are called hard. Permanent magnets have a
wide range of application, such as in hard-disk drive, microphones, electromotors, and toys. Most permanent magnets were made from steel before 1950. At present most high performance magnets are made from rare-earth transition-metal intermetallics such as Nd$_2$Fe$_{14}$B, and SmCo$_5$. Magnetic recording media are utilized in computer and audio-visual technology. The moderate coercivity and the rectangular loop shape ensure the stability of the stored information. Traditional storage media are made from granular Fe$_2$O$_3$ and CrO$_2$. Advanced high-density recording media are made from magnetic thin films containing Co. Soft magnetic materials are widely used for flux guidance in permanent-magnet, transformer cores for high-frequency and microwave application, and recording heads. Iron-based metallic magnets have long been used as soft magnetic materials. Recently amorphous and nanostructured metals have been a new interest. Their composition is $M_{100-x}I_x$ (M=Fe, Co, Ni, and I=B, C, P,…) where $x$=10–20. Impurity elements such as C, S, N, and O distort the crystal lattice and hinder the easy formation of domains and their motion.

Quantum mechanics is essential to interpret magnetism. The behavior of materials in magnetic fields leads to the classification of diamagnetic, paramagnetic, ferromagnetic, antiferromagnetic based on the magnitude, sign and effect of temperature on their magnetic properties. The magnetic moment of a free atom has three principal sources: the spin with which electrons are endowed; their orbital angular moment around the nucleus; and the change in the orbital moment induced by an applied magnetic field. The first two effects contribute to paramagnetic magnetization, while the third gives a diamagnetic contribution.
Magnetic susceptibility is defined as $\chi = \frac{M}{H}$ where magnetization $M$ is the magnetic moment per unit volume; $H$ is the applied magnetic field. Substances with a positive susceptibility are called paramagnetic, and substances with a negative magnetic susceptibility are diamagnetic. According to the Langevin theory, paramagnetic susceptibility is inversely proportional to the temperature. This is described by Curie law: $\chi_p = \frac{C}{T}$ ($C$ is Curie constant). Compared to diamagnetic and paramagnetic materials, ferromagnetic materials show a very strong response to the presence of an applied magnetic field. Fe, Co, Ni, Gd are the most well-known ferromagnetic metals. A ferromagnet has a spontaneous magnetic moment, called saturation moment. The existence of a spontaneous moment indicates that the electron spins and magnetic moments are arranged in an ordered manner. Ferromagnetism is dominantly used in industry and commercially for magnetic recording devices. In an antiferromagnet the spins are ordered in an anti-parallel arrangement with zero net moment at temperatures below the ordering. All of the spin arrangements are showed in Figure 3.1. Domains are the small regions, within each of which the local magnetization is saturated. The magnetization directions of different domains do not need to be parallel. There is a transition layer in the crystal between domains that separates adjacent domains called Bloch wall (Figure 3.2). The spins contained in the wall are mostly directed away from the axes of easy magnetization. So the anisotropy energy limits the width of the wall (anisotropy energy is roughly proportional to the wall thickness). Ferromagnetic particles will be a single magnetic domain if they are small enough. Assuming that the small particles are separated far enough apart so that interparticle interaction can be neglected, single domain ferromagnetic particles at elevated temperatures can behave in a manner
like a paramagnet. However, the independent moments are not atomic moments but large groups of moments. The moments of the particle may be $10^5$ times the atomic moment. Such a system is called superparamagnet.

Figure 3.1 Arrangements of electron spins.36

Figure 3.2 The structure of the Bloch wall separating domains.36
Magnetic hysteresis is the most important micromagnetic phenomenon. Technical terms can be defined by a magnetic hysteresis curve\textsuperscript{36} as illustrated in Figure 3.3. A good permanent magnet shows: a) large saturation and remnant inductions, $B_s$ and $B_r$. A large saturation magnetization, $M_s$, and induction $B_s$, are desired for both hard and soft magnetic materials; b) large coercivity, $H_c$. The coercivity is the reverse field $H_c$ required to reduce the magnetization or the induction $B$ to zero; c) high Curie temperature $T_c$. Curie temperature is the temperature above which the spontaneous magnetization vanishes; it separates the disordered paramagnetic phase at $T>T_c$ from the ordered ferromagnetic phase at $T<T_c$. Soft magnetic materials have: (a) high permeability $\mu$, $\mu=B/H=(1+\chi)$, $B$ is the flux density, $H$ is a given applied field; (b) low hysteresis loss per cycle (or low hysteretic power loss); (c) large $B_s$ and $B_r$; (d) high Curie temperatures $T_c$.

![Figure 3.3. Schematic of hysteresis curve for a magnetic material.\textsuperscript{36}](image-url)
The shape of the magnetization curve (Figure 3.3) is determined by the magnetic free energy. The magnetic free energy includes four parts: field (Zeeman) energy, self-field (demagnetization) energy, wall energy, and magnetic anisotropy energy. The magnetic Helmholtz free energy \(^{35,37}\) can be formulated as:

\[
F_m = \int \left[ A(r) \left( M/M_s \right)^2 - K_1(r) \left( M \cdot n / M_s \right)^2 - \mu_0 M \cdot H \right] dr
\]  

(1)

where \(A(r)\) is the local exchange stiffness related to the exchange energy \(J\), and spin dipole moment, \(S \approx CJS^2/\alpha \) at 0 K, with \(C\sim1\) depending on crystal structure and \(\alpha\) is the interatomic spacing, \(M_s\) is the saturation magnetization, \(K_1(r)\) is the local magnetic anisotropy energy density, \(M\) is the magnetization vector, \(n\) is a unit vector parallel to the easy direction of magnetization, and \(H\) is the sum of the applied field and demagnetization field vectors. The magnetic anisotropy represents a barrier to switch the magnetization. A small magnetic anisotropy is desired for soft magnetic materials in order to minimize the hysteretic losses and maximize the permeability. A large magnetic anisotropy is desirable for hard magnetic materials.

Anisotropy energy or magnetocrystalline energy is the energy in a ferromagnetic crystal that directs the magnetization along certain crystallographic axes called directions of easy magnetization. Co is a hexagonal crystal. The hexagonal axis is the direction of easy magnetization at room temperature,\(^{36}\) Figure 3.4.

### 3.1.2 Magnetic Thin Films Application in Recording Media

Magnetic thin films have been widely used in various devices, such as, magnetic and microwave circuits, magneto-optical recording, Faraday effect devices, microwave and millimeter wave applications in communications and radar systems, miniature magnetic inductive components for use in portable communications, computer systems etc. By far,
the most significant application for magnetic thin films is the magnetic recording/memory technology. Magnetic storage has played a key role in audio, video and computer development since its invention. The fundamental technology of recording media has a developing history from particulate to thin film. The early tape media (1955-1985) were composed of $\gamma$-Fe$_2$O$_3$ particles and their variations are still used today in the tape media industry. Since 1985, magnetic thin films had replaced magnetic oxide particles as a source of magnetic flux. The switch and thin film development were driven by the requirement for high recording densities. In the 20 years before 1990, the real density increased at approximately 25% annually.\textsuperscript{38} The first thin film magnetoresistive (MR) heads in 1990 further impacted the magnetic recording technology. The storage density was able to increase at 60% per year. Giant magnetoresistance (GMR) was first discovered in Fe/Cr multilayers\textsuperscript{39} and subsequently in many other multilayers (Co/Cu, Fe/Cu)$^{40-43}$ and sandwiches (Co/Au/Co).\textsuperscript{44} Nonmultilayer GMR was also reported.\textsuperscript{45} Due
to the introduction of GMR, storage densities are increasing at 90-100% annually. The storage density in 2004 was at \(~20\text{ Gbits/inch}^2\).

It is known that there are two kinds of thin film media. If the medium has its magnetization primarily in the plane of the film, it is called \textit{longitudinal recording}. If the magnetization is primarily out of the plane of the film, it is called \textit{vertical recording}. Currently data are recorded longitudinally in a Co-based thin film. The storage density increases by reducing the area occupied by one bit of data. The final limit to storage density is the superparamagnetic limit, where thermal energy is able to overcome coercive energy of the magnetic bit. At present the limit is about 100 Gbits/inch$^2$. However, 1000 Gbits/inch$^2$ is possible by using vertical recording.

A typical structure of a magnetic recording medium is shown in Figure 3.5. Data are stored in a magnetic layer of Co-based alloy. Its underlayer is Cr-based texture layer and a Ni-P base layer on Al$_2$O$_3$-TiC or a glass substrate. A diamondlike carbon coating is applied over the magnetic layer as a protective layer, and a molecular lubricant is used on the overcoat. High density recording keep on pursuing low layer thickness. Therefore, the thickness of layers in Figure 3.5 is an approximate value.

As for the Co-based alloys, various alloy additions to the Co change some of its intrinsic magnetic properties. Pt increases the magneto-crystalline anisotropy constants. Cr tends to segregate to the grain boundaries and decrease the exchange coupling between the grains. Ta can promote the segregation of Cr.

In magnetic tape or hard disk drives, the thin films with low intrinsic coercivities are used in the read heads while thick films with high moments and high intrinsic coercivities are used for storage media.
3.1.3 Crystallographic Texture

For longitudinal media, it is desired that there are as many of grains as possible with their c-axis in the plane of the film. For example, hcp-Co or its alloy films usually take on a crystalline texture with its c-axis being vertical to the plane of the film. The control of the crystallographic orientation of the magnetic layer is obtained by controlling the crystallographic orientation of the underlayer. The polycrystalline magnetic layer is often grown epitaxially grain-to-grain on the underlayer. The epitaxial relationship for deposited Co alloys on a Cr underlayer with crystallographic texture is (10\bar{1}1)Co//(110)Cr (Figure 3.6).\textsuperscript{37,46,47} The angle between the (10\bar{1}1) and the [0001] is 28°. The (0001) plane is the basal plane for the hcp structure. So the crystallographic c-axis is out of the plane of the film. Depositing Cr underlayers at elevated temperatures...
Figure 3.6 Schematic showing the epitaxial relationship of \((10 \overline{1} 1)\text{Co}//(110)\text{Cr}\).\(^{37,46,47}\) will result in (002) crystallographic textures. This causes the c-axis to lie in the plane of the film.

### 3.1.4 Chemical Segregation

Exchange coupling among the Co grains is a significant factor in determining the magnetic and recording properties of Co alloys films. A Co alloy with smaller exchange coupling has larger \(H_c\), low squareness and smaller noise. Non-magnetic elements in the Co alloy such as Cr, Mn, W, B, C can effectively reduce the exchange coupling. On the other hand, Pt seems to promote a more exchange-coupled medium while it significantly increases the magneto-crystalline anisotropy.

### 3.1.5 Future Media

The grain size of the media needs to reduce in order to obtain higher recording densities. When the grains are isolated from each other, it is possible that they will reach the size limit-superparamagnetism.\(^{48}\) This loss of thermal stability can be overcome by
increasing the magnetocrystalline anisotropy. High anisotropy media like CoSm, CoPt and FePt are candidates for extremely high density recording media.\textsuperscript{37}

Ordered arrays of magnetic nanoparticles and patterned magnetic media are currently the most promising materials for developing in high density magnetic storage media, due to the sharp distribution of their magnetic properties and high reproducibility nanoparticle arrays.\textsuperscript{49-52} The Co-C60 film has been anticipated to be another promising nanocomposite with advanced magnetic and electronic properties.\textsuperscript{53,54}

The thin-film technology integrates a new set of magnetic, materials science, and manufacture challenges. The major issue is the reduction of intrinsic media noise. Reduction of the media noise is usually obtained by magnetic isolation of the media grain; the isolation weakens or eliminates the exchange coupling between the grains. Carbon encapsulation can serve the dual role of reducing the magnetic coupling between grains, and protecting magnetic grains from surface oxidation. Nanogranular Co-C thin films have potentially opened the way for ultra-high-density magnetic recording media.\textsuperscript{1,55,56}

### 3.1.6 Experimental Techniques to Study Magnetization of Thin Films\textsuperscript{57}

(a). Mössbauer spectroscopy

The Mössbauer effect was discovered in 1957. The principle can be illustrated in Figure 3.7. $^{57}$Co nucleus decays slowly to excited $^{57}$Fe nucleus. Subsequently, 91% of $^{57}$Fe decays to the $I=3/2$ state which decays to ground state $I=1/2$. The decay releases a 14.4 keV $\gamma$-ray. The $\gamma$-ray can excite a transition in the sample if it is absorbed resonantly. The frequency of the $\gamma$-ray can be slightly adjusted by moving the $^{57}$Co source at a speed $\nu$ relative to the sample which contains some $^{57}$Fe nuclei. The $\gamma$-rays are measured by the
detector through the sample which can deduce the absorption. Any splitting in the ground state in the source or absorber nucleus might result from magnetic or other interactions.

(b). Magneto-optic methods

The method is extremely useful in magnetic recording. Mageto-optical effects involve Faraday effects and Kerr effects. Faraday effects occur in transmission while Kerr effects occur in reflection. Surface magneto-optic Kerr effect (SMOKE) technique is particularly used for thin magnetic films and surfaces.

(c). Polarized neutron reflection (PNR)

---

**Figure 3.7 Schematic illustration of the principle of the Mössbauer method.**

---
Spin-polarized neutrons are reflected at grazing incidence from magnetic multilayers. The reflectivity can be used to infer the depth-dependent magnetization (direction and magnitude).

(d). Magnetic force microscopy (MFM)

A magnetic moment on a cantilever is scanned across the surface of a thin film. There is a force on the tip whenever there is a gradient in the magnetic field above the sample. Therefore the method is sensitive to domain wall.

(e). Scanning electron microscopy with polarization analysis (SEMPA)

This technique utilizes a conventional scanning electron microscope to study the ejection of secondary electrons. These secondary electrons retain their spin polarization and give information on the magnetization of the surface.

Other techniques include Kerr microscopy and scanning SQUID microscopy.

3.2 \textit{a-C:H} Films

Diamondlike carbon is a form of amorphous carbon (\textit{a-C}) or hydrogenated amorphous carbon (\textit{a-C:H}) containing a significant fraction of sp\textsuperscript{3} bonds. DLC films have been used as protective coatings in areas such as magnetic storage disks, optical windows, car parts, biomedical coatings, tribological coatings and in microelectromechanical systems (MEMS).

The composition of the various forms of amorphous C-H alloys is best expressed on a ternary phase diagram,\textsuperscript{58} Figure 3.8. The fraction of sp\textsuperscript{3} bonding in \textit{a-C} can be controlled by the deposition method. The \textit{a-C} with high fraction of sp\textsuperscript{3} bonding is denoted as tetrahedral amorphous carbon (\textit{ta-C}). A highly sp\textsuperscript{3} bonded material with hydrogen is called hydrogenated tetrahedral amorphous carbon (\textit{ta-C:H}).\textsuperscript{59} The \textit{ta-C} and \textit{ta-C:H} films
can be produced by PECVD (plasma-enhanced chemical vapor deposition). The deposition method for DLC includes ion beam, mass selected ion beam, sputtering, cathodic arc, pulsed laser deposition and PECVD.

3.2.1 Deposition Mechanism of a-C:H

The present Co-DLC films mainly belong to the a-C:H type. The various processes taking place during deposition of a-C:H films are illustrated in Figure 3.9. The a-C:H can be deposited from different hydrocarbon gases such as CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{2}, C\textsubscript{2}H\textsubscript{4} and C\textsubscript{6}H\textsubscript{6}. The plasma deposition includes three general stages.\textsuperscript{60}

(a) Plasma reactions

Plasma reactions are driven by the energetic electrons. Energetic electrons are defined as the electrons with energy above some threshold energy that colliding with neutral species will ionize or dissociate it according to the convolution:

\[ N_i = \int n_0 (E, T_e) f_i(E)dE \]  \hspace{1cm} (2)

where \(N_i\) is the number of energetic electrons, \(n_0\) is the plasma density, \(T_e\) is the electron temperature, \(f_i\) is the ionization probability. Over a limit energy range, there is

\[ N_i \approx N_0 \exp(-E_i/kT_e) \]  \hspace{1cm} (3)
where $E_i$ is the ionization potential.

(b) Plasma-surface interaction

Other species will form in secondary reactions such as polymerization. These reactions are not significant at low pressures.

(c) Subsurface reactions in the film

The plasma incident species on the growing film consist of ions and neutrals. The neutrals are closed shell unsaturated species ($\text{C}_2\text{H}_4$ or $\text{C}_2\text{H}_2$). Plenty of atomic hydrogen $\text{H}'$ is also contained in the plasma. Neutral species contribute to growth since the mass deposition rate exceeds the rate from ions alone. The growth rate decreases with increasing temperature. This temperature dependence results from the etching of the atomic hydrogen. Growth itself is independent of the temperature, and the etching rate increases with temperature. Thus, the net growth rate decreases with temperature\textsuperscript{60-63} Figure 3.10.

![Figure 3.9 Component processes in the growth mechanism of $a$-C:H\textsuperscript{60}](image-url)
Figure 3.10 Temperature dependence of net growth rate.\textsuperscript{60-63}

The contribution of each neutral species to the growth rate is relevant with their sticking coefficient. The $a$-C:H is chemically passive since its surface is fully covered with C-H bonds. Closed shell neutrals (CH\textsubscript{4}) have low sticking coefficients usually under $10^{-4}$ and their effects are negligible. Diradicals and unsaturated species react strongly with the film and sticking coefficients approach 1 because they can insert directly into surface C-C or C-H bonds. The monoradicals have a moderate effect. They cannot insert directly into a bond. If there is an existing dangling on the film surface, they will add to this bond to form a C-C bond. The dangling bond is created as follows:

\[
\equiv C\ldash + H' \rightarrow \equiv C' + H_2 \quad \text{or} \quad \equiv C\ldash + CH_3' \rightarrow \equiv C'+CH_4
\]

Then, the CH\textsubscript{3} adds to the dangling bond,

\[
\equiv C' + CH_3' \rightarrow \equiv C-CH_3
\]

Atomic H' is the most efficient species for abstraction. So, the effective sticking coefficient of CH\textsubscript{3} is small. However, it is high in the presence of atomic hydrogen.\textsuperscript{64,65} Neutral hydrocarbon species cannot penetrate the film. The H atoms can penetrate about
2 nm into the film. In that region, they can abstract H from C-H bonds and create subsurface dangling bonds. Carbon and hydrogen ions can cause subplantation. Ions in a-C:H displace H from C-H bonds. Then, the H can recombine with other H' to form H₂, and desorbs from the film. Therefore, increasing bias voltage will decrease the H content of PECVD a-C:H. Some of the H' will find dangling bonds to re-saturate.

Hydrogen ions interact weakly with C atoms due to their low mass. H⁺ ions will penetrate deeper into the film. Thus, a-C:H films have three characteristic depths, the surface is controlled by reaction of hydrocarbon and hydrogen species; reactions of atomic H' control the upper 2 nm; H⁺ ions control a larger depth depending on ion energy.

### 3.2.2 Structure and Characterization

(a) Bonding

Carbon can exist in three hybridizations, sp³, sp², sp¹ as shown in Figure 3.11. In sp³ configuration, as in diamond, a carbon’s four sp³ orbital form strong σ bonds to adjacent atoms. In sp² configuration as in graphite, a carbon atom can form three σ bonds by its three sp² orbital, and the fourth pπ orbital forms a π bond with a neighbor π orbital. In the sp¹ configuration, there are two σ bonds and two pπ bonds.

(b) Properties of DLC films

DLC has some extreme properties like diamond. The properties of various forms of the carbon structure are summarized in Table 3.1. Here only bulk properties of hydrogenated DLC are discussed.
Figure 3.11 The three hybridizations of carbon\textsuperscript{60}: sp\textsuperscript{3}, sp\textsuperscript{2}, sp\textsuperscript{1}.

Figure 3.12 shows the sp\textsuperscript{3} fraction, hydrogen content, mass density, and optical gap as a function of the bias voltage for $a$-C:H films deposited from different source gases.\textsuperscript{60,69-71} Based on the ion energy or bias voltage, the bonding and properties of $a$-C:H films can be classified into three regimes.\textsuperscript{72,73} At low bias voltage, the films are called polymeric $a$-C:H or soft $a$-C:H, which possesses a large hydrogen content, a large sp\textsuperscript{3} content and a low density. At intermediate bias voltages, the films demonstrate their highest diamond-like character since the amount of C-C sp\textsuperscript{3} bonding is maximum in this regime. The H content has fallen, the sp\textsuperscript{2} content is less and the films have a maximum density. At high bias voltages, the films are called graphitic. In this regime, the H content has fallen further and the sp\textsuperscript{2} bonding has become increasing higher. Raman spectra show that some sp\textsuperscript{2} sites are aromatic.

Table 3.1 Comparison of major properties of different C states.\textsuperscript{60,67,68}

<table>
<thead>
<tr>
<th></th>
<th>Density g/cm\textsuperscript{3}</th>
<th>sp\textsuperscript{3} %</th>
<th>H at%</th>
<th>Hardness GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>3.515</td>
<td>100</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>$a$-C:H hard</td>
<td>1.6-2.2</td>
<td>40</td>
<td>30-40</td>
<td>10-20</td>
</tr>
<tr>
<td>$a$-C:H soft</td>
<td>1.2-1.6</td>
<td>60</td>
<td>40-50</td>
<td>&lt;10</td>
</tr>
<tr>
<td>$ta$-C:H</td>
<td>2.4</td>
<td>70</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>$ta$-C</td>
<td>3.1</td>
<td>80-88</td>
<td>0</td>
<td>80</td>
</tr>
<tr>
<td>Graphite</td>
<td>2.267</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Sputtered C</td>
<td>2.2</td>
<td>5</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.12 The $sp^3$ fraction, hydrogen content, density and optical gap as a function of deposition voltage for PECVD $a$-C:H.\textsuperscript{60,69-71}

In $a$-C:H, the C $sp^3$ sites form a network of C-C bonds. A large fraction of the $sp^3$ bond in $a$-C:H results from the saturation of bonding of hydrogen. The $sp^2$ sites form small clusters in the matrix. The cluster sizes or $sp^2$ site distortions increase with the increase of bias voltage, which causes the band gap to decrease. Most properties of $a$-C:H depend on the incident ion energy per C atom\textsuperscript{74}. The depositing species is $C_mH_n^+$, the effective energy per C atom is $E = E_i/m$, where $E_i$ is the molecular ion energy.
The maximum in density for α-C:H prepared from acetylene occurs at about twice the bias voltage of that from methane. The H content prepared from methane is higher than that prepared from other precursors because of its high H/C. On the other hand, the optical gaps vary in the same manner against bias voltage for all the precursor gases. That is, the gap depends on $E_i$, not on the number of the carbons. Refractive index attains a maximum at the bias voltage where the density reaches a maximum.

The ta-C:H has been deposited from high plasma density reactors. The source gas is acetylene. It was found that the sp$^3$ fraction reached a maximum at an ion energy of ~100 eV per C atom. The H content is below 30% at any circumstance and fall slowly with increasing ion energy. Compared with α-C:H, there is a lower H content and higher fraction of C-C sp$^3$ bonds in ta-C:H. There is no polymeric regime in ta-C:H because its hydrogen content is low. At low ion energy, the ta-C:H network is sp$^2$-like. At 100 eV, there is highly tetrahedral C-C bonding in ta-C:H. At higher ion energy, the ta-C:H becomes graphite-like.

(c) Characterization techniques for bonding in amorphous carbons

The ratio of sp$^3$/sp$^2$ is the most crucial factors determining the properties of diamond-like carbon thin film. Various characterization methods have been used to determine the sp$^3$/sp$^2$ bonding ratio of DLC film. Table 3.2 shows these techniques.

3.2.3 Mechanical Properties

(a) Elasticity

The elastic constants for some DLC films are shown in Table 3.3. The ta-C with 88% sp$^3$ bonding has a Young’s modulus of 757 GPa. The Young’s modulus of ta-C:H is lower with values around 300 GPa. So hydrogen decreases the network
Table 3.2 Techniques for sp³ measurement.⁶⁰

<table>
<thead>
<tr>
<th>Method</th>
<th>Comparison</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMR (Nuclear magnetic resonance spectroscopy)</td>
<td>Direct measurement of sp³ by C¹³, need large sample</td>
</tr>
<tr>
<td>XRR (X-ray reflectivity)</td>
<td>Nondestructive, linear correlation of density and sp³ fraction of DLC</td>
</tr>
<tr>
<td>EELS</td>
<td>Preferred, destructive, time-consuming</td>
</tr>
<tr>
<td>XAES (Auger electron spectroscopy)</td>
<td>Fingerprint of the C bonding configuration</td>
</tr>
<tr>
<td>IR (infrared spectroscopy)</td>
<td>Only identify C-H</td>
</tr>
<tr>
<td>Raman spectroscopy</td>
<td>Widely used, non-destructive</td>
</tr>
<tr>
<td>X-ray photoelectron spectroscopy</td>
<td>Chemically specific, small peak shift from homopolar bonding, affected by the sp² surface layer</td>
</tr>
<tr>
<td>Optical spectra and ellipsometry</td>
<td>Real-time or on-site measurement, but limited to a small spectral range</td>
</tr>
<tr>
<td>NEXAFS (Near-edge x-ray-absorption spectroscopy)</td>
<td>Most reliable technique to determine the sp³</td>
</tr>
<tr>
<td>HEELS (high-energy electron energy loss spectroscopy)</td>
<td>Most reliable technique to determine the sp³</td>
</tr>
</tbody>
</table>

coordination of ta-C:H. The relationship between the bias voltage and the Young’s modulus of a-C:H is illustrated in Figure 3.13.⁶⁰,⁸⁰ The maximum Young’s modulus is observed for deposition with a bias around -100 V.

(b) Hardness

The hardness is a measure of the yield stress of a material. Hardness (H) is related to the yield stress (Y) and Young’s modulus (E) by:

\[
\frac{H}{Y} = 0.07 + 0.06 \left( \frac{E}{Y} \right)^{60}
\]

Table 3.3 Elastic properties of various forms of carbon.⁶⁰,⁶⁷,⁷⁸,⁷⁹

<table>
<thead>
<tr>
<th></th>
<th>ta-C: H</th>
<th>ta-C</th>
<th>100% sp³ ta-C (calculated)</th>
<th>Diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g.cm⁻³)</td>
<td>2.35</td>
<td>3.26</td>
<td>3.5</td>
<td>3.515</td>
</tr>
<tr>
<td>H (at%)</td>
<td>30</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>sp³ (%)</td>
<td>70</td>
<td>88</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
<td>300</td>
<td>757</td>
<td>822.9</td>
<td>534.3</td>
</tr>
</tbody>
</table>
The $H/Y$ value for diamond and other ceramics is $\sim 1.8$. Yield occurs by bond cleavage in brittle materials like DLC. Based on Orowan’s approximation, $E/Y = \pi$ and $H/E = 0.16$. The $H/E$ value for DLC films is about 0.16.

The hardness of $a$-C:H deposited by PECVD is low at low bias voltage corresponding to the polymeric films. Then, the hardness rises to a maximum in the maximum diamond-like regime, followed by a decrease at the more graphitic regime. The maximum nano-hardness of $a$-C:H is 17 GPa. The nano-hardness of $ta$-C with 85-90% sp$^3$ bonds is about 80-88 GPa.

(c) Adhesion

The inherent compressive stresses developing in DLC films during processing increase with film thickness and thus, limit their maximum achievable thickness. The relationship between film thickness ($h$) and adhesive strength ($\sigma$) is as follows:

$$2\gamma > \sigma^2 h / 2E \quad \text{or} \quad h < 4\gamma E / \sigma^2$$

(5)
where $\gamma$ is the surface energy and $E$ the elastic modulus. Metal alloying is one of the ways to reduce internal stresses in DLC films\textsuperscript{83,84} and also improve hardness, thermal stability, toughness, and increase the maximum film thickness.

(d) Friction

DLC films are notable for their low friction. The lowest friction coefficient of $a$-C:H in a vacuum is found to be $<0.01$.\textsuperscript{60,85} Friction behavior of DLC is strongly related to the relative humidity. For $a$-C:H, the friction coefficient increases with high humidity. The DLC surface is inert since the broken bonds are passivated by C-H bonds.\textsuperscript{67} DLC surfaces are hydrophobic, closed-shell bonded systems, and they contact with van der Waals forces. The contact is elastic under pressure. The van der Waals bonds instead of the bulk C-C bonds will break as the contacts shear. Therefore, the friction force has an adhesive/deformation nature.

For $a$-C:H, contact with a different surface results in the formation of a transfer layer of $a$-C:H on the counter surface or between the two surfaces in contact. The friction is low since the contact is between two similar hydrophobic $a$-C:H surfaces. High humidity interferes with the formation of the contact layer and causes oxidation /hydration without formation of van der Waals bonds. So the friction coefficient is much higher because there is no transfer layer and no hydrophobic counter surface.

The $ta$-C films exhibit a somewhat different behavior, wear-induced graphitization mechanism. The $ta$-C is transformed into graphitic layers at the contact area. The graphitic layers behave as a solid lubricant. Water between the graphite layers lowers the friction coefficient. The friction coefficient of $ta$-C will decrease with increasing humidity.
(e) Wear

Wear is the removal of material as two solid surfaces contact. Wear results from adhesion, abrasion and/or corrosion/oxidation. The volume of wear over a unit track length is $V = KA$, where $K$ is the wear coefficient, $A$ is the real contact area, and $A = L/H$, $L$ is the applied load, and $H$ is the hardness. Combining the above equations result in $V = KL/H = kL$, where $k$ is wear rate in units of mm$^3$N$^{-1}$m$^{-1}$. Based on the equation $V = KL/H$, the wear coefficient is inversely proportional to the hardness of the surface. The wear rate of $a$-C:H is at the order of $10^{-6}$~$10^{-7}$ mm$^3$N$^{-1}$m$^{-1}$ which is a couple of orders of magnitude higher than that of $ta$-C at $10^{-9}$ mm$^3$N$^{-1}$m$^{-1}$. During wear, $a$-C:H forms a C:H transfer layer on the counter surface while $ta$-C is transformed to a graphitic overlayer which acts as a lubricant. More sp$^2$ bonded $a$-C was found to wear by oxidation to CO$_2$.87 DLC films are characterized by unique combination of low friction and high wear resistance.

3.3 Co-C Films

Magnetic grains encapsulated in carbon have gained increasing interests for their potential application as high-density magnetic recording media.1 Carbon encapsulation can reduce the media noise, and can provide protection against surface oxidation of magnetic grains. Recently, we have successfully synthesized Co-C nano composite thin films in our laboratory.3,4

3.3.1 Deposition Techniques

Since the discovery of the Huffman–Kratschmer carbon arc process for production of fullerness,88 there has been significant attention in the study of carbon-coated nanoparticles. Different methods have been utilized in the synthesis of Co-C film. Based on a recent survey, the methods include the following:
Nanodot arrays were produced by direct interferometric laser annealing.\textsuperscript{126,127} It was found that the structure and morphology of Co-C thin films are sensitive to preparation methods, and so are their magnetic properties. Thus, we review the structures and properties with respect to the deposition methods.

### 3.3.2 Structure

The published results demonstrate that carbon in Co-C films exists in the form of either amorphous or cobalt carbides or graphite-like. Co crystals in Co-C films are in one or two of the three structures: hcp-Co, fcc-Co and $\varepsilon$-Co. There is a substantial difference in the structure and magnetic properties between the as-deposited Co-C films and annealed ones.

(a) DC magnetron sputtering

The results by Shimamoto \textit{et al.}\textsuperscript{90} showed that the as-deposited Co-C films by DC magnetron sputtering were amorphous and they changed to hcp Co particles embedded in
the graphitic carbon after annealing. Konno and Sinclair\(^2\) demonstrated that the reaction of Co-C film with less than 35% C is:

\[
\text{amorphous} \xrightarrow{250-350^\circ C} \delta' - \text{Co}_2\text{C} + \text{hcp Co} \xrightarrow{380-420^\circ C} \text{hcp Co} + \text{graphite}.
\]

(b) Ion beam sputtering

A thin film of Co nanocrystals isolated and embedded in graphite–like carbon has been prepared first by Hayashi \textit{et al.}\(^1\) The Co-C films were deposited at 200°C and annealed at 300°C. XRD and TEM indicated that the films mainly consisted of hcp Co nanocrystals wrapped by several layers of graphite-like carbon. However, the study by Delaunay \textit{et al.}\(^98\) revealed that the cobalt phase in Co-C films obtained by IBD depended on the carbon concentration and substrate temperature. \(\delta' - \text{Co}_2\text{C}\) formed at 27 \(\text{at}\% \leq \text{C} \leq 36\) at\% and substrate temperature of \(100^\circ C \leq T_s \leq 200^\circ C\). After annealing at 350°C, \(\delta' - \text{Co}_2\text{C}\) decomposed into hcp Co and graphite C. When \(T_s = 200^\circ C\), \(\text{C} = 46-57\)\% and annealing was conducted at 350°C, the cobalt phase had a faulted close-packed structure or random stacking structure.

(c) Modified arc discharge

Modified arc charge was invented by Dravid \textit{et al.}\(^103\) The intention was to decrease the carbon debris in the carbon arc method. Jiao and Seraphin were the first to study the carbon-coated Co produced by a modified arc discharge process\(^104\). Based on their study, the as-deposited particles were carbon-coated fcc-Co nanocrystals covered by graphite layers without Co carbide. Annealing and immersion into HNO\(_3\) resulted in further graphitization of the carbon coating. After annealing at 1100°C, the structure changed to numerous empty polyhedral shells of carbon and all the Co particles were ejected from the carbon coating. Host \textit{et al.}\(^106\) reported that the fcc-Co phase can be stable in the film.
due to the small particle nature, and Co particle size increased with annealing. Banhart et al.\textsuperscript{108} showed that high temperature electron irradiation promotes a heavy contraction of the carbon onions. The contraction forces the Co atoms to migrate outwards through the carbon layers. Spherically curved graphite layers are permeable to Co atoms. Films have been also produced by another modified arc charge method.

(d) Pulsed filtered vacuum arc deposition

TEM and Raman spectra\textsuperscript{117} showed that the Co-C reaction under annealing is:

\[
\text{Amorphous} \rightarrow \text{cobalt carbide} + \text{hcp Co (metastable stage 250-350°C)} \rightarrow \text{hcp Co} + \text{graphitelike C (cobalt carbide decomposes at 350-400°C)}.
\]

Another work showed that the as-deposited films consisted of amorphous Co clusters and $a$-C.\textsuperscript{118} After annealing in vacuum at 350°C for 1 h, the Co clusters crystallized.

(e) Electron beam evaporation

Electron beam evaporation was utilized to obtain 3 nm Co clusters randomly dispersed in electrically insulating C matrix. Similarly, work in our laboratory showed that the Co-C film synthesized by dual e-beam evaporation consisted of $\varepsilon$-Co embedded in an amorphous C matrix.\textsuperscript{3} After annealing, coalescence of Co clusters formed a continuous cluster-network modifying the magnetic properties of the film.\textsuperscript{4} Another film was prepared from Co and C60 co-deposition. Electron diffraction analysis revealed that the film consists of fcc Co crystals and C60-based substance containing diamond, graphite, Co$_2$C and Co$_3$C.\textsuperscript{116}

(f) Carbon arc

Both XRD and TEM demonstrated that the carbon coated Co produced by carbon arc contained nanocrystalline fcc-Co spherical particles, hexagonal graphite and a minority
Co$_2$C. High-resolution TEM (HRTEM) showed stacking faults in individual Co crystals. The method also produced carbon debris.

(g) RF magnetron sputtering

XRD studies show that RF magnetron sputtering can produce amorphous-like fcc Co$_x$C at 150°C and crystalline fcc Co$_x$C at 350 °C, and an unknown structure at 300°C.92

3.3.3 Properties

(a) Magnetic Properties

Optimum magnetic properties with saturation magnetization of 380 emu/cc and coercivity of 400 Oe were obtained by DC magnetron sputtering for a Co-C film with 50 at% C after annealing at 350°C. Small monodomain Co particles produced by carbon arc exhibit superparamagnetism, Hayashi et al. were the first to deposit Co-C films using ion beam sputtering.1 Their results showed that the magnetic property of Co-C films was: $M_s = 550$ emu/cm$^3$ and $H_c = 370$ Oe. Delaunay et al.98 deposited samples with different Co contents by the same method, and they found that the phase of Co crystals was changed from hcp to a highly faulted closed-packed phase by increasing the atomic C content from 36 % to 57%. The magnetic hysteresis was also changed and found to have low coercivity and low squareness. $H_c$ decreased from 630 to 40 Oe. Squareness $S$ decreased from 0.6 to 0.05. Wang et al. conducted several investigations on Co-C magnetic films produced by pulsed filtered vacuum arc deposition. They reported that the magnetization of Co$_{65}$C$_{35}$ after annealing at 350°C in vacuum for 1 h is $M_s = 500$ emu/cm$^3$, $H_c= 460$ Oe, $M_r/M_s = 0.68$ (300 K), $H_c = 1380$ Oe (3 K) based on MFM images and magnetic hysteresis loops.115 In another report118 it was revealed that the as-deposited films were soft ferromagnets. The coercivity $H_c$ of as–deposited and annealed
Co-C film is: $H_c = 2$ (as-deposited), 70 (350°C) for Co$_{44}$C$_{56}$, $H_c = 3$ (as-deposited), 460 (350°C) for Co$_{65}$C$_{35}$, $H_c = 10$ (as-deposited), 90 (350°C) for Co$_{71}$C$_{29}$. The low coercivity is due to the low anisotropy. After annealing, the films become magnetically harder due to enhanced magnetic anisotropy. MFM shows there was perpendicular magnetic anisotropy. As-deposited carbon coated Co by modified arc discharge technology shows ferromagnetic property. Host et al.\textsuperscript{110} reported the dependence of room temperature saturation magnetization, remnant magnetization and coercive field of the Co particles on annealing temperature. Transition of particles from single domain to multidomain resulted from particle growth due to annealing. As-deposited film by electron beam evaporation shows superparamagnetic behavior.\textsuperscript{115} After annealing at 600°C, it shows ferromagnetic behavior with a formation of an unusual perpendicular anisotropy.

(b) Electrical properties

Temperature-independence electrical resistance was observed in Co-C thin films produced by pulsed filtered vacuum arc deposition. The samples with 39 at% Co are metallic. Those with low Co atomic composition (18% and 25%) after annealing are near the metal-insulator. As-deposited films by electron beam evaporation\textsuperscript{115} show insulating resistant behavior. After annealing at 600°C, they gradually change to metallic behavior.

(c) Hardness

The hardness was found to decrease linearly with increasing carbon content (decreasing Co content) in the Co-C films produced by ion beam co-sputtering.\textsuperscript{128}

3.4 Co-a-C:H Films

Laurent et al. utilized rf capacitively coupled diode system to deposit a film in which Co clusters were dispersed in a polymeric matrix.\textsuperscript{29,30} In their study, films with different
Co concentrations were prepared by controlling the ratio of the mass spectrometer peaks C$_2$H$_5^+$/Ar$^+$. Based on their research, the Co atoms coalesced into clusters that were roughly spherical and isolated by polymeric matrix for 5% and 15% Co volume fractions, and then more wormlike as cobalt concentration was increased to 40 at%. Electron diffraction pattern showed that cobalt was in hcp structure. The electrical percolation threshold (the metal volume fraction at which the film undergoes the insulator-conductor transition) was 22 at%±5%. The films showed superparamagnetic property below 25% Co volume fraction, and showed ferromagnetic property above that. Similar observations have been made in our laboratory on Co-C films deposited by dual e-beam evaporation.$^{3,4}$ It is apparent that in spite of their importance at present there is very little information on nanocomposite Co-DLC films.

Chua et al.$^{31}$ produced cobalt containing tetrahedral amorphous carbon (ta-C:Co) by an off-plane double bend filtered cathodic vacuum arc technique. Their interest focused on the surface properties of ta-C:Co films. Two sets of films were deposited on silicon wafer by varying Co content and the applied bias. Their study indicated that the sp$^3$ content was in inverse relation to the Co content. The maximum sp$^3$ was obtained when Co content was lower than 5% under -80V bias. With the increase of %Co, sp$^2$ content increased and predominated in the entire film. Similarly, an increase in bias from -120V to -500V caused a decrease of sp$^3$ content in the film. Co incorporation reduces the surface energy through two mechanisms.

Recently, some interesting results were reported on the structure of Co nanocrystals embedded in amorphous hydrogenated carbon (a-C:H(Co)) by Ivanov-Omskii’s group.$^{32-34}$ The samples were prepared by magnetron co-sputtering of graphite and Co targets in
an Ar-H₂ plasma. IR absorption identified hydroxyl groups which could be related to the formation of hydrates of metastable cobalt carbide. Further study by combined IR spectroscopy and Raman scattering revealed three types of interactions between Co and C: (a) a strong interaction related to the formation of a metastable chemical bond in methyl derivatives of cobalt carbide; (b) an interaction associated with the formation of benzene derivative of cobalt carbide; (c) a weak interaction of Co-C not in carbide. Thermal annealing at ~350°C suppressed these interactions and favored the formation of cobalt nanoclusters. EXAFS indicated that in as-deposited samples, a majority of Co atoms were dispersed in α-C:H matrix with a fraction of them forming the Co nanocrystalline phase.

The studies on Co-DLC films discussed above present us with the information on magnetic property, electric property, surface energy and interactions between Co and C. However, in multifunctional DLC related films, mechanical, tribological and electrochemical properties are significant evaluation parameters in view of functional application. Although Laurent et al. found a relationship between composition and structures, there is no report on the relationship of synthesis-structure-properties which help us to unveil the nature of Co-DLC systems. Based on the knowledge of Co-C films, Co in Co-α-C:H is expected to undergo phase transition upon annealing which results in enhancement in magnetism. The architecture of DLC is subject to the annealing effects. Graphitization under thermal attacking might happen and cause properties deterioration. A thermal stability study would uncover the environmental limitation of Co-DLC application. Moreover, we obtain an unique nanocolumnar Co-α-C:H film which was never reported before. This Co nanocolumnar structure may possess different properties
from other microstructures such as nanoparticle or elongated particles. Studies on nanocolumnar Co-\textit{a}C:H will widen our knowledge on nano materials. Finally, the understanding on the Co-DLC films can be a basis to prepare other functional adaptive systems by changing or adding doped elements. Therefore, we set up the target to conduct systematic in-depth research on Co-\textit{a}-C:H thin films.
4.1 Deposition of Co-\textit{a}-C:H Films

A series of Co-DLC nanocomposite films have been deposited on Si (100) substrate. All processing was conducted in an intensified plasma-assisted processing (IPAP) system that is capable of plasma, dual magnetron sputtering and ion beam deposition described elsewhere\textsuperscript{129} (Figure 4.1). This is a hybrid process involving PECVD and plasma-enhanced PVD by magnetron sputtering. Based on this process, it is more appropriate to name the films Co-\textit{a}-C:H. Thus, the notation Co-\textit{a}-C:H will be used instead of Co-DLC. Before the deposition, the chamber was first evacuated down to $10^{-6}$ Torr and purged with Ar several times. Then, samples were sputter-cleaned for 20 min using Ar\textsuperscript{+} at a pressure of 25 mTorr and -1000 V bias voltages. Co-\textit{a}-C:H deposition was performed by magnetron sputtering of a Co target (99.95%), under magnetron current control in a

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{ipap_system.png}
\caption{Schematic illustration for the IPAP system.\textsuperscript{129}}
\end{figure}
discharge composed of Ar and CH$_4$ with a ratio ranging from 3.8-13 at a chamber pressure varied in the range of 8 to 20 mTorr. The bias voltage applied to the substrate was -500 V. After processing, the substrate was cooled inside the chamber in an Ar atmosphere.

4.2 Microstructural Characterization of Co-$\alpha$-C:H Films

(a) Composition

Composition of the films was measured by wavelength-dispersive spectrometer (WDS) on a JEOL JXA-733 electron microprobe with four automated wavelength dispersive spectrometers. WDS measurement was conducted under the accelerating voltage of 15 kV and beam current of 10 nA. Standards for Co, C, Si were pure Co, diamond, and pure Si respectively. Also, x-ray photoelectron spectroscopy (XPS) was used for composition analysis on a Kratos AXIS 165 high performance electron spectrometer. In XPS analysis, a monochromatic Al K$_\alpha$ excitation source was utilized to acquire the spectra. Survey scans were conducted in the 0-1200 eV at 0.5 eV steps and high-resolution scans for Co 2$p$ and C 1$s$ at 0.1 eV steps. The surface contamination was sputter cleaned by a 5 kV and 10 mA Ar$^+$ ion beam.

(b) Microstructure

TEM was mainly used to study the Co-$\alpha$-C:H microstructure and structure of the various phases present. Plan-view and cross-sectional TEM images were utilized to characterize the three-dimensional microstructure of the films. Electron diffraction was used to identify the crystal structure of the various phases.
Selected-area electron diffraction (SAED) patterns, bright-field, dark-field and high-resolution TEM images were recorded in a JEOL 2010 electron microscope operating at 200 keV (point-to-point resolution 0.23 nm).

(c) Chemical state analysis

Based on the ternary phase diagram of the C:H system, the structure and properties of DLC depended on two key parameters: the fraction of sp$^3$ and bonded carbon sites and the hydrogen content. XPS on core levels is a surface analysis technique for detailed information in electronic structures. High-resolution of XPS C 1s spectra provided the means to study the electron structure of Co-a-C:H, such as fraction of sp$^3$, sp$^2$, and other C bonds. The instrumental information refers to XPS composition measurement.

Table 4.1 present a summary of the C 1s peaks affected by its chemical states$^{29,117,119,120,130-134}$. The determination of Co 2p peaks was shown in Table 4.2$^{29,117,119}$. On the basis of the table combined with the instrumental specifics, the C 1s signal is deconvoluted into four components: sp$^2$ at 284.3 eV, sp$^3$ at 284.8 eV, C-O at 286.5 eV, Co-C at 283.5 eV. The ratio of sp$^3$/sp$^2$ was calculated by the equation as follows: sp$^3$/sp$^2$ = integrated areas of sp$^3$/integrated area of sp$^2$. Similarly, the atomic fractions of other components were calculated by measuring the integrated areas of the corresponding peaks. In hydrogenated amorphous carbon, the composition of C-C sp$^2$ and C-C sp$^3$ cannot be calculated since XPS cannot separate C-C from C-H bonding. The hydrogen content is hard to measure by common methods used in the measurement for other elements. Table 4.3 shows some techniques for the hydrogen measurements$^{60}$. The hydrogen content of Co-a-C:H films was determined by the nuclear reaction analysis (NRA) technique. The analysis was conducted by using a nitrogen -15 ion ($^{15}$N) beam.
from the accelerator to react with protons. The $^{15}$N beam energy was increased from 6.38 MeV to 7 MeV in steps of 100 keV.

**Table 4.1 Binding energies of the C $1s$ electron.**

<table>
<thead>
<tr>
<th>Material</th>
<th>Binding energy (eV)</th>
<th>Chemical bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-C:H (Polymer-like,</td>
<td>284.3</td>
<td>C-C $sp^2$ or $C_6H_6$</td>
</tr>
<tr>
<td>Diamond-like, Middle)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>285</td>
<td>C-C $sp^3$ or -CH$_3$</td>
</tr>
<tr>
<td></td>
<td>286.4</td>
<td>C-O</td>
</tr>
<tr>
<td></td>
<td>287.7</td>
<td>C=O</td>
</tr>
<tr>
<td></td>
<td>289.1</td>
<td>O=C=O</td>
</tr>
<tr>
<td>$\alpha$-C:H</td>
<td>284.4-284.75</td>
<td></td>
</tr>
<tr>
<td></td>
<td>284.3</td>
<td>$sp^2$</td>
</tr>
<tr>
<td></td>
<td>284.8</td>
<td>$sp^3$</td>
</tr>
<tr>
<td></td>
<td>286.1</td>
<td>C=O</td>
</tr>
<tr>
<td>$\alpha$-C</td>
<td>284.3±0.1</td>
<td>$sp^2$</td>
</tr>
<tr>
<td></td>
<td>285.2±0.1</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>Graphite</td>
<td>284.36, 285.6</td>
<td>$sp^2$</td>
</tr>
<tr>
<td>Diamond</td>
<td>285.35, 290.45</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>Co/C multilayer</td>
<td>283.2</td>
<td>C-Co (i.e., carbide)</td>
</tr>
<tr>
<td></td>
<td>284.1</td>
<td>C-C (graphite)</td>
</tr>
<tr>
<td>Co-polymer</td>
<td>284.6</td>
<td>C-C, C-H</td>
</tr>
<tr>
<td></td>
<td>286.2</td>
<td>C-O-C, C-OH</td>
</tr>
<tr>
<td></td>
<td>288.2</td>
<td>O-C=O</td>
</tr>
<tr>
<td>Co$<em>{65}$C$</em>{35}$ film</td>
<td>283.5/283.1</td>
<td>C-Co (carbide)</td>
</tr>
<tr>
<td></td>
<td>284.1</td>
<td>C-C</td>
</tr>
</tbody>
</table>

**Table 4.2 High-resolution XPS spectra for Co $2p$ electron.**

<table>
<thead>
<tr>
<th>Binding energy (eV)</th>
<th>Identified species</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co $2p_{3/2}$ in Co-</td>
<td>778.2</td>
<td>Co</td>
</tr>
<tr>
<td>polymer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co $2p$ in Co$_{65}$</td>
<td>781/782</td>
<td>$Co_{6}O_6$, Co(OH)$_2$</td>
</tr>
<tr>
<td>C$_{35}$</td>
<td></td>
<td>Pure Co</td>
</tr>
<tr>
<td>Co$<em>{65}$C$</em>{35}$</td>
<td>778.3</td>
<td>Co in Co-carbide</td>
</tr>
</tbody>
</table>

The Co $2p$ peaks in pure Co and Co carbides almost coincide with each other.
Table 4.3 Various techniques for hydrogen content measurement.\textsuperscript{60}

<table>
<thead>
<tr>
<th>Method</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nuclear reaction analysis</td>
<td>Widely used, need special facilities</td>
</tr>
<tr>
<td>Elastic recoil detection NMR</td>
<td>Rarely used</td>
</tr>
<tr>
<td>Combustion</td>
<td>Difficult</td>
</tr>
<tr>
<td>Hydrogen evolution</td>
<td>/</td>
</tr>
<tr>
<td>IR</td>
<td>Difficult</td>
</tr>
</tbody>
</table>

4.3 Property Characterization

(a) Magnetic property

Samples with a size of 3 mm x 8 mm were cut from Co-\(a\)-C:H films for magnetic property measurements. A MPMS Quantum Interference Devices (SQUID) magnetometer was utilized for the measurements of the films: hysteresis loops at 10 K and 300 K and zero-field-cooled and field-cooled magnetizations from 10 K to 300 K. These studies were performed in collaboration with Dr. Leonard Spinu (AMRI-UNO).

(b) Wear and friction

Pin-on-disc experiments were involved in the tribological behavior study utilizing a computer-controlled ICS-200 tribometer made by Implant Sciences Corp. Tests were performed on bulk Co, Co film and Co-\(a\)-C:H films on Si (100) wafer. The tests on Co-\(a\)-C:H films were conducted at a sliding velocity of 10 cm/s, 1 N applied load and a sliding distance of 250m utilizing an Al\(_2\)O\(_3\) pin (9.5 mm in diameter). The average wear rate (W) was calculated by the equation as follows:

\[
W = \frac{V}{LS} \quad (6)
\]

\(V\) is the volume of Co-\(a\)-C:H films removed by the wear action, \(L\) is the applied load and \(S\) the sliding distance.
(c) Mechanical property

Co-$a$-C:H films on Si (100) wafers were used for investigation of mechanical properties. Nanoindentation was used to measure reduced elastic modulus and hardness of the films on a Hysitron Triboscope combining Digital Instrument Scanning Probe Microscopy - SPM 3000.

(d) Electrochemical test

The potentiodynamic scanning technique was utilized to obtain polarization curves with a scan rate of 1mV/min in 3.5% NaCl unstirred and aerated solution. The electrochemical measurements were conducted on a EG&G Poterntiostat/Galvanostat Model 273 which communicates with 352 SoftCorr™ III software running on an IBM compatible personal computer.

4.4 Annealing Experiments

(a) Thermal stability

The thermal stability was investigated by modulated differential scanning calorimetry (DSC) using a TA instrument Q100 DSC system. Initial and final temperatures were 30°C and 600°C, and the heating rate was 10°C/min. The experiments were conducted in a ceramic pan purged by N₂.

(b) Annealing treatment

A temperature around 350°C was a sensitive phase changing temperature for Co-C films since amorphous carbon transforms to graphite. Therefore, temperatures at and below 350°C were selected for the annealing treatments that will be conducted at various periods of time in order to follow the evolution of the microstructure. Also, preliminary DSC work showed that there were reactions or phase changes at the peak temperatures.
Annealing at the peak temperature helped to better understand the structure and phase changes in these films.

The annealing treatment was conducted under vacuum. The vacuum sample was prepared as following: a 3mm×10mm Co-a-C:H thin film on Si 100 was cut by a diamond knife. Then the small sample was inserted into Pyrex glass tube. The glass tube was pumped to vacuum after purging with Ar for several times. Then the sample was sealed in the glass tube utilizing a torch. Subsequently, samples were annealed at the designed temperature.
CHAPTER 5. RESULTS AND DISCUSSION

5.1 Effect of Processing Parameters on Film Composition

Table 5.1 presents the main deposition parameters and composition for six selected Co-$\alpha$-C:H thin films. In addition, the effect of the processing parameters on the film composition (measured by WDS) is shown in Figure 5.1. The error bars in Figure 5.1 represent standard deviation. A number of interesting observations can be made. Both chamber pressure and the Ar/CH$_4$ flow rate ratio significantly affect the film composition. The increase of the chamber pressure while keeping the same Ar/CH$_4$ ratio (either at 4.3 or 3.8) causes an increase in the C content. Higher pressure reduces plasma density and thus sputtering, and drives more hydrocarbon to the substrate thus increasing C content (decreasing Co content) in the film. Furthermore, increasing the Ar/CH$_4$ ratio while keeping the same pressure (either at 11 or 9 mTorr), sputtering from the metal target is enhanced thus, resulting in a higher Co content. The variation of Co content along with H content is shown in Figure 5.2. The error bars in Figure 5.2 represent standard deviation. The results show an inverse relationship between Co and H content in the film. Similar effects have been observed in other Me-DLC films. Since H is attached

Table 5.1 Processing parameters and composition of Co-$\alpha$-C:H thin films. For all experiments, the bias voltage and magnetron current were constant at –500 V and 120 mA, respectively.

<table>
<thead>
<tr>
<th>Films</th>
<th>Pressure, mTorr</th>
<th>Ar/CH$_4$</th>
<th>H, at% (NRA)</th>
<th>Co, at% (WDS)</th>
<th>% in film</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Co-C</td>
<td>sp$^3$</td>
</tr>
<tr>
<td>Film 1</td>
<td>9</td>
<td>13</td>
<td>/</td>
<td>70±0.52</td>
<td>24.3</td>
</tr>
<tr>
<td>Film 2</td>
<td>9</td>
<td>4.3</td>
<td>16.3</td>
<td>55±0.25</td>
<td>21.6</td>
</tr>
<tr>
<td>Film 3</td>
<td>9</td>
<td>3.8</td>
<td>18.5</td>
<td>54±0.6</td>
<td>23.7</td>
</tr>
<tr>
<td>Film 4</td>
<td>11</td>
<td>4.3</td>
<td>22.6</td>
<td>50±0.67</td>
<td>20</td>
</tr>
<tr>
<td>Film 5</td>
<td>11</td>
<td>3.8</td>
<td>25.7</td>
<td>45±0.45</td>
<td>/</td>
</tr>
<tr>
<td>Film 6</td>
<td>14</td>
<td>4.3</td>
<td>62.4</td>
<td>28±1.52</td>
<td>15.8</td>
</tr>
</tbody>
</table>

+ Based only in presence of C and Co in the film.
Figure 5.1 The effects of chamber pressure and Ar/CH$_4$ on C fraction of Co-$a$-C:H films (C fraction was measured by WDS).

Figure 5.2 The relationship between the Co and H content in Co-$a$-C:H films.
only to C, by increasing Co content, the C content decreases and subsequently reduces H content. Another contributing reason may be the larger percentage of hydrogen deficient hydrocarbon produced under the enhanced sputtering conditions. Maximum H content is obtained in Co free films when the sputtering process is not operational. Previous studies in our laboratory showed that under the latter conditions H content can reach up to 63 at.%\textsuperscript{135} Thus, the Co content in the a-C:H film is controlled by the pressure and Ar/CH\textsubscript{4} ratio.

In addition, the fractions of the various carbon chemical states present in these films were also studied by obtaining C 1s high-resolution XPS spectra. The high-resolution C 1s spectrum for these films can be deconvoluted into four components sp\textsuperscript{2} (C-C and C-H bonds), sp\textsuperscript{3} (C-C and C-H bonds), Co-C and C-O, Table 4.1. Table 5.1 lists the content of the various major C states (C-O is not listed). The percentage of a C state (type of bonding) in the film was obtained by multiplying its fraction in the C 1s peak by the total C content in the film. The general trend shows that both the sp\textsuperscript{3} and sp\textsuperscript{2} C bonding are decreasing with increasing Co content. However, the effect on the sp\textsuperscript{3} bonding seems to be more significant with the exception of Film 1. Table 5.1 shows a general decline in the sp\textsuperscript{3}/sp\textsuperscript{2} ratio along with the raising of Co content. However, Film 1 exhibits a highest sp\textsuperscript{3}/sp\textsuperscript{2} ratio. Since most of the C are bonded with Co in Film 1, the rest of C is less in the bulk and exists in sp\textsuperscript{3} bonding. Also, the increase in the Co content is causing an increase in the Co-C bonding. Considering the inverse relationship between Co and H content, it can be inferred that Co atoms mostly replace H atoms in sp\textsuperscript{3} C-H to form Co-C bonds. This is consistent with the increasing tendency of the Co-C fraction along with the rising of the Co percentage. Table 5.1 also reveals a trend between deposition parameters and
Increasing the pressure while keeping the Ar/CH4 constant at 4.3, causes an increase in the sp³/sp² ratio. Under the present deposition conditions, a higher pressure produces lower energies in the plasma (short collision distance) and thus, lower probability to break the $C - H_3^+$ species produced from the ionization of CH4. Raising the Ar/CH4 ratio while keeping the pressure constant (9 mTorr) seems to increase the sp³/sp² ratio. In view of the higher ionization efficiency of Ar compared to CH4, a higher Ar/CH4 ratio is expected to result in a more energetic plasma and more Co sputtering as observed experimentally. But at the same time, the latter plasma is also expected to cause more break down of sp³ C-H bonds. Furthermore, the latter conditions favor more Co sputtering and a higher Co content along with a lower H content. Therefore, in view of the above discussion the present observation seems to suggest that a higher Ar/CH4 ratio promotes sp³ C-C bonding. In summary, since the sp² and sp³ C bonding involves C-C and C-H bonds, the two process parameters affect them in different ways. High pressures are expected to enhance high C-H sp³ formation, while high Ar/CH4 ratios to promote sp³ C-C bonding.

5.2 Effect of Processing Parameters on Microstructural Evolution

Several typical microstructures of Co-a-C:H films have been prepared as a function of various deposition parameters, which are listed in Table 5.2. The table mainly involves the films shown in Table 5.1 along with a couple of additional films. The results are consistent with the previously discussed trend of increasing Co content with decreasing pressure when the Ar/CH4 ratio remains constant (Film 2, 4, 6, 7).

Cross-sectional and plan-view TEM examinations were conducted on these films and their general morphology is described in Table 5.2. A self-assembled nanocolumnar
Table 5.2 Microstructures of six Co-α-C:H films and their processing parameters. The bias voltage and magnetron current were constant at –500 V and 120 mA, respectively.

<table>
<thead>
<tr>
<th>Films</th>
<th>Pressure, mTorr</th>
<th>Ar/CH₄</th>
<th>Co, at%</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WDS</td>
<td>XPS</td>
<td>Cross-section</td>
<td>Plan-view</td>
</tr>
<tr>
<td>Film 2</td>
<td>9</td>
<td>4.3</td>
<td>55</td>
<td>60 Nano column</td>
</tr>
<tr>
<td>Film 7</td>
<td>10</td>
<td>4.3</td>
<td>/</td>
<td>55 Nano column</td>
</tr>
<tr>
<td>Film 4</td>
<td>11</td>
<td>4.3</td>
<td>50</td>
<td>49 Nano column+ multilayers</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Slightly elongated particle</td>
</tr>
<tr>
<td>Film 8</td>
<td>14</td>
<td>10</td>
<td>42</td>
<td>40 Elongated particle</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Column cluster</td>
</tr>
<tr>
<td>Film 1</td>
<td>9</td>
<td>13</td>
<td>70</td>
<td>78 Column cluster</td>
</tr>
</tbody>
</table>

Structure was discovered in Film 2 shown first in Table 5.2. Therefore, a detailed study on this film was carried out and is presented first. Thereafter, in order to follow the microstructural evolution four films are selected (1, 2, 6 and 8) and their microstructural characteristics are presented in detail. Two more structures are also discussed, which seem to be transitional structures. XPS/AES and TEM are utilized to provide information on chemical state and microstructures of the films.

In addition, the composition of the films has been characterized by two techniques, WDS and XPS, Table 5.2. There is a 2-20% difference in the information provided by these two methods. The analysis by WDS essentially probes the bulk composition with a depth of analysis of ~1 µm since the emitted radiation is x-ray. XPS provides a quantitative evaluation of surface composition with an analysis depth of 3-10 nm through emitting electron radiation. The incident radiation in WDS is electron beam and in XPS is
x-ray. Therefore, it is reasonable to expect a difference in composition between these two methods considering the surface state and uniformity of the film. WDS possesses high resolution and sensitivity through correction for absorption of fluorescence. XPS can eliminate the contamination effects by sputtering, and describe vertical composition variation through non-destructive depth profiling. In the present work, XPS is applied only in 5.2.2, while WDS is utilized to analyze the composition in all the remaining sections. Five measurements were conducted on each film to obtain statistically valid values in WDS analysis.

5.2.1 Self-assembled Nanocolumnar Co-a-C:H Films

(a) Microstructural Studies

Cross-sectional and plan-view bright filed TEM micrographs of Film 2 are shown in Figures 5.3 and 5.4 (a), respectively. The bright field cross sectional TEM image

![Figure 5.3 Cross sectional TEM image of Film 2 on Si (100) showing nanocolumnar structures](image-url)
Figure 5.4 (a) Plan-view TEM of Film 2. (b) Statistical distribution of the long and short axis of the columns.
shows that Film 2 exhibits helical-like column nanostructure. The dark column structures initiate at and grow continuously from the film/substrate interface up to the top surface of the film (~250 nm long for the film shown in Figure 5.3) and are separated by a bright matrix. Their lateral size varies from 6 nm to 10 nm and thus has an aspect ratio of ~25. Growth of thicker films can result in higher aspect ratios. Figure 5.4(a) is a plan-view TEM image of Film 2 showing the cross-sectional shape and the in-plane distribution of the column structures in the film. The dark regions in Figure 5.4(a) represent cross-sections of the columns showing round shape morphology and can be identified to be Co-rich structures. The cross-sections of the Co grains are slightly elongated, as evidenced in Figure 5.4(b) that shows a statistical distribution of a large number of grains. Most Co grains in Figure 5.4(a) have a long axis between 7 nm and 15 nm and a short axis between 4 nm and 10 nm. This suggests that the elongated columns are produced by coalescence of adjacent columns. Nearly all of the Co grains are well separated with respect to each other by a uniformly thick layer of matrix (bright layer) that has a thickness of about 1-2 nm.

Figure 5.5(a) is a high-resolution TEM image of the plan-view of Film 2. Bright contrast from the matrix can be clearly recognized to have an amorphous-like structure that corresponds to $a$-C:H. No lattice fringes were observed in the high-resolution TEM image of the Co grains that are encapsulated by the $a$-C:H matrix, which indicates that Co grains have an amorphous-like or a defect-rich structure. This conclusion is consistent with the SAED pattern shown in the inset in Fig 5.5(a). The two intense diffuse diffraction rings show that atoms in the Co grains have a good short-range ordering rather than a long-range ordering. Annealing of the TEM foil was conducted by e-beam
Figure 5.5 Plan-view HRTEM image of Film 2 with an inset of SAED of (a) as-deposited and (b) after heat treatment.
radiation. Figure 5.5(b) is a high-resolution TEM image that was taken from the same area under the same imaging condition as Figure 5.5(a) but after 10 min electron beam illumination. Compared with Figure 5.5(a), lattice fringes in the Co regions were clearly observed indicating that the Co grain structure is transformed from amorphous-like or a defect-rich structure to a crystalline structure. It was observed that after annealing, each Co nanorod cross-section typically contains three or four nanocrystals.

The SAED pattern of the Co grains after e-beam annealing is shown in the inset in Figure 5.5(b). Diffraction rings 1, 2, 3 and 4 have a \( d \) spacing of 2.48 Å, 2.10 Å, 1.60 Å and 1.49 Å, respectively. These data are consistent with the lattice spacing of the (211), (220), (321) and (400) planes of the \( \varepsilon \)-Co which is a \( \beta \)-Mn structure with a lattice constant of \( a = 6.07 \) Å\textsuperscript{137}. Recently, we have also observed formation of \( \varepsilon \)-Co in Co/C nanocomposite films\textsuperscript{4}. The \( \varepsilon \)-Co is a soft phase with the magnetocrystalline anisotropy constant of \( 1.5 \times 10^6 \) erg/cm\(^3\) at room temperature. The typical lattice fringes frequently observed in Figure 5.5(b) have a spacing of 2.1 Å corresponding to the (220) planes of the \( \varepsilon \)-Co. On the other hand, lattice fringes were clearly observed in the matrix regions in Figure 5.5(b). The latter lattice fringes have a spacing of \( \sim 3.4 \) Å that very well corresponds to the (0002) spacing of graphite. Previously, we have also observed transformation of DLC to graphite during wear of pure DLC films\textsuperscript{138}. Frictional heat generated during the wear process has a similar annealing effect as that of e-beam. The structural transition of the Co grains that occurred under the electron beam illumination indicates that the as-deposited Co nanorods are a defect-rich \( \varepsilon \)-Co phase.

The above local structural transition maybe ascribe to the collision interaction between the incident electrons and the film. When the electron beam illuminates the TEM
sample, beam/specimen interactions occur within a column of the material. Heat and defects are generated in the entire column. The relative role of beam heating and defect generation processes are not known at the moment. The present work shows that radiation-stimulated annealing can result in local recrystallization. This is in agreement with previous reports in the literature. For example, it was reported that under focused electron beam radiation, Ge₄₈Te₅₂ amorphous thin films can be crystallized at an average film temperature of 300 K, which is about 150 K lower than the corresponding annealing crystallization temperature in the absence of electron beam radiation. The Co-α-C:H nanocomposite thin films prepared in this study contain hydrogen as confirmed by NRA. Thus, the electron bombardment can be envisioned to cause liberation of hydrogen from the α-C:H matrix leading to graphitization and annihilation of defects in the Co nanorods enhancing their crystallinity. In fact, the fundamental wear mechanism of α-C:H involves hydrogen liberation under the frictional heat and formation of thin lubricious graphitic layer (friction coefficient \( f = 0.01 \)) between the countersurfaces.

Although the exact mechanism for growth of such Co nanorods in the DLC matrix is not yet completely understood, it is known that sputtered metal species arrive at the growing film surface as atoms. The subsequent nucleation and growth processes depend on arrival rate and surface migration that in turn is determined by plasma conditions. Present results show that the major processing parameters affecting Co content in the films are the Ar/CH₄ partial pressure ratio and chamber pressure. For example, by monitoring the Ar/CH₄ partial pressure ratio, synthesis of the entire composition spectrum of Co-containing films can be achieved. A lower ratio enhances the Co sputtering process resulting in a higher Co content. Formation of self-organized
nanocolumns in the present study can also be attributed to the relatively low magnetron power used that lowers deposition rate (arrival rate) and surface mobility of Co atoms. Under these conditions and in view of the large surface tension of Co (1520 erg/cm²), defect-rich columns form.

XRD (Cu $K_\alpha = 1.542$ Å) in Figure 5.6 also shows that the structure of Co in Film 2 is different from that in pure Co films, which is hcp Co. In the XRD of pure Co film, there are two peaks of hcp-Co, and two peaks from the Si substrate. As for Film 2, there are only two peaks for the Si substrate. The amount of crystal Co in as-deposited Film 2 is undetectable since most of the Co is amorphous or in a defect-rich structure that cannot be resolved by this probe. Electrons at 200 keV have a wavelength of 0.0251 Å that provides the most appropriate probe for this type of structural analysis.

![Figure 5.6 XRD for as-deposited Co thin film and Film 2.](image)
(b) XPS/AES Characterization Studies

Figure 5.7 shows an XPS survey spectrum of an as-deposited film with the top contamination layer removed by Ar-ion sputtering for 150s. This spectrum exhibits peaks of Co and C only. It should be noted that no O was found in the spectrum indicating that in the as-deposited films the Co is not oxidized. General Auger spectra show no contamination in the films and only presence of Co and C, Figure 5.8(a). Narrow window scans reveal differences in the Auger transitions for Co, Figure 5.8(b), and additional transitions for C in $a$-C:H, Figure 5.8(c). Thus, the $a$-C:H environment provides protection from oxidation and results in the formation of Co in metallic state. Co oxidation is one major drawback of wet techniques for synthesizing Co nanoparticles.\textsuperscript{137}
Figure 5.8 (a) General Auger spectrum from a Co-\textit{a}-C:H film showing only presence of Co and C (no contamination). Narrow window scans of (b) C and (c) Co transitions, respectively.
In summary, self-assembled, high aspect ratio nanorods in Co-α-C:H thin films have been successfully synthesized by plasma-assisted magnetron sputtering. The nanorods are continuously grown along the growth direction and have a relatively narrow distributed lateral size. The nanorods in the as-deposited thin films have an ε-Co structure with a high density of defects and are encapsulated by a 1–2-nm-thick amorphous α-C:H matrix.

5.2.2 Relationship between Process Parameters and Microstructure

Four films (Table 5.3) are selected to study the effects of deposition conditions on film microstructure. Typical XPS survey spectra of the four films exhibit the same characteristics as that in Figure 5.7. The Co content was found to vary from 35 at % to 78 at %. Very little O (<1 at %) was detected in the films, indicating the absence of Co oxide in the as-deposited film and that the α-C:H environment is effective in providing protection.

Figure 5.9 shows high-resolution spectra of the Co2p peak for all four Co-α-C:H films and pure Co target. The peaks for Co 2p3/2 and Co 2p1/2 show binding energies at 778.3 and 793.3 eV, respectively, that are very close to those obtained from metallic Co target (778.2 and 793.2 eV). The peak position of Co present as an oxide is around 780.9 and 796.4 eV. Thus, no Co oxide was observed in the four Co-α-C:H films. Regarding

Table 5.3 The effects of deposition parameters on components and structure of Co-α-C:H films.

<table>
<thead>
<tr>
<th>Pressure mTorr</th>
<th>Ar/CH4</th>
<th>Co at% XPS</th>
<th>Deposition Rate nm/min</th>
<th>% in C 1s peak</th>
<th>% in film</th>
<th>Intensity of ε-Co (321)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Co-C sp² sp³</td>
<td>Co-C sp² sp³</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>4.3</td>
<td>35</td>
<td>5.5</td>
<td>21.9 33.1 39.7 14.2</td>
<td>21.5 25.8</td>
<td>Medium</td>
</tr>
<tr>
<td>14</td>
<td>10</td>
<td>40</td>
<td>4.4</td>
<td>31.1 24.6 39.2 18.7</td>
<td>14.8 23.5</td>
<td>Absent</td>
</tr>
<tr>
<td>9</td>
<td>4.3</td>
<td>60</td>
<td>4.1</td>
<td>48.1 25.3 21.3 19.3</td>
<td>10.1 8.5</td>
<td>Strong</td>
</tr>
<tr>
<td>9</td>
<td>13</td>
<td>78</td>
<td>3.3</td>
<td>81 1.2 12.2 17.8</td>
<td>0.3 2.7</td>
<td>weak</td>
</tr>
</tbody>
</table>
the possibility of some Co to be present as Co carbide, it has been reported that the difference in binding energy between these two states of Co is very small and may not be resolved in the spectra\textsuperscript{117}. Thus, the slight difference (0.1 eV) in binding energies between Co in $a$-C:H and metallic Co is attributed to some presence of Co carbide or defected structure of the nanoparticles.

Figure 5.10 shows high-resolution spectra of the C\textit{I}s peak for the four films. The C\textit{I}s peaks can be decomposed into four components with binding energies at 283.5 eV for Co-C bond,\textsuperscript{117} 284.3 eV for sp\textsuperscript{2} C-C and/or C-H bond ($C\textsubscript{6}H\textsubscript{6}$), 284.8 eV for sp\textsuperscript{3} C-C

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Figure 5.9 High-resolution XPS spectra of Co 2\textit{p} peak from Co and Co-$a$-C:H films.
and/or C-H bond (-CH₃) and 286.5 eV for C-O and/or –CH₂O- bond. The percentage of each one of these four C states in the C 1s peak and in the overall composition of the four films is shown in Table 5.3.

Deposition of a-C:H films is typically produced by using a hydrocarbon containing discharge. It is well established that such a-C:H films are mainly amorphous, composed of sp² -and sp³ -bonded C domains. Recent NRA measurements show that all the films
contain hydrogen. The \textit{a}-C:H matrix encapsulates the Co rich nanostructures, and thus an interaction is expected between Co atoms on the surface and C atoms across the interface. In addition, during the present plasma-assisted hybrid CVD/PVD process, the Co target is bombarded by the gas discharge, and thus hydrocarbon and Co components are co-deposited on the biased substrate. Therefore, a relatively fast cooling rate pertains, restricting adatom mobility at the surface. It is also expected that a fraction of Co atoms are dispersed in the \textit{a}-C:H matrix. It is difficult to envision hydrocarbon molecules within the Co nanoparticles, but the presence of some C in the Co nanostructures can not be ruled out. Thus, the Co-C may result from interactions at the nanoparticle/matrix interface; Co atoms dissolved in the matrix and C atoms dissolved in the Co nanoparticles. As the Co content increases (C content decreases), the contribution of the Co bonded C in the C 1s peak increases and finally dominates the C 1s peak in the film while the remaining C contributions decrease. In fact, in the case with the highest Co content, the film has the lowest C content and most of the C atoms are expected to face Co atoms at the surface of the nanoparticles.

The microstructures of the four films have been studied by plan-view and cross sectional TEM. Figure 5.11 shows plan-view TEM images of the four Co-\textit{a}-C:H films. The dark regions in the images represent Co-rich nanostructures, while the bright regions correspond to \textit{a}-C:H matrix. The size and morphology of the Co nanostructures is associated with the Co content in the films. The average cross sectional area of the Co nanostructures increases with increasing Co content in the four films from 6 to 20, 25, and 1500 nm$^2$. A similar trend is also followed by the area fraction of Co nanostructures.
Cross-sectional TEM images of the four films are present in Figure 5.12. Co nanostructures in Film 6 (Figure 5.12(a)) are slightly elongated with their long axis parallel to the growth direction of the film. These Co nanostructures have an average lateral size of ~3 nm and length of ~4 nm (aspect ratio about 1.3). Increasing Co content of the film causes a size increase (coalescence) of the Co nanostructures preferentially along the growth direction. Thus, the Co nanostructures in Film 8 (Figure 5.12(b)) have an average lateral size of ~5 nm and length of ~20 nm (aspect ratio ~4). In Film 2, Figure 5.12(c), the lateral size of the Co nanostructures is about 7 nm, but their length is equal to the thickness of the film. The results suggest that at this point, the arrival rate of Co
atoms is sufficient to form complete columns along the entire film thickness. By increasing the Co content further to 78 at % Co (Film 1), the lateral growth of the nanocolumns is continuous, and very thin boundaries (~1 nm) are produced, Figure 5.12(d). However, all the Co atoms arriving at the surface cannot be accommodated by the latter growth process, and in view of the lower film growth rate (3.3 nm/min, Table 5.3), a “banded” film morphology is produced, Figure 5.12(d), to accommodate the Co atoms. This banded morphology has a variation in Co content, as evidenced by energy-dispersion spectroscopy analysis in conjunction with the TEM, giving rise to the electron absorption contrast shown in Figure 5.12(d). Therefore, it is clear that the present results indicate that nanorods formation is under kinetic control. Indeed, Table 5.3 shows that nanorods evolution depends on the deposition rate, and full column formation (through the entire film thickness) is achieved at a rate of 4.1nm/min.

![Cross-sectional TEM image of Co-a-C:H films](image)

**Figure 5.12** Cross-sectional TEM image of Co-a-C:H films: (a) 35 at% Co, (b) 40 at% Co, (c) 60 at% Co and (d) 78 at% Co.
Figure 5.13 (a)-(d) show SAED patterns of the four Co-α-C:H films correspondingly. The diffuse diffraction rings in the diffraction patterns show that atoms in the Co nanostructures have a short-range ordering rather than a long-range ordering. The five diffraction rings 1, 2, 3, 4, and 5 in Figure 5.13 (a) are identified to have a $d$-spacing of 2.1, 1.6, 1.2, 1.04, and 0.88 Å, respectively. The first intense ring in Figure 5.13(a) may correspond to the broad peak of either the (002) reflection of the α-Co or the superposition of the (220) and (300) reflections of the ε-Co. The $d$-spacing of the weak ring 2 and the intense ring 3 in Figure 5.13(a) agrees well with the lattice spacing of the (321) and (500) of the ε-Co. Ring 4 may correspond to the (201) reflection of the α-Co or the (522) reflection of the ε-Co. The $d$-spacing of ring 5 agrees well with the lattice spacing of the (321) and (500) of the ε-Co.

![SAED patterns](image)

**Figure 5.13** SAED pattern of the Co-α-C:H films: (a) 35 at% Co, (b) 40 at% Co, (c) 60 at% Co and (d) 78 at% Co.
spacing of the (631) of ε-Co. It is noticed that the weak diffraction ring 2 in the SAED pattern of Film 8 disappeared, Figure 5.13(b). The intensity of the diffraction ring 2 in Figure 5.13(a) is weaker than that in Figure 5.13(c) and stronger than that in Figure 5.13(d). These results show that a decrease in the chamber pressure and/or Ar/CH₄ flow rate ratio improve the weak reflection intensity, indicating the enhancement of the long-range ordering.

These results indicate that both the chamber pressure and Ar/CH₄ significantly influence the composition, crystallinity, and morphology of the Co-a-C:H films. As mentioned previously, the Co content of the films decreases by increasing the chamber pressure while keeping the Ar/CH₄ ratio constant or by decreasing the Ar/CH₄ ratio while keeping the chamber pressure constant. Such effects on the film composition by the two processing parameters can be understood by considering the sputtering process. Increasing the chamber pressure while keeping the Ar/CH₄ ratio constant increases the deposition of the hydrocarbon. The decrease of the Ar/CH₄ while keeping the chamber pressure constant results in a lower sputtering rate of the Co target from Ar⁺ and also an increase in the CH₄ partial pressure. Both of these effects decrease the Co content of the film. It is also interesting to note in Table 5.3 that decreasing the processing pressure and increasing the Ar/CH₄ flow ratio increases the Co content, but the overall deposition rate decreases. The deposition rate seems to exercise an effect in the evolution of the nano columns. Formation of nano columns in the entire film thickness is expected to be under kinetic control and involve interplay between atom arrival rate and adatom diffusion. It is interesting to note that in an earlier study, faster film growth rates (7.8-12nm/min) produced spherical Co nanoclusters (~1nm) in a hydrocarbon matrix. Similar results were
observed in Cr-DLC films, in which a film growth rate >10nm/min produces spherical Cr nanoparticles (~5nm). On the other hand, very low deposition rates are expected to produce coarse and irregular Co particles.

As mentioned previously, the Co nanostructures are defect-rich structures. It can be assumed that such defects arise from the ion bombardment on the growing surface and the fast cooling rate during deposition. The plasma encapsulating the film surface is composed of hydrocarbon and Ar ions, among which hydrocarbon will be deposited onto the film. The bombardment of the Ar plasma on the growing surface is expected to introduce defects in the films, which will deteriorate the atomic order of the Co nanostructures. It is expected that Ar plasma density will influence the atomic order of the structure. Such kind of effect is observed in the present experimental results by examining the intensity variation of (321) weak reflection of ε-Co (Table 5.3). Reducing the Ar/CH₄ ratio while keeping the chamber pressure constant, will reduce the Ar plasma density, which will introduce fewer defects in the films. The intensity of the (321) weak reflection of ε-Co is expected to increase, which agrees with the present experimental observations: Film 6 deposited using an Ar/CH₄ ratio of 4.3 and a chamber pressure of 14 mTorr shows a stronger ε-Co (321) reflection than Film 8 deposited using an Ar/CH₄ ratio of 10 and a chamber pressure of 14mTorr; Film 2 deposited using an Ar/CH₄ ratio of 4.3 and a chamber pressure of 9 mTorr shows a stronger ε-Co (321) reflection than Film 1 deposited using an Ar/CH₄ ratio of 13 and a chamber pressure of 9mTorr. Similarly, reducing the chamber pressure while keeping the Ar/CH₄ ratio constant will reduce the Ar plasma density and will produce the same effect as reducing the Ar/CH₄ ratio. This is also consistent with the experimental observation: Film 6 deposited using an
Ar/CH\(_4\) ratio of 4.3 and a chamber pressure of 14 mTorr shows a weaker \(\varepsilon\)-Co (321) reflection compared to Film 2 deposited using an Ar/CH\(_4\) ratio of 4.3 and a chamber pressure of 9 mTorr.

**5.2.3 Transitional Microstructures**

Two additional films were deposited at the same Ar/CH\(_4\) as Film 2 (nanocolumns) and Film 6 (elongated particles) but at an intermediate pressure in order to refine the process of nanocolumn formation. Thus, they acquired the term “transitional microstructures”. Film 7 in its cross sectional image, Figure 5.14(a), exhibits a similar columnar structure to that of Film 2. However, Film 7 consists of more wormlike Co rich clusters, which are shown in the plan-view of Figure 5.14(b).

The analysis about the trend of structure transition is as follows. As Co content decreases, the size of the Co nanocolumns decreases which eventually become elongated grains and finally spherical particles. This change is attributed to deposition conditions, which affect the deposition rate of different atoms. Processing at high power>150 W has been found to result in spherical particles.\(^{29}\) However, lower power as in the present work, reduces the sputtering rate of Co allowing atomic rearrangement (self organization) that under the magnetic field of the magnetron results in a “directional” deposition or self-assembly in the form of columns. If the power is high, the deposition rate is significantly increased resulting in spherical nanoparticles. Another effect is expected from the Co content. As the Co content decreases, the Co requirements for building up columns cannot be met thus sequentially formation of interrupted columns, elongated grains and eventually spherical nanoparticles takes place. Thus, for low metal volume fractions spheroidization of metal clusters occurs whereas for low hydrocarbon volume
Figure 5.14 (a) Cross-sectional TEM image of Film 7-Si showing columnar structures. (b) Plan-view TEM image of Film 7 showing wormlike structures.
fraction the Co is round or wormlike column. This is consistent with previous observations on Au-DLC and can be attributed to surface energy effects. The surface energy of Co and Au is $\gamma_{\text{Co}} = 1520$ erg/cm$^2$ and $\gamma_{\text{Au}} = 1200$ erg/cm$^2$. The $a$-C:H films typically exhibit $\gamma_{\text{a-C:H}} = 30$ erg/cm$^2$. Thus, it is expected that metallic particles in $a$-C:H will tend to spheroidization to minimize their surface to volume ratio. On the contrary, a low fraction of DLC will tend to wet the metal particles showing a worm-like microstructure. However, at the present conditions, the fraction of $a$-C:H is not the only factor since wormlike structure does not exist in the Co-$a$-C:H with higher Co content (>60 at%). The deposition rate for the wormlike Co-$a$-C:H is lower (3 nm/min). The lower deposition rate maybe promoting the coalesce of columns.

Observation of bright field images in Figures 5.15 (a) and (b) show that Film 4 structures are similar to those in Film 2, i.e., Film 4 shows a columnar structure in cross-section view and slightly elongated Co-rich particles in plan-view. Also, the nanocolumns seem to be finer in size due to lower Co content. However, Film 4 also shows a multilayer structure that can be observed clearly in Figure 5.15(b). Elemental mapping in Figure 5.16 indicates that the multilayer is composed of Co-rich layer and a C-rich layer in alternating sequence. This effect is attributed to higher pressure (11 mTorr in Film 4 compared to 9 mTorr in Film 2) that can produce a periodic building up of a hydrocarbon layer on the Co target (poisoning) that is sputtered off when a critical accumulation is reached resulting in a compositional variation (gradient). When the pressure is further increased (14 mTorr in Film 6), Co sputtering is reduced and the periodic layers are composed of $a$-C:H while the Co columns are interrupted resulting in
Figure 5.15 (a) Plan-view TEM image of Film 4. (b) Cross-sectional TEM image of Film 4 showing columnar and multilayer structure.
Figure 5.16 (a) STEM image of multilayer Film 4, (b) C map in (a), (c) Co map in (a) and (d) EDS spectrum in (a).

elongated particles. It is not clear at present how this modulation can be utilized. However, a higher sputtering rate (power or Ar/CH₄ ratio) can alleviate this effect resulting in compositionally uniform films. Similar modulation has been observed in our laboratory on Cr-Fe-C:H films. Also, a recent report presents evidence for other systems such as Ni-DLC. These effects are attributed to poisoning of the metal target as mentioned above.

Although one factor to affect the structure is composition of the film, it is difficult to correlate the composition with the structure changes. Laurent and Kay concluded that size and shape of Co clusters changed as a function of volume fraction. Since they only
changed the Ar/C$_2$H$_6$ to obtain films with different Co fractions, their conclusion is limited to a specific parameter. On the other hand, we can conclude that pressure is a rather sensitive parameter to affect the structure. A 10-20% variation in pressure results in different structures (nano-column, elongated particles, wormlike, multilayer). The Ar/CH$_4$ ratio can also affect the Co-$a$-C:H structure by changing the Co content in the Co-$a$-C:H films.

The structure of Film 3 is similar to Film 2 in both plan-view and cross-section view. Thus, it can be concluded that the column structure can be produced when the Ar/CH$_4$ ratio is 3.8–4.3 while the rest of the parameters remain the same as shown in Table 5.1.

5.3 Properties of Co-$a$-C:H Films

5.3.1 Magnetic Properties

Based on the transmission electron micrographs obtained from the Co-$a$-C:H films, both Film 1 (70 at% Co) and Film 2 (55 at% Co) have columnar structures. The mean diameter of Film 1 is about 40 nm in short axis and 55 nm in long axis. The mean diameter of the columns in Film 2 is about 7.2 nm of short axis and 9.6 nm of long axis. The Co nano columns are embedded in the $a$-C:H matrix. The metal Co columns are well separated from each other in Film 2, while the Co columns coalesce to clusters in Film 1.

The magnetic properties for Film 1 and Film 2 are summarized in Table 5.4 on the basis of the magnetization behavior. Figures 5.17 (a) and (c) present the in-plane M-H curves of Film 2 and Film 1, respectively, measured at 10 K and 300 K. Their zero-field-cooled (ZFC) and field-cooled (FC) scans are shown in Figure 5.17 (b) and (d), respectively. Film 1 possesses ferromagnetic property, while Film 2 is superparamagnetic. The hysteresis loop of Film 2 at 300 K is too narrow to be
Table 5.4 Magnetic parameters of Co-a-C:H films measured at 10 K and 300 K. 
\(M_s\) = saturation magnetization, \(H_c\) = coercivity, and \(M_r/M_s\) = the ratio of the remanence to the saturation magnetization.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature K</th>
<th>(M_s) emu/cm(^3)</th>
<th>(M_r) emu/cm(^3)</th>
<th>(H_c) Oe</th>
<th>(M_r/M_s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film 2 in-plane</td>
<td>10</td>
<td>276</td>
<td>31</td>
<td>32</td>
<td>0.11</td>
</tr>
<tr>
<td>Film 1 in-plane</td>
<td>300</td>
<td>6</td>
<td>2</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>Film 2 perpendicular</td>
<td>10</td>
<td>409</td>
<td>22.5</td>
<td>145</td>
<td>0.055</td>
</tr>
<tr>
<td>Film 1 perpendicular</td>
<td>300</td>
<td>960</td>
<td>0</td>
<td>0</td>
<td>\</td>
</tr>
</tbody>
</table>

Figure 5.17 In plane magnetic behavior: (a) hysteresis loops for Film 2, (b) ZFCFC curve for Film 2, (c) hysteresis loops for Film 1 and (d) ZFCFC curve for Film 1.
distinguished. The superparamagnetic property of Film 2 results from its small Co-rich column diameter. On the basis of in-plane M-H curves for Co-\(a\)-C:H thin films, at low temperature (\(\leq 300\) K), the coercivity \(H_c\) is independent of composition and temperature; \(H_c\) for these samples is almost the same, 16-32 Oe. At 10 K, the saturation magnetization, \(M_s\), for Film 1 is 731 emu/cm\(^3\), while \(M_s\) for Film 2 is 276 emu/cm\(^3\). At higher temperature measurement (300 K), \(M_s\) of Film 1 and Film 2 decreases to 545 and 6 emu/cm\(^3\), respectively. Raising thermal energy increases the spin of the Co nanocrystals, and thus decreases the magnetization. The sharp drop in saturation magnetization from Film 1 to Film 2 might result from the decrease of Co ratio in the films and the decrease of the size of the columns distributed in the hydrogenated C matrix. We have reported that as-deposited Co-\(a\)-C:H thin films are composed of defect-rich \(\varepsilon\)-Co. Film 2 possesses a stronger \(\varepsilon\)-Co (321) reflection than Film 1. \(\varepsilon\)-Co is a soft magnetic phase that displays a magnetocrystalline anisotropy that is lower than uniaxial hcp-Co\(^{137}\). This might be another contributing factor. Decreasing column size causes an increase of the surface-to-volume ratio in the columns. The squareness, \(M_r/M_s\), of Film 2 at 10 K is significantly small, which is an indication that phase separation is incomplete in the Co-rich composition. In ZFC scans, a sample is cooled in a zero applied field, and the magnetization is recorded by rising temperature in the presence of a field (200Oe). As the thermal energy increases, nano-structured \(\varepsilon\)-Co in Film 2 becomes unpinned and aligns with the applied field; the film’s net magnetization is increased. At the blocking temperature \(T_b=120\) K, \(\varepsilon\)-Co moments begin to fluctuate in the field due to the thermal energy, reducing the net magnetization. In FC scans, a sample is cooled in a field (200Oe), freezing-in a net alignment of the nano structured \(\varepsilon\)-Co moments. After the field
is removed, the magnetization is measured as the sample is slowly heating up. The freezing-in net alignment is not broken up by thermal energy at the temperature lower than $T_b$, and a “self-sustained” field is formed. Active moments resulted from thermal energy align with the “self-sustained” field, while increasing the net magnetization. When the temperature is higher than $T_b$, nano crystal $\varepsilon$-Co moments randomized from alignment under thermal energy, lowering the net magnetization. The ZFC and FC curves converge at 120 K. Net magnetization is close to zero at 250 K. Murray et al. reported similar results for 9.5 nm $\varepsilon$-Co nano particles. In both ZFC and FC scans for Film 1, the magnetization decreases smoothly, as temperature increases, which is the typical feature of a ferromagnet. Ferromagnetic order is reduced by enhancing thermal activity. The spontaneous magnetization is vanished above the Curie temperature, $T_c$. The ZFC and FC curves almost coincide in both Film 1 and Film 2 since the films possess the simple cubic, soft magnetic $\varepsilon$-Co phase and the applied field is not strong enough to produce a difference. The freezing-in net alignment produces a similar magnetization behavior to that with the presence of the field.

Figures 5.18 (a) and (b) present the perpendicular M-H curves of Film 2 and Film 1 measured at 10 K and 300 K. Film 1 does not show any perpendicular magnetization under both 10 K and 300 K. Its $M_r$ and $H_c$ are negligible. Film 1 possesses anisotropic magnetism with in-plane ferromagnetism. The Film 2 demonstrates a hard perpendicular magnetic property at 10 K with a $H_c$ of 145 Oe and a $M_r$ of 22.5 emu/cm³. When the temperature increases to 300 K, Film 2 shows superparamagnetic behavior. Therefore, the magnetic orientation of the domains in Film 2 prefers to be along the growth orientation.
Figure 5.18 Perpendicular magnetic hysteresis loops of (a) Film 2 and (b) Film 1.

Based on the theory of superparamagnetism\textsuperscript{48,57}, for $k_BT>>KV$, small particles well separated by a non-magnetic matrix will behave like a paramagnet, and a particle is a single-domain. They can be termed as “single domain particles”. The single domain particles have anisotropy of cubic symmetry. Bean \textit{et al.}\textsuperscript{48} stated that “single domain particle” means a particle being in a state of uniform magnetization at any field. Since both in-plane and perpendicular magnetization in Film 2 show superparamagnetic behavior, one column can be a single-domain. Therefore, superparamagnetism is related to two-dimensional rather than three-dimensional structure. This may be a way to synthesize magnetic materials since one of the dimensions is unlimited. Kittel\textsuperscript{48} and others estimated the critical particle size for spherical samples to be a radius of 150 Å. Synthesis of single domain columns might be a complement for the superparamagnetism.

The present results provide the opportunity to tailor these films by changing Co content, nanostructure size and annealing for various applications, such as soft magnet, magnetic recording and hard magnet. However, superparamagnetism is an important limitation in magnetic recording. Perpendicular magnetic thin film is one of the prospect
candidates for extremely high density recording media. Therefore, it is possible to overcome the superparamagnetic property of Co-\(a\)-C:H by doping other elements such as Sm and Pt, and take advantage of the perpendicular magnetic property of columnar structure. Bean et al. suggested some applications of superparamagnetism\(^4\), which are also applicable for Co-\(a\)-C:H films.

**5.3.2 Wear and Friction Behavior**

Pin-on-disc wear testing has been carried out on the Co-\(a\)-C:H films to study the frictional behavior. Also, the wear rate was evaluated by measuring the cross sectional area of the wear track by profilometry. Figure 5.19 shows the friction variation of Co-\(a\)-C:H films as a function of the sliding distance. Pure Co film is also shown here for

![Figure 5.19 Friction behavior for various Co-\(a\)-C:H films.](image-url)
comparison. After about 50 m sliding, the friction coefficient for all Co-\(a\)-C:H film stabilizes. The friction coefficient of pure Co film is significantly higher than all the Co-\(a\)-C:H films and reaches a value close to 0.65.

Figure 5.20 shows the effects of Co content on wear rate and friction. In general, the wear rate increases with increasing the Co content. The tendency for the friction coefficient with Co content is similar. Again, a higher C content (low Co content) is translated into larger volume fraction of \(a\)-C:H that exhibits low friction and wear rate. The Co-\(a\)-C:H film with 45 at% Co exhibits a good compromise between wear behavior and Co content. It shows significant decrease in wear rate and friction coefficient compared with pure Co film and the same time has a significant Co content. Such a film constitutes a good multifunctional candidate film.

Figure 5.21 presents the wear track morphology in 3D and 2D view for bulk Co, pure Co film and Co-\(a\)-C:H films. The wear track morphology for films with high Co content (70% Co) is similar to that of pure Co. The wear is mainly between the Co and \(\text{Al}_2\text{O}_3\) ball. The wear mode is adhesive. The Co-\(a\)-C:H film with 55 at % Co or less show abrasive wear. The film wears by a layer-by-layer process and the wear debris adheres to \(\text{Al}_2\text{O}_3\) ball. A low shear strength graphitic interlayer (transfer layer) is formed between the ball and the film. This transfer layer allows for low friction. Increasing the C content in the film reduces the depth and width of wear track. Co-\(a\)-C:H film with 45 at% Co exhibit very low wear and the wear track is weak, Figure 5.21 (m). Thus, a significant presence of Co in the film impedes transfer layer formation, which can be observed on the wear track of Co-\(a\)-C:H with 70 at% Co in Figure 5.21 (e). On the other hand, at a Co content \(\leq 45\) at% the transfer film can maintain coherency and friction retains low.
Figure 5.20 Variation of the wear rate and friction coefficient with Co content in the Co-a-C:H thin films (Co content measured by WDS).

Figure 5.21 Wear track image along with corresponding profile of the track cross-section for Co and different Co-a-C:H films: (a) wear track image for bulk Co, (b) profile for (a), (c) wear track image for Co film, (d) profile for (c), (e) wear track image for Film 1 (70 at% Co), (f) profile for (e), (g) wear track image for Film 2 (55 at% Co), (h) profile for (g), (i) wear track image for Film 3 (54 at% Co), (j) profile for (i), (k) wear track image for Film 4 (50 at% Co), (l) profile for (k), (m) wear track image for Film 5 (45 at% Co), (n) profile for (m).

(Figure cont’d)
Figure 5.21 (Continued)
Figure 5.21 (Continued)
5.3.3 Mechanical Properties

The variation of nanohardness and elastic modulus of the Co-α-C:H films as a function of Co content is shown in Figure 5.22. Hardness decreases with increasing Co content in the films since that corresponds to a decreased volume fraction of α-C:H. This indicates that the hardness increases with the increase of the fraction of α-C:H in Co-α-
Figure 5.22 Variation of reduced elastic modulus and nanohardness with Co content of Co-\textit{a}-C:H thin films (Co content determined by WDS).

C:H films, which is an evidence of the presence of \textit{a}-C:H not the common Co-C structure. Indeed, previous analysis showed that incorporation of Co in \textit{a}-C:H causes reduction of H and sp\textsuperscript{3} bonding. The maximum nano-hardness observed for the present Co-\textit{a}-C:H films is 12.5 GPa, while the value for typical \textit{a}-C:H is 17 GPa\textsuperscript{67,81}. Thus, it is significant that the Co-\textit{a}-C:H films can maintain up to 70\% of the hardness of pure \textit{a}-C:H. The Co doping and low sp\textsuperscript{3} fraction produces a decrease in hardness. Based on Table 3.1, Co-\textit{a}-C:H belongs to hard \textit{a}-C:H. The relationship between the Co content and the modulus is complex. There should be several factors involved. Two important factors affect the hardness and modulus of Co-\textit{a}-C:H are the sp\textsuperscript{3} and Co content in the film.

Although we know that the sp\textsuperscript{3} fraction in C \textit{1s} peak of Co-\textit{a}-C:H thin films is in the range of 10-40 \% (Table 5.1), the ratio of contribution from C-H and C-C bonding is unknown.
5.3.4 Corrosion Behavior

Figure 5.23 shows potentiodynamic polarization curves for pure \(a\)-C:H, pure Co, Film 2, and Film 6 in 3.5% NaCl aqueous solution. The corresponding corrosion properties are listed in Table 5.5. The corrosion potential, \(E_{\text{corr}}\), for \(a\)-C:H is 142 mV (SCE) while the values for the rest of the films are negative and close to each other. Thus, the corrosion potential of Co-\(a\)-C:H is controlled by the presence of Co. The corrosion potential of Co-\(a\)-C:H is controlled by the presence of Co. The corrosion potential of Co-\(a\)-C:H is controlled by the presence of Co.

![Corrosion Behavior Graph](image)

**Figure 5.23 Corrosion behavior of Co-\(a\)-C:H thin films in 3.5% NaCl solution compared with pure Co and pure \(a\)-C:H thin film.**

**Table 5.5 Relationship between the electrochemical behavior and the structure of Co-\(a\)-C:H samples in comparison with \(a\)-C:H, and pure Co.**

<table>
<thead>
<tr>
<th>samples</th>
<th>Microstructure</th>
<th>(E_{\text{corr}}) mV</th>
<th>(i_{\text{corr}}) mA/cm²</th>
<th>(R_p) kΩ cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>Micro crystal</td>
<td>-378.8</td>
<td>0.014</td>
<td>1.5</td>
</tr>
<tr>
<td>Film 2</td>
<td>Nano column</td>
<td>-304.9</td>
<td>2.5x10⁻³</td>
<td>11.2</td>
</tr>
<tr>
<td>Film 6</td>
<td>Nano particle</td>
<td>-246</td>
<td>8.3x10⁻⁴</td>
<td>61.1</td>
</tr>
<tr>
<td>(a)-C:H</td>
<td>amorphous</td>
<td>142</td>
<td>2.0x10⁻⁷</td>
<td>*</td>
</tr>
</tbody>
</table>

* The value is beyond the detecting range of the instrument.
current density of \( a\)-C:H is very low \((1.95\times10^{-7}\text{ mA/cm}^2)\), which indicates that \( a\)-C:H is stable and electrochemically inert in NaCl environments. Both current density \((1.4\times10^{-2}\text{ mA/cm}^2)\) and resistivity \((1.5\text{ k}\Omega\text{ cm}^2)\) reveal a high corrosion rate for pure Co. In comparison, the corrosion rate of Co-\( a\)-C:H is a compromise between \( a\)-C:H and pure Co (about 1 order of magnitude enhancement compared to pure Co). Therefore, \( a\)-C:H protects Co from corrosion when nanostructured Co is embedded in \( a\)-C:H. This protection can be further improved by depositing a pure \( a\)-C:H thin film (overlayer \( \sim2\text{nm} \)) after Co-\( a\)-C:H deposition. Film 2 and Film 6 have a corrosion current density of \(2.5\times10^{-3}\) and \(8.3\times10^{-4}\text{ mA/cm}^2\), and a resistivity of 11.2 and 61.1 \(\text{k}\Omega\text{cm}^2\) respectively (Table 5.5). Film 6 was found to be superior to Film 2 in terms of corrosion resistance. One important reason is that nano Co particles are well encapsulated in the diamondlike carbon matrix in Film 6 while the top sides of nano Co columns in Film 2 are exposed to the electrolyte. Another reason is that the Co fraction in Film 6 is lower. Polarization curves demonstrate that passivation zones exist in both films. Compared to Film 2, the zone for Film 6 is wider, and its passivation current density is lower when the applied potential is below 1000 mV (SCE). Above 1000 mV (SCE), the corrosion rate of Film 6 increases. Below 1000 mV (SCE), Film 2 undergoes three passivation stages. This indicates that Film 2 “passivated” in a different way. During the corrosion experiment of pure Co, evolution of \( \text{H}_2 \) bubbles was observed from the cathode and a greenish CoO layer covered the sample surface. During the testing of Co-\( a\)-C:H films, there was no \( \text{H}_2 \) evolution observed and a greenish surface layer was present only on Film 2, but not on Film 6. There was also no \( \text{H}_2 \) formation in \( a\)-C:H. Therefore, the corrosion behavior of Co in Film 2 is similar to that of pure Co resulting in CoO production. The passivation
phenomena in Film 2 result from the nanostructure and \( a-C:H \) matrix which hindered the corrosion process. The passivation of Film 6 comes from the well encapsulation particle structure and thus Co are well protected by \( a-C:H \) from oxidation to CoO.

5.3.5 Surface Roughness

Roughness is a surface characteristic that can affect tribological and other functions such as electrical and thermal performance. Roughness is also one of the important evaluation factors in magnetic storage devices. Therefore, the Co-\( a-C:H \) thin films were characterized in terms of roughness by measuring the roughness average \( R_a \) by profilometry. The results are shown in Table 5.6. The roughness of all Co-\( a-C:H \) films is low, and remained closed to that of the Si substrate. Thus, the present processing conditions do not exercise an adverse effect on surface roughness.

5.4 Annealing Effects

5.4.1 Modulated DSC Characterization

The modulated DSC results for Film 2 are presented in Figure 5.24 (a). The reaction temperatures fall in the range of 300-470 °C. The response can be analyzed with three overlapping exothermal peaks in the heat flow. The first peak is at about 343°C. The

<table>
<thead>
<tr>
<th>Films</th>
<th>Co, at%</th>
<th>( R_a, \text{nm} )</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film 4</td>
<td>50</td>
<td>2.3</td>
<td>0.7</td>
</tr>
<tr>
<td>Film 5</td>
<td>45</td>
<td>2.7</td>
<td>0.6</td>
</tr>
<tr>
<td>Film 1</td>
<td>70</td>
<td>3.2</td>
<td>0.8</td>
</tr>
<tr>
<td>Film 3</td>
<td>54</td>
<td>3.6</td>
<td>0.7</td>
</tr>
<tr>
<td>Film 2</td>
<td>55</td>
<td>2.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Film 8</td>
<td>42</td>
<td>1.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Co</td>
<td>100</td>
<td>1.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Si</td>
<td>0</td>
<td>1.9</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Figure 5.24 DSC results for (a) Co-\(a\)-C:H film and (b) Pure \(a\)-C:H film.
second is at about 407°C. The third reaction peak is at 459 °C. The reactions at the three peaks are nonreversible. The total heat flow is the combination of reversible and non-reversible heat flows.

The DSC results from pure \(a\)-C:H film are shown in Figure 5.24(b). From the reversible and nonreversible heat flow, it can be observed that a transition occurs at about 402 °C. Based on previous annealing studies of \(a\)-C:H, this behavior can be attributed to the graphitization process. This process starts at about 350 °C with liberation of hydrogen and gradual conversion of all \(sp^3\) bonds into \(sp^2\) graphitic bonds\(^{143}\). The results show that this process ends at about 500 °C.

The heat flow of the graphitization reaction is relatively small compared to that involved in the reactions of the Co-containing \(a\)-C:H films, Figure 5.24(a). Thus, the DSC studies indicate other major transitions in Co-\(a\)-C:H films with that of graphitization of the matrix being buried in this response. The first peak can be attributed to \(\varepsilon \rightarrow \text{hcp}\) transition of Co, the second to the decomposition of \(\delta' - \text{Co}_2\text{C}\), and the third to \(\text{hcp-Co} \rightarrow \text{fcc-Co}\) transition, which will be discussed later with the TEM results.

### 5.4.2 TEM Analysis

Various annealing treatments were applied to Film 2 as follows: 200 °C×24 hrs, 300 °C×2 hrs, 350 °C×2 hrs and 500 °C×2 hrs. Figures 5.25 (a)-(f) show bright field TEM plan-view and cross-section images for the annealed Film 2 at different temperatures and durations along with the corresponding electron diffraction pattern as inset in the micrograph. The results also show that annealing at or below 350°C does not damage the columnar structure. There is no evidence of Co column coalescence upon annealing.
Figure 5.25 Phase changes under various vacuum annealing treatments observed by TEM: (a) plan-view after 200°C×24hrs, (b) plan-view after 300°C×2hrs, (c) cross-section after 300°C×2hrs, (d) plan-view after 350°C×2hrs, (e) cross-section after 350°C×2hrs. (f) plan-view after 500°C×2hrs. Insets are the diffraction patterns.

(Figure Cont’d)
Figure 5.25 (Continued)
under these conditions. Both the microstructural observations and electron diffraction patterns indicate that the matrix in the Film 2 remains amorphous for 200°C×24 hrs.

The SAED pattern in Fig 5.25 (a) reveals that the five diffraction rings with a d-spacing of 2.45, 2.15, 1.49, 1.16 coincide with the lattice spacing of (211), (220), (410), (511) of ε-Co. Therefore, ε-Co is stable under annealing at 200 °C×24 hrs. Since there is no CoO present, the results show that the a-C:H matrix provides protection to the Co columns from oxidation. Annealing the film at 300 °C×2 hrs causes crystal lattice spacing to appear. There are lattice fringes in some of the Co column and discrete fringes in the matrix. The SAED pattern of the film is shown as inset in Figure 5.25 (b). The diffraction rings corresponding to a d spacing of 2.07, 1.6, 1.51, 1.33, 1.14 Å, fit well with the lattice spacing of the (221), (321), (400), (420), (520) planes of ε-Co. The other diffraction rings have a d spacing of 2.04, 2.18, 3.08, 4.39, 4.32, 2.41, 1.59, 1.23 which corresponds to (001), (011), (020), (022) planes of δ’-Co2C. The formation of δ’-Co2C was first reported by Konno et al. It has a type of orthorhombic structure. Therefore, the electron diffraction demonstrates that ε-Co along with δ’-Co2C co-exist in Co-a-C:H films up to annealing at 300°C×2 hrs.

The crystal formation is fully realized under 350 °C×2 hrs, Figures 5.25 (d) and (e). Each column contains a crystal with broad fringes. The lattice fringes in a-C:H matrix are also apparently displayed. Columns also seem to grow in a parallel direction. Observations on the cross-sectional images indicate that the crystal fringes in different columns also follow the same direction. The five diffraction rings in the SAED after 350 °C×2 hrs, inset in Figure 5.25(d), have a d spacing of 2.04, 2.18,
1.91, 1.49, 1.15, 1.09, 1.03, which is consistent with the (002), (100), (101), (102), (103), (200), (201) plane of hcp-Co, respectively. The SAED also demonstrates that the structure is close to single crystal and suggests long-range ordering. The electron diffraction shows that hcp-Co and δ'-Co₂C are present in the films. The ε-Co has changed to hcp-Co fully upon annealing at 350 °C×2 hrs. Figure 5.25(f) presents a plan-view image and SAED for Film 2 annealed at 500 °C×2 hrs. The plan-view indicates a uniform distribution of spherical Co nanostructures in the matrix. Six diffraction rings with d-spacing of 2.07, 1.81, 1.29, 1.07, 1.03, 0.80 match well with the (111), (200), (220), (311), (222), (420) planes of fcc-Co. The diffraction rings with a d-spacing of 2.41 2.07, 1.93, 1.49, 1.45 can be indexed as (110), (111), (012), (003) (031) planes of δ'-Co₂C, respectively. Also, it can be observed that the diffraction rings for δ'-Co₂C become weak, suggesting a reduction in the amount of δ'-Co₂C.

5.4.3 Electron Structure Transition Characterized by XPS

Figures 5.26 (a)-(d) are high-resolution XPS C 1s spectra for as-deposited and annealed Film 2 at 250°C×2hrs, 350°C×2hrs and 500°C×2hrs. The C 1s peak can be decomposed into five components with binding energies 283.4±1eV, 284.3±1eV, 285.0±1eV and 286.4±1eV and 287.7±1eV, which can be ascribed to Co-C, sp² C-C or C-H, sp³ C-C or C-H, C-O and C=O bonds, respectively. Table 5.7 summarizes the fractions of the different C chemical states in the annealed films. Along with the raise of annealing temperature to 350°C, the fraction of Co-C bonding and the ratio of sp³/sp² tend to increase slightly. When the temperature attains 500°C, the amount of sp² bonding rises significantly to 87%, while the sp³ bonding disappears while still 10 % Co-C bonding remains, in agreement with the TEM results.
The structure of Co-\(a\)-C:H involves embedded Co-rich nano columns, \(a\)-C:H matrix and the interface structure between Co and \(a\)-C:H. The structure is discussed in the following three aspects.

(a) Co/\(a\)-C:H interface

The TEM observations reveal that Co atoms in the film (with high Co content) form Co clusters embedded in the amorphous hydrogenated carbon matrix. High-resolution XPS C 1s spectra trace the existence of Co-C bonds in as-deposited films. However,

Figure 5.26 Deconvolution of high-resolution C 1s spectra for as-deposited and annealed Co-\(a\)-C:H films: (a) as-deposited, (b) annealed at 250°C ×2hrs, (c) 350°C ×2hrs, and (d) 500°C ×2hrs.
Table 5.7 High-resolution C 1s spectra showing annealing effects on the chemical state of Co-α-C:H films.

<table>
<thead>
<tr>
<th>Condition</th>
<th>%Co-C</th>
<th>%sp²</th>
<th>%sp³</th>
<th>%C-O</th>
<th>%C=O</th>
<th>sp³/sp²</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>50.28</td>
<td>30.21</td>
<td>16.98</td>
<td>2.51</td>
<td>0.56</td>
<td></td>
</tr>
<tr>
<td>Annealed at 250°C ×2hrs</td>
<td>53.61</td>
<td>25.34</td>
<td>15.97</td>
<td>2.64</td>
<td>2.44</td>
<td>0.63</td>
</tr>
<tr>
<td>Annealed at 350°C ×2hrs</td>
<td>57.23</td>
<td>20.65</td>
<td>15.38</td>
<td>5.12</td>
<td>1.61</td>
<td>0.74</td>
</tr>
<tr>
<td>Annealed at 500°C ×2hrs</td>
<td>9.33</td>
<td>87.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TEM can only acquire the information of Co and C without any cobalt carbide evidence in the as-deposited film. Moreover, TEM identifies the δ’-Co₂C after the film is annealed at 300 °C×2 hrs, 350 °C×2 hrs and 500 °C×2 hrs. Therefore, most of the interface structure is probably a kind of hydrate of cobalt carbide. This has been shown previously in the literature.³⁴ Annealing removes the water from the film leaving behind δ’-Co₂C. However, this is not likely since no O was detected in the films by XPS after sputter cleaning. It is more likely that there might be some organocobalt compound formed from cobalt atoms and α-C:H matrix in the interface during deposition. The π-complexes Co(C₂H₄)₁₋₃ have been reported in the literature.¹⁴⁴ A previous report³³ also identified the existence of methyl derivatives of cobalt-carbide and benzene derivatives of cobalt-carbide. Since this Co-C interaction exists only at the interface in the form of a single atomic interaction, it cannot be identified by TEM. After annealing, the Co in the organometallic compound reacts further with C for the formation of cobalt carbide domains. Then, such domain structures can be detected by TEM. In that case, XPS also shows a slight increase in the fraction of Co-C bonding. XPS reveals that only 10% of Co-C bonding remains in the C 1s peaks after 500 °C×2 hrs annealing. TEM shows that δ’-Co₂C decomposes under annealing of 500 °C×2 hrs, which is discussed next.

(b) The embedded Co structure transition
According to the TEM observations and composition analysis, as-deposited Co-α-C:H is composed of a defect-rich ε-Co structure and hydrogenated amorphous carbon. The ε-Co structure is stable after the annealing treatment of 200°C×24 hrs. Crystallization initiates when the film is annealed at 300°C×2 hrs, although it is just traceable. Co exists in two phases, ε-Co and δ'-Co₂C after the 300 °C×2 hrs annealing. ε-Co fully changes to ordered hcp-Co upon annealing at 350 °C×2 hrs. The hcp-Co and δ'-Co₂C co-exist in the Co-α-C:H film annealed at 350°C×2 hrs. Following annealing at 500°C×2 hrs, hcp-Co changes to fcc-Co, while a small amount of δ'-Co₂C remains. Therefore, the temperature range for ε-Co to exist is ≤300°C. The δ'-Co₂C phase can exist at temperatures >300°C, which agrees with the results of Konno et al.² However, based on their studies, the as-deposited Co-C film was amorphous, and the ε-Co phase was not detected in any annealing stage. The only difference for Co-α-C:H and Co-C films is that they possess a different matrix. Since the Co atom can act as a type of catalyst for a-C:H or polymer, it is easy to coalesce to metal clusters embedded in the a-C:H or polymer. The metastable ε-Co phase is protected by the a-C:H matrix from its nucleation stage. On the other hand, in the Co-C amorphous films, the Co atoms are randomly dispersed with no structure. If annealed, then formation of the hcp-Co is expected. The formation of ε-Co is also related to the synthesis method and processing condition. The DSC analysis showed that the first nonreversible peak is at around 343°C. On the basis of SAED in TEM, the first peak refers to the nonreversible phase change from ε-Co to ordered hcp Co, which is consistent with the results of the annealing behavior of Co in Co-C film⁴. Hibbard et al. reported a grain growth emerged at 346°C for electrodeposited nanocrystalline Co¹⁴⁵. However,
there is no evidence for Co grain growth in Co-α-C:H. The difference can be ascribe to the presence of α-C:H which hinder the grain growth of nanocolumnar Co.

The second peak in DSC is at around 407 °C. The reaction is exothermic and nonreversible. TEM analysis demonstrates that hcp-Co and δ′-Co2C co-exist upon 350°C×2hrs annealing while fcc-Co and small amount δ’-Co2C co-exist under 500°C×2hrs annealing. It has been demonstrated that δ′-Co2C decomposes to hcp-Co and graphite at 380-420°C^2. Moreover, it is well known that the hcp-Co is stable below 425 °C and the fcc phase is stable at higher temperatures. Therefore, the phase change shown in the second peak reflects the δ′-Co2C decomposition. Pure hcp Co exhibits an exothermic partial reversible reaction in DSC (not shown here) exactly at the same temperature as the third peak in DSC for Co-α-C:H film, 459 °C. It is the phase change of hcp-Co → fcc-Co. Thus, the third peak should reflect the same phase change from hcp-Co to fcc-Co, which has been confirmed by the TEM analysis. Apart from the phase change of hcp-Co to fcc-Co, plan-view TEM observations reveal that Co nanostructures change from an elongated round shape to spherical, which will reduce the ratio of surface/volume, and thus the surface energy of Co in α-C:H is reduced. The energy reduction reflects an exothermic behavior in DSC. The graphitization of α-C:H matrix is also in that temperature range (402°C, Figure 5.24 (b)). Therefore the second peak reflects the decomposition of δ′–Co2C and the graphitization reaction, and the third peak reflects mainly the phase change of hcp-Co to fcc-Co.

(c) Thermal stability of α-C:H

High-resolution XPS C Is spectra indicate that annealing of Co-α-C:H below 350 °C does not break the sp^3 and Co-C bonds. The fractions of the different species remain
almost the same below this temperature. The sp$^3$ carbon is fully graphitized at 500 °C×2 hrs.

In summary, Film 2 undergoes the following phase transitions:

\[
\text{as-deposited Co-}\alpha\text{-C:H (defect-rich } \varepsilon\text{-Co + Co carbide derivative + } \alpha\text{-C:H)} \xrightarrow{300°C} \varepsilon\text{-Co + }\delta'\text{-Co}_2\text{C + }\alpha\text{-C:H} \xrightarrow{343°C} \text{hcp-Co + }\delta'\text{-Co}_2\text{C + }\alpha\text{-C:H} \xrightarrow{407°C} \text{hcp-Co + graphite} \xrightarrow{459°C} \text{fcc-Co + graphite.}
\]

**5.5 Multifunctional Co-\(\alpha\)-C:H Films**

The previous sections showed that processing conditions can be manipulated to synthesize Co-\(\alpha\)-C:H films with magnetic properties while the films possess good wear resistance, high hardness, low roughness and corrosion resistance. As mentioned earlier, deposition of a thin pure \(\alpha\)-C:H overlayer can further improve corrosion resistance and tribological performance. At present, corrosion and wear are two major problems in perpendicular data storage films. Another advantage is that all the processing steps can be conducted in a single system (no transfer of wafer is required). In that case, upon completion of the nanocolumnar Co-\(\alpha\)-C:H film deposition, the magnetron is turned off and deposition of pure \(\alpha\)-C:H takes place to produce the thin overlayer. This design concept is shown in Figure 5.27. Furthermore, annealing can be used to control magnetic properties through microstructural control of the magnetic Co phase (soft \(\varepsilon\) or hard hcp).

In the future, co-deposition of Pt and Co can be attempted to develop the hcp Co$_3$Pt phase. The latter is a magnetically hard phase with great interest for perpendicular data storage.
Figure 5.27 Schematic representation of Co-$a$-C:H film overlayer design.

5.6 Mechanism of Co-$a$-C:H Film Formation

The mechanism proposed is a generalization based on limited regulation involving two major processing parameters. The pressure is controlled in the range of 4–15 mTorr. The change of the Ar/CH$_4$ mass flow ratio is realized by fixing the flow rate of Ar at 30 sccm and changing the CH$_4$ flow rate in the range of 2–8 sccm. One of the films was deposited with the flow rate of Ar at 58 and CH$_4$ at 7 sccm. Other parameters are constant (bias voltage of -500V and magnetron current of 120 mA). It is worth noting that the effect of bias voltage on the structures has also been carried out. The change of bias voltage in the range from -50V to -500V did not affect the film microstructure noticeably. Thus, pressure and gas flow ratio are considered as the major two processing parameters.

Within the above conditions, deposition of embedded Co nanoparticles or nano columns in $a$-C:H matrix is a competitive growth mode, where simultaneous depositions of $a$-C:H and Co occur and growth of embedded Co is significantly influenced by the coincidental growth of $a$-C:H. Therefore, the size and shape distribution of the embedded Co nano particles or nano columns can be adjusted by altering sputtering parameters.
At low pressure, a high voltage between the cathode and the anode in magnetron triggers the magnetron plasma formation of ionized Ar and CH$_4$. The plasma is sustained by the ionization caused by secondary electrons emitted from the Co cathode due to ion bombardment of Ar and CH$_4$ ions. The emitted secondary electrons are confined in the closed $\vec{E} \times \vec{B}$ drift loop. Therefore, the plasma density is much higher. The higher plasma density and its proximity cause a high discharge current, which sputter the Co cathode at a high rate. Co atoms and ions are ejected. Co atoms are ionized in the magnetron plasma. The negative bias voltage on the substrate attracts Co ions to the Si substrate, especially the Co$^{2+}$. DC plasma near the substrate also forms under the high bias voltage between the substrate (cathode) and the chamber wall (anode). Due to energetic collisions, under the magnetron plasma and the DC plasma, the CH$_4$ molecules change to CH$_3$, CH$_5^+$, C$_2$H$_5^+$, CH$_3^+$, CH$_3^+$ and CH$_4^+$. The Co ions pass through and thus enhance the DC plasma, which improves the ionization of CH$_4$. Due to higher mobility of Co ions and low pressure, it is expected that a layer of Co-rich islands forms first. After an incubation period, ionized CH$_4$ molecules mentioned above are subsequently trapped by the negative substrate over and between the Co islands. From that point on, based on the relative arrival rate of Co and hydrocarbon ions, columnar, elongated or spherical Co particles embedded in a-C:H matrix nucleate and grow up continuously. The collision among Ar ions, Co ions and hydrocarbon ions is expected to catalyze the formation of a-C:H or polymer molecules. In principle, a-C:H and plasma polymer can be deposited in the same way. However, the energy density for the a-C:H deposition is much higher. If there is significant arrival rate of Co ions, under the local magnetic field of the Co islands (nuclei) nano columns will grow. If the arrival rate of the Co ions is lower, continuous
growing of nanocolumns cannot be sustained and the continuity break resulting in elongated or spherical nano grain formation.

During the nucleation stage, the impinging Co⁺ Co²⁺ ions with some hydrocarbon ions are thermally accommodated on the cold substrate, Figure 5.28.¹⁴⁶ Co adatoms diffuse on the surface to interact with other Co adatoms or re-evaporate. Co atoms coalesce to small stable clusters which nucleate directly on the substrate surface and grow in three dimensions to form islands. Covalently bonded hydrocarbon ions are deposited in the form of \( a-C:H \) due to its low packing density and strong bonding directionality. \( a-C:H \) fill the space between the Co islands. The Co atoms and \( a-C:H \) in the interface are attracted with each other by van der Waals forces to form an organocobalt compound or “localized” cobalt carbides.

Certain rules have been suggested for the nucleation and microcrystallite growth during metal atom deposition. Layer growth is favored if \( \nabla_0 \leq 3(E_{ds} - E_{df}) \); and island growth is favored if \( \nabla_0 \geq 3E_{ds} \). [\( \nabla_0 \) is the metal sublimation energy; \( E_{ds} \) is the energy of atomic desorption from the substrate; and \( E_{df} \) is the energy of diffusion on the substrate.]

Figure 5.28 Schematic description of 3-D nucleation and growth process.¹⁴⁶
surface. The reduction of surface energy is the driving force to cause the islands to increase in height and become rounded, which is apparent in the present Co-\textit{a-C:H} system. The difference of surface energy between Co and \textit{a-C:H} is significant. Therefore, Co structures tend to be in the form of round particles or covered by \textit{a-C:H} in order to decrease the surface area of Co due to its high surface energy. However, surface energy is not the only factor that affects the structure formation. Otherwise, all the processes should produce the same structure, that is, spherical Co particles embedded in an \textit{a-C:H} matrix. Another factor that should be considered is the magnetic field. Upon nucleation of Co particles the local magnetic field may attract incoming Co atoms and thus the particles continue to grow in size under the influence of the local magnetic field and develop into columns. Thus, the final shape is determined by the combined surface energy and magnetic field forces.

Apparently, the composition of the film is the third factor to affect growth mode since it involves simultaneous depositions of the \textit{a-C:H} and Co. It has been mentioned that \textit{a-C:H} fills the space between the islands. The filling factor is related to the relative deposition rates of the two components (Co and \textit{a-C:H}). The deposition rates for different atoms are controlled by the nature of the components and the deposition parameters (pressure, Ar/CH$_4$ and others). The filling factor is equivalent to the composition of the film to some extent. If the filling factor is below a percolation threshold $f<f_0$, Co islands grow continuously to column structure. If the $f>f_0$, the Co clusters exist separated from each other as particles. This type of filling growth can be attributed to two reasons (i) Co atoms are more strongly bound to each other than to the Si substrate and \textit{a-C:H}; (ii) Co as
a transition metal is a good catalyst for the formation of \( \alpha \)-C:H, that is, Co prefers to bond with Co, and C prefers to bond with C and H.

Regarding Co bonding, it is evident that it is hard to form Co-C bonds and the bonds should be weak. It is known that metal atoms tend to form two types of materials. One is metals and alloys by metallic bond. Second, strongly electropositive metal elements combine with strongly electronegative nonmetal elements to form a compound by ionic bonding. Co is a mild electropositive metal element, and C/H is a mild electronegative nonmetal element (molecule). It is hard for Co and C/H to form ionic bonding. Most of the bonds between Co and C/H should be based on van der Waals forces. Even if there are some strong bonds, the number is insignificant, and they possess the characters of both ionic and covalent bonds. There is very limited information on the compounds \( \text{Co}_2\text{C} \), \( \text{Co}_3\text{C} \), \( \text{Co}(\text{C}_2\text{H}_4)_3 \), that are produced by special methods, although the Co-C bond in Vitamin B\(_{12}\) has been studied widely. The Co-H bond has been reported in organometallic compound (Co hydroperoxide). Therefore, Co bonding with C or H can take place by replacing either one H or C or forming a complex.

In view of the thermodynamics, net deposition requires that the condensate pressure in the gas phase \( P \) is equal to its equilibrium vapor pressure \( P_0 \) over the solid. In fact, the supersaturation \( P/P_0 \) should be larger than one since nuclei have a larger vapor pressure than that of bulk material due to their high surface-to-volume ratio. Homogeneous nucleation lowers the volume free energy while increasing the surface free energy. There is an activation free energy barrier \( \Delta G^* \) to nucleation. Therefore, a large surface-to-volume ratio also requires that clusters must be greater than a certain minimum critical size. From the capillarity theory, the critical size for Co can be inferred\(^{146, 147} \):
\[ r^* = \frac{-2(a_1 \Gamma_{CoV} + a_2 \Gamma_{SiCo} - a_2 \Gamma_{SiV})}{3a_3 \Delta G_v} \] (7)

where \( r^* \) is the critical radius; \( \Gamma_{CoV} \) is the free surface energy related to the condensate Co nucleus in vapor; \( \Gamma_{SiCo} \) is the surface free energy between the Si substrate and the Co nucleus; \( \Gamma_{SiV} \) is the free surface energy of the substrate Si in vapor. Parameters \( a_1 = 2\pi(1-\cos \theta) \); \( a_2 = \pi \sin^2 \theta \); \( a_3 = \pi \frac{(2-3\cos \theta + \cos^3 \theta)}{3} \), are geometric constant as shown in Figure 5.29; and \( \Delta G_v \) is the chemical free energy change per unit volume. The size of \( r^* \) decreases along with the decrease of the growth temperature. Nuclei can grow to islands by direct impinging of vapor phase species and by the capture of Co adatoms diffusing across the substrate surface.

High-resolution cross-sectional TEM observations of Co-\( a \)-C:H thin films showed the presence of a layer of Co islands on the amorphous Si substrate and subsequent nanocolumn (or other nanostructure) formation on the islands. Figure 5.30 is a conceptual illustration of the nanocolumnar Co-\( a \)-C:H growth. On the basis of the TEM observations, Co grows initially in an island mode on the Si substrate. After the initiation, Co nanocolumns embedded in \( a \)-C:H continue to grow under the influence of the

![Figure 5.29 Basic atomic processes on Si surface during Co deposition.](image)
Figure 5.30 Schematic illustration for the growth of columnar Co-\textit{a}-C:H thin film.
localized magnetic field and the energetic considerations discussed earlier (surface energy, etc). When the fraction of $a$-C:H is increased by regulating the processing parameters (pressure and/or Ar/CH$_4$), the columns are interrupted to form elongated nanoparticles, spherical nano particles, wormlike or multilayer nanostructures. Also, due to energetic impingement and the constriction by the $a$-C:H matrix, the Co nanoparticles are not allowed to grow laterally and have a highly defected structure.

A zone diagram for metal films prepared by magnetron sputtering was proposed by Movchan and Demchishin and extended by Thornton,\textsuperscript{146} Figure 5.31. The diagram illustrates the microstructure of single-element films that is worth discussing in view of the present nanocomposite films. Co-$a$-C:H films cannot be described well by the zone models. These models predict the film microstructure based on the $T_s/T_m$ ratio ($T_s=$ substrate temperature; $T_m=$ melting point). The Co melting temperature is $T_{Co}=1495$ °C, and in view of the present deposition temperature ($\sim$60 °C), $T_s/T_{Co}<0.05$. According to this model, all the Co nanostructure in Co-$a$-C:H films in the present study should be tapered crystals with dome tops and void boundaries, as shown in Zone1. However, different structures have been obtained by only changing pressure in the range of 10-20mTorr. In fact, the C/H additions hinder the Co grain growth, and stimulate the formation of columnar or elongated or spherical particle structures. Therefore, we also need to consider another parameter, the Ar/CH$_4$ ratio which affects the composition of the films. The effect of chamber pressure becomes protruding compared to the substrate temperature since it is also a key factor to control the film composition through affecting Co plasma near the magnetron and CH$_4$ glow discharge in the Ar-CH$_4$ atmosphere. We can predict the microstructures obtained by combining the Thornton model with the
At last, based on the XPS results in Table 5.2, an initial attempt has been made to correlate the Co content to the processing parameters:

$$C_{Co} = 96.4 - 5p + 2R$$  \hspace{1cm} (8)

where $p$ is the chamber pressure (in mTorr) and $R$ the Ar/CH$_4$ ratio.

The expression simply states that a higher ratio $R$ and lower pressure favor deposition of Co in the film. Furthermore, the expression shows that pressure has a stronger effect on the Co content than the ratio $R$. Co nanocolumns can be developed for a range of $p$ and $R$ combinations. Finally, this predictive diagram can be utilized to design Co-$a$-C:H microstructures (spherical, nano particles, nanocolumns, etc.) and select the appropriate processing parameters for their fabrication.
Figure 5.32 The effects of Ar/CH₄ and chamber pressure on microstructure of Co-α-C:H films, dark area filled with Co while bright area represents the α-C:H matrix.
CHAPTER 6. CONCLUSIONS

The synthesis-structure-property relationship in multifunctional nanocomposite Co-
a-C:H thin films has been investigated. The as-deposited films consist of defect-rich ε-Co
nanostructures embedded in an amorphous diamond-like a-C:H matrix. The films are
multifunctional since the Co nanostructures provide magnetic properties while a-C:H
matrix provides high wear resistance, low friction, high hardness, corrosion resistance
and protection of Co from oxidation. The following conclusions can be made based on
the results of the present study:

• Pressure and Ar/CH₄ ratio are two major parameters that affect composition,
  microstructure, crystallinity of Co nanostructure, chemical state of C and thus
  properties. The effect of pressure is more sensitive on composition and
  microstructure of the nanocomposite films.

• Various self-assembled Co nanostructures (column, elongated particles
  spherical particles, wormlike and multilayers) in Co-a-C:H films can be
  obtained by appropriately controlling the processing parameters. Surface
  energy, local magnetic field and relative arrival rate of ionized Co atoms and
  hydrocarbon molecules control the nucleation and formation of these
  nanostructures. It is suggested that the surface energy drives the Co grains to
  be spherical while the local magnetic field attracts Co atoms resulting in
  column formation. Ion arrival rate affects the competitive deposition of a-C:H
  and Co.

• The Co-a-C:H films were found to possess good tribological, mechanical and
  electrochemical properties. These properties can be further improved by
increasing the $a$-C:H content (decreasing Co content) or depositing a pure $a$-C:H overlayer.

- The thermal treatment of Co-$a$-C:H films causes partial formation of $\delta'$–Co$_2$C at 300°C, the phase change from $\varepsilon$-Co to hcp-Co at 343°C, the decomposition of $\delta'$–Co$_2$C at about 407°C, the phase change from hcp-Co to fcc-Co at 459°C and the graphitization of $a$-C:H mingling in the reactions in the range of 350-500°C.

- The films were found to be ferromagnetic and change to superparamagnetic as the size of the Co nanostructures is decreasing. The as-deposited films with $\varepsilon$-Co nanocolumns were superparamagnetic above 120K but thermal treatment can change the structure to hcp and produce magnetically hard columns.

- Thus, Co-$a$-C:H nanocomposite films can be designed and synthesized through appropriate control of processing parameters and thermal treatment to possess desirable tribological, mechanical, electrochemical and magnetic properties. Due to their versatility, these films can find a broad spectrum of potential applications ranging from MEMS, and NEMS to electronics and perpendicular data storage.
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VITA

Fengli Wang was born in a small northeastern town of China in 1968. Before she entered the university in 1986, she did not leave the town. In July 1990, she received her bachelor degree of petrochemical engineering from Daqing Petroleum Institute. Fengli worked as an assistant engineer in Harbin Petrochemical Factory during 1990-1994. Then she was enrolled as a graduate in Harbin Institute of Technology with the first rank in the entrance exam in September 1994. Two years later, she acquired a master’s degree in applied chemistry (applied electrochemistry). The University of Science and Technology, Beijing, offered her a position just before she got her master’s degree. She mainly did research as an assistant professor in department of Surface Science and Corrosion Engineering. In the meanwhile, she was awarded ‘excellent instructor’. On July 6, 2000, she arrived at Baton Rouge to pursue a doctoral degree with a four-month son left in China. She anticipates receiving the degree in Engineering Science from Louisiana State University and Agriculture and Mechanical College in 2004. She hopes to be a good mother and wife thereafter.