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Thermomechanical, Electromagnetic and Material Issues in Heat-assisted Magnetic Recording Technology

By

Shengxi Wang

A dissertation submitted in partial satisfaction of the requirement for the degree of Doctor of Philosophy

in

Engineering – Mechanical Engineering

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Kyriakos Komvopoulos, Chair Professor Eli Yablonovitch Professor Grace Gu

Fall 2020

Thermomechanical, Electromagnetic and Material Issues in Heat-assisted Magnetic Recording Technology

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Abstract

Thermomechanical, Electromagnetic and Material Issues in Heat-assisted Magnetic Recording Technology

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Doctor of Philosophy in Engineering-Mechanical Engineering

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Professor Kyriakos Komvopoulos, Chair

Amorphous carbon (a-C) possessing exceptional physical, chemical and mechanical properties is one of the most important building blocks for numerous technical applications. Specifically, a-C films have widespread applications as protective coatings in mechanical parts, biomedical instruments, microelectromechanical devices and magnetic recording, because of their high hardness and excellent chemical inertness. At present, the urgent demands for higher data areal density in magnetic recording industry have generated high interest in acquiring fundamental understanding of the structure and properties of a-C ultrathin films.

The most promising magnetic recording technique to achieve higher data areal density is heat-assisted magnetic recording (HAMR). HAMR solves a critical problem in high data areal density or high data stability associated with the superparamagnetic limit. In HAMR, an integrated optical system is used to focus a laser beam to a sub-diffraction-limit spot in order to locally heat the magnetic media above its Curie temperature, thus enabling data writing in the fine-grained, high-magnetic-anisotropy magnetic media and allowing both high data areal density and data stability. The incorporation of laser heating in magnetic recording creates a major challenge, i.e., the durability and stability of ultrathin *a*-C films (a few nanometers thick) under high temperature. Thus, the principal objective of this dissertation was to address the thermomechanical, electromagnetic, and material issues relevant to *a*-C films used in HAMR technology.

Device-level simulations using the finite element method (FEM) were performed to elucidate the heat transfer process in HAMR. The thermal protrusion and the surface temperature distribution in a typical HAMR head were examined under various heat sources and read/write conditions to understand the near-field heat transfer at the head/disk interface. The effects of material optical properties of various stack layers on the thermo-plasmonic performance of a HAMR head/disk stack were also investigated. The device-level simulations provide insight into the unique heat transfer process in HAMR and an effective means of tuning the optical properties of stacking layers in HAMR devices to optimize their energy transmission performance.

After obtaining the representative temperature distribution in a HAMR device via the device-level simulations, the thermal stability and diffusion characteristics of *a*-C films were studied experimentally. The growth and thermal stability of ultrathin *a*-C films synthesized by filtered cathodic vacuum arc on a crystalline Si substrate with and without a SiN_x over layer formed by nitrogenation of the Si substrate in a radio-frequency sputtering system were investigated. The samples were thermally annealed for various durations and, subsequently, characterized by high-resolution transmission electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS). The HRTEM images revealed the continuity and uniformity of the *a*-C films and the morphology of the SiN_x layer. The EELS analysis of cross-sectional samples confirmed the thermal stability of the *a*-C films and the efficacy of the SiN_x layer to prevent carbon migration from the *a*-C film into the Si substrate.

Despite several experimental studies dealing with the thermal stability of *a*-C films, basic understanding of the structure evolution of ultrathin *a*-C films during film growth and heating is highly empirical, presumably due to the lack of high-resolution instruments that can probe structural changes at the atomic level and in real time. Thus, molecular dynamics (MD) simulations were performed to provide insight into changes in the structure of ultrathin *a*-C films during deposition and annealing. Simulation results revealed a multi-layer film structure, even for *a*-C films as thin as ~20 Å, the existence of a deposition energy that yielded *a*-C films with the highest *sp*³ content, the transient and steady-state stages of the structure evolution during annealing at different temperatures, and insight into the changes in the hybridization state encountered during annealing.

The correlation between internal stress, film structure, and temperature in ultrathin a-C films was also analyzed by MD. The physical mechanisms of a-C film growth and stress built-up under energetic particle bombardment and stress relief due to thermal annealing were examined. Simulations of film growth revealed a correlation between internal stress and energy of incident carbon atoms. A significant stress relief was observed mainly in the bulk layer of the multilayered a-C film structure at a critical annealing temperature, which intensified with the further increase of the temperature.

Besides a high temperature, *a*-C films may experience oxidation and sliding contact during operation. MD simulations of oxidation and sliding of *a*-C films were performed to elucidate the oxidation and tribo-oxidation processes of the films in the presence of oxygen. The simulations demonstrated oxygen kinetic energy thresholds for continuous carbon loss and saturation of oxygen surface adsorption, a surface dominated oxidation process, significant interfacial adhesion of the active film surface and significant changes of the tribological behavior and film structure during sliding. Tribo-induced *a*-C film oxidation was observed in sliding simulations with surface oxygen adsorption.

Graphene is another carbon form that shows outstanding mechanical properties and a high potential as a protective and lubricious coating in various industrial applications. In this dissertation, the synthesis of graphene on *a*-C films was explored and a facile single-step method for fabricating thin *a*-C layers containing graphitic structures was developed. By annealing thin-film stacks of Si/NiFe/*a*-C, a thin layer with a hybrid *a*-C-planar graphene (PG)-orbicular graphitic carbon (OGC) structure was produced. Raman spectroscopy and cross-sectional TEM confirmed the transformation from amorphous to

graphitic structure in the *a*-C film during thermal annealing. The obtained results indicated that the development of this hybrid *a*-C-PG-OGC microstructure is due to a metal-catalyzed PG nucleation mechanism and a mismatch-induced OGC growth mechanism.

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Chapter 1. Introduction

1.1 Amorphous carbon overcoats

Carbon is one of the most remarkable elements on Earth. It exists in more than 90% of all known substances and is the fundamental composition in the vast field of organic matter. Carbon has many allotropes, including diamond, graphite, carbon nanotube, buckyball, graphene, glassy carbon and carbon fibers. Its versatile nature has made carbon one of the most important building blocks for a wide range of technology applications.

During the last three decades, the exceptional properties of carbon-based materials have attracted significant interest from both science and engineering communities [1-5]. Among these materials, amorphous carbon (*a*-C) film is an important class of overcoat materials because of the attractive properties, such as high hardness, good optical transparency in the visible and near-infrared wavelength range, thermal stability, chemical inertness, and biocompatibility [6-10]. In principle, carbon atoms can form three different bonding configurations, i.e., sp^3 , sp^2 , and sp^1 atomic carbon hybridizations, and most *a*-C films contain graphite-like (sp^2) and diamond-like (sp^3) carbon structures. Various studies have shown that the desirable properties of *a*-C, such as high hardness, low friction, and good thermal stability, are mainly determined by the fraction of sp^3 bonding [11]. The *a*-C films with significant fractions of sp^3 bonding demonstrate superior mechanical and tribological properties and, therefore, are widely used as protective overcoats and solid lubricant layers in those industries demanding excellent tribomechanical properties.

Advances in thin-film deposition technologies have been critical to the integration of thin films in various technology sectors where maintaining the surface integrity is of critical importance to device functionality and reliability. Specifically, the growth of *a*-C films can be accomplished by a wide range of deposition methods, such as ion beam deposition [12], pulsed laser beam deposition [13,14], chemical vapor deposition [15,16], sputtering [17-21], and cathodic arc deposition [22-25]. The common feature of these methods is that film growth occurs by energetic carbon particle bombardment, which is conducive to the *sp*³ hybridization. Among the aforementioned techniques, sputtering is the most common deposition because of its versatility. The deposition conditions can be easily controlled by the plasma power and gas pressure. Moreover, many variants of sputtering, such as radiofrequency (RF) sputtering [26], magnetron sputtering [27], reactive sputtering [28], and ion-assisted sputtering [29], have been developed to enable the growth of *a*-C films with improved properties and desired functionalities.

Filtered cathodic vacuum arc (FCVA) is a plasma-based deposition technique that is also widely used in thin film applications. In FCVA, an arc is instigated by striking the graphite target (cathode) with a striker electrode in high vacuum. The arc produces a cathode spot of very high current density causing the explosion of ions, electrons, and particles. The produced plum is filtered by a toroidal magnetic filter duct to remove the

particles and increase carbon ionization to nearly 100%. Thus, only carbon ions arrive at the substrate surface to be coated. The advantages of FCVA include high fraction of carbon ionization, fairly narrow ion energy distribution, high film growth rate, and low cost. FCVA is the only demonstrated low-temperature deposition method for synthesizing ultrathin *a*-C films with high sp^3 contents, good mechanical properties, and high wear resistance [30,31].

The structure of *a*-C films depends strongly on deposition conditions, such as vacuum level, deposition time, substrate temperature, carbon ion energy, and substrate bias voltage. Thus, tuning the structure and properties of *a*-C films by adjusting the deposition conditions enables the deposition of high sp^3 *a*-C films exhibiting high hardness and excellent wear resistance. The incidence carbon ion energy can be easily varied by applying DC or RF self-bias to the substrate, thus providing an effective way to control the sp^3 content of *a*-C films. An optimal deposition process of *a*-C films should possess several key conditions: a carbon ion energy of about 80-100 eV, a narrow ion energy distribution, and predominantly ion species [32,33]. FCVA is much more effective in growing continuous, smooth, and ultrathin (e.g., <5 nm) *a*-C films than sputtering because the film precursors are energetic carbon ions rather than carbon atoms and/or carbon clusters.

1.2 Magnetic recording and amorphous carbon overcoats

Ultrathin *a*-C films are of importance for current magnetic recording devices to maintain the device reliability. In a typical magnetic recording device, namely hard-disk drive (HDD), a read/write head is used to read data stored in a ferromagnetic medium located on a hard disk platter with the read element and to write data to the medium by applying a magnetic field with the write element, as shown in Fig. 1.1. During the operation of HDD, the head flies only 2-5 nm above the disk surface at a linear speed of 10-20 m/s relative to the rotating disk. These extremely small flying height and high linear speed are needed to achieve high data areal density and read/write speed. However, intermittent head-disk interaction becomes inevitable under the operation conditions of the HDD. The head-disk interaction can damage the device, significantly undermining the durability and functionality of the device and leading to catastrophic device failure and data loss. In response to this issue, ultrathin *a*-C films with high hardness are deposited onto the head and disk surfaces to mitigate damage from head-disk asperity contact interactions and corrosion.

1.3 Heat-assisted magnetic recording

The overall data storage demand has grown rapidly over the past several decades. Especially in the recent decade, the digitalization of the world and the proliferation of smart platforms have created unprecedented amount of data. The global data sphere will grow from 33 Zettabytes (ZB) in 2018 to 175 ZB by 2025 (1 ZB = 10^9 TB; the maximum single device capacity of conventional HDD in 2020 is ~18 TB). To keep up with the storage demands stemming from this tremendous rate of generated data, over 22 ZB of storage capacity must ship across all media types from 2018 to 2025, with nearly 59% of that capacity supplied from the HDD industry, although solid-state drives (SSD) are

gaining significant market share [34]. To satisfy this data storage demand, the areal density of HDDs has been doubled roughly every two years. This profound increase in areal density has been achieved by shrinking the area of bits in the magnetic media and reducing the physical spacing between the read/write element of the head and the magnetic medium of the disk. Major advances have contributed to the shrinking of the area of bits, including perpendicular magnetic recording (PMR) [35], tunneling magnetoresistance (TMR) [36], bit-patterned magnetic recording (BPMR) [37], 3D magnetic recording [38,39], heat-assisted magnetic recording (HAMR) [40], and microwave-assisted magnetic recording (MAMR) [41]. Reducing the physical spacing is achieved by decreasing the flying height of the head and the *a*-C film thickness to enhance the areal density.

When the areal density reaches about 1 Tbit/in², problems associated with low signal-tonoise ratio (SNR), data stability, and writability tradeoff due to the superparamagnetic limit are encountered, which limit the ability to continue to scale traditional magnetic recording technology to higher storage densities. When the size of the magnetic domains (bits) is reduced below a few nanometers, magnetization becomes unstable and the bits can randomly flip direction under thermal fluctuation, resulting in data loss. To circumvent this problem, a high-magnetic-anisotropy medium with small grains is used to preserve data stability and the desired SNR. However, the use of a high-magneticanisotropy medium inhibits data writing due to the high coercivity of the magnetic medium and the magnetic flux saturation of the write element. Novel magnetic recording techniques are needed to overcome this limit and increase the areal density beyond 1 Tbit/in².

Among the magnetic recording techniques mentioned above, the HAMR is the most promising technique that can lead to a projected areal density of the order 10 Tbit/in² and has been developed over the past decade. In HAMR, the magnetic medium is heated for a short duration by a laser beam focused by an integrated waveguide/near-field transducer (NFT) optical system that is embedded in the read/write head to increase the temperature of a bit-region beyond the Curie temperature of the magnetic medium. At that juncture, the coercivity of the heated region experiences a sudden and non-linear decrease, thereby allowing data writing by the relatively weak magnetic field of the write pole on the head. However, the introduction of laser heating in HAMR brought new challenges. To locally heat a one-bit region, the NFT must focus the laser to a size smaller than the diffraction limit. This implies a power density of ~10¹¹ W/m² at the magnetic medium surface, resulting in excessive heating. High temperature in HAMR devices due to direct laser heating and heat transfer has raised concerns about the reliability and durability of HAMR devices.

Both the high temperature and the decrease of *a*-C overcoat thickness bring up great challenges in the pursuit of HAMR technology. First, a HAMR device must exhibit good optical and thermal performance, i.e., the NFT must enable heating of the magnetic medium beyond the Curie temperature, and the laser energy transmission efficiency must be high enough to reduce laser energy dissipation. Second, the thermal stability of the ultrathin *a*-C overcoat at this high temperature is critical to the durability of the HAMR device. This is even more significant for the read/write head than for the disk platter. Compared to transient heating in the fast rotating disk platter, heating of the read/write

head is more formidable due to constant heating by the NFT. Under the high temperature, the *a*-C overcoat may undergo graphitization, oxidation, carbon loss, and other structure/morphology evolutions, all of which impair the mechanical and tribological properties of the overcoat and weaken the protection capability. Moreover, due to the complexity of the HAMR device, the foregoing challenges are intertwined. A HAMR design with high energy transmission efficiency and less undesirable heat dissipation is beneficial to maintain the protection capability of the *a*-C overcoat. Consequently, a thermally stable *a*-C overcoat is essential for maintaining the functionality of the device under high temperature.

The required laser spot size for an areal density of 1 Tbit/in² is about 25 nm, which is much smaller than the diffraction limit and cannot be realized by traditional highnumerical-aperture lenses due to the lack of high refractive index materials. Therefore, the greatest difficulty in designing a HAMR device is the design of the waveguide/NFT optical system. The purpose of using the NFT is to create surface plasmons that can achieve a laser spot size less than the diffraction limit. Plasmons are quanta of surfacecharge-density oscillations [42]. Plasmon excitation by the electric field of an electromagnetic (EM) wave does not occur in the bulk of metals because the dimensions exceed the metal skin depth. However, specific plasmon modes can be excited by the electric field of external EM waves generated at the interfaces of different materials, a phenomenon known as surface plasmons [43]. If the dimensions of the NFT are designed to generate plasma resonance excited by the external far-field EM wave delivered by the dielectric waveguide, the efficiency of the NFT will be significantly improved. For a metallic NFT whose size is comparable to the laser wavelength, the electric field of the laser generates surface plasmons that are confined within the surface nanostructure of the metal, which are referred as localized surface plasmons. The localized surface plasmons can couple with the magnetic medium in the disk that is only several nanometers away from the NFT tip, resulting in energy transmission through the air gap between the head and the disk and, ultimately, heating of the magnetic medium. Following this principle, HDD industry has proposed several types of optical system designs in their technique demonstrations, including dielectric waveguide with rectangular cross-section/plasmonic E-antenna [44], rectangular dielectric waveguide/plasmonic nanobeak antenna [45], and planar solid immersion mirror (parabolically shaped waveguide)/ "lollipop" transducer [46], as shown in Fig. 1.2. The common feature of these designs is the use of dielectric waveguides and plasmonic NFTs made of gold.

1.4 Motivation and thesis organization

Since the optical system is the most crucial component in HAMR disk drives, a basic understanding of the energy transmission process is of paramount importance. The laser energy dissipation determines the temperature distribution and the thermal deformation of the HAMR device, influencing its reliability and functionality. The nanometer scale air gap in HAMR drives produces a unique heat transfer process across the head-disk interface (HDI), namely near-field heat transfer, where classical heat conduction or radiation theory breaks down due to nonlinear energy coupling [47]. A simulation of the heat transfer process in HDI using the finite element method (FEM) is presented in Section 3.1 and the temperature distribution and the thermal protrusion in the head are

analyzed. An FEM model of a HAMR stack used to investigate the laser energy transmission process is introduced in Section 3.2 and the electrical field distribution and temperature distribution at different positions of the stack are obtained. Furthermore, the effects of selecting materials with different optical properties on the thermal/optical performance of the stack are studied using the developed FEM model. The simulations provide insight into the heat transfer process at the head-disk interface of HAMR drives and a general framework for investigating the performance of a HAMR device.

In addition to the device-level thermomechanical and EM issues in HAMR technology, material issues relating to the structure, stability, and tribology of ultrathin *a*-C films are also addressed. Structure changes and interfacial diffusion in ultrathin *a*-C films are significant at a high temperature. The most representative structure change of *a*-C films exposed to a high temperature is a phase transformation characterized by sp^3-sp^2 rehybridization that degrades the film hardness and wear resistance. Under a high temperature, carbon diffusion to the neighboring materials, such as the gold NFT, may alter the thermal/optical properties of the neighboring materials and compromise the functionality of the HAMR device. An experimental investigation of structure changes and diffusion behavior of ultrathin *a*-C films synthesized by FCVA under high temperature is presented in Chapter 4.

It is well established that a-C films grown by deposition methods wherein the film precursors are energetic particles, like FCVA, exhibit a multi-layer structure consisting of three main layers, namely intermixing, bulk, and surface layer [48], of which the intermediate sp^3 -rich bulk layer is principally responsible for the excellent mechanical properties and thermal stability demonstrated by *a*-C films synthesized by FCVA [4]. The multi-layer amorphous structure of nanometer-thick films makes the characterization challenging. Lacking crystallinity impairs the efficiency of diffraction-based techniques like X-ray diffraction. Extremely high spatial resolution (ideally, sub-nanometer) is needed to probe the through-thickness multi-layer structure of an ultrathin a-C film. This resolution requirement rules out X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy, which only yield the overall film composition. As shown in Chapter 4, high resolution transmission electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS) were used to map the through-thickness morphology and structure of ultrathin a-C films with a spatial resolution of ~0.2 nm. The EELS analysis of crosssectional samples was found to be an effective means for evaluating the thermal stability of the *a*-C films and the efficacy of a diffusion barrier after prolonged heating.

Despite the experimental studies mentioned above and the voluminous literature dealing with structure changes in thin *a*-C films, basic understanding of the structure evolution during film growth and under a high temperature is still limited and quite empirical, presumably due to the lack of time sensitive characterization techniques that can directly observe structure changes at the atomic scale in real time. Molecular dynamics (MD) is a powerful computational method for studying material structure and interactions at atomic and femtosecond scales. Thus, MD simulations of the deposition and thermal annealing process of ultrathin *a*-C films are performed in Chapter 4. The simulation results reveal a multi-layer film structure, even for *a*-C films as thin as ~20 Å, the existence of an optimal deposition energy that yields *a*-C films with the highest sp^3 content, the transient and steady-state stages of the structure evolution and internal stress relief during annealing at

different temperatures, and the changes in the hybridization state (mainly in the bulk layer) encountered during annealing. The simulations of film deposition process also illuminate the correlation between internal stress and deposition energy.

The operation environment of ultrathin *a*-C films involves not only high temperature but also oxidation and mechanical contact. In Chapter 5, MD simulations of ultrathin *a*-C films with different sp^3 contents subjected to energetic oxygen atom bombardment or undergoing normal and sliding contact against each other in vacuum and oxygen atmosphere are discussed. The hyperthermal oxidation of the *a*-C films, the dependence of contact deformation and surface attractive forces (adhesion) on surface interference, and the evolution of friction and structural changes (rehybridization) of the *a*-C films during sliding are interpreted in the context of MD simulation results.

Carbon-based overcoats beyond *a*-C films are explored from a new perspective in Chapter 6. Graphene, as an allotrope of carbon, is one of the strongest materials in nature. The exceptional tribological properties, low oxygen/water permeability, and high optical transmission of graphene make it a potential candidate for transparent protective overcoats operated in environments involving sliding contact and oxidation. A facile single-step synthesis method for fabricating thin *a*-C films with incorporated graphene of different morphologies by thermal annealing in inert atmosphere using an *a*-C film as a precursor is presented in Chapter 6. The growth mechanisms of graphene exhibiting different morphologies are analyzed using multiple characterization methods. The obtained results reveal that the development of this composite microstructure is due to a metal-catalyzed nucleation mechanism and a mismatch-induced growth mechanism. The present method paves the way toward the fabrication of complex micro-assemblies where high strength and good thermoelectric properties are of paramount importance.

The main findings of this thesis are summarized and an outlook of the research in this field are discussed in Chapter 7.

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Read/write head & recording layer



Figure 1.1 A picture of a HDD and cross-sectional schematics of head/disk stack.



Figure 1.2 Different HAMR designs. (a) Schematic showing the head concept, including light delivery, waveguide, plasmonic antenna, magnetic writer, TMR reader, and disk motion direction. (b) Schematic of integrated head. Cross section of the head, including near-field optical transducer, waveguide, and magnetic pole (left) and perspective view of near-field optical transducer and magnetic pole (right). (c) Schematic of the integrated recording head incorporating the HAMR optics: a grating coupler, a PSIM waveguide and a lollipop NFT, as well as the magnetic components including the recording pole and TMR reader.

Chapter 2. Methods and procedures

This chapter introduces the computational and experimental methods used in this dissertation. In the computational studies, finite element analysis (FEA) and molecular dynamics (MD) modelling were used to study energy transmission process in HAMR and ultrathin *a*-C films, respectively. In the experimental investigation, filtered cathodic vacuum arc (FCVA) and radiofrequency (RF) sputtering were used for film deposition. Microanalysis techniques, including HRTEM/EELS, scanning electron microscopy (SEM), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS), were used to characterize the structure, composition, and stability of the synthesized films.

2.1 Finite element analysis

2.1.1 Near field heat transfer simulation

Several physical processes occur simultaneously during the operation of a HAMR head. First, self-heating of the NFT due to laser energy dissipation creates a heat source in the head. Second, the high-frequency current applied to the write coil (shown in Fig. 1.1) produces resistive heating and eddy current heating. Third, a resistive heater in the head is used to actively control the distance between the read element and the disk and to maintain their proximity. All of these three heat sources contribute to the temperature rise in the head. Heat transfer in the head includes heat conduction within the head, heat convection at the surface of the slider, and near-field heat transfer at the air bearing surface (ABS). Besides temperature rise and heat transfer, there is also thermal deformation in the head due to thermal expansion. Thus, the combined thermomechanical (heat transfer and thermal deformation) and EM (eddy current heating) process must be simultaneously dealt with.

The thermomechanical process follows governing equations of heat transfer and linear elastic deformation:

$$\rho c \frac{\partial T}{\partial t} + \nabla \cdot \boldsymbol{q} = Q \tag{2.1}$$

$$\nabla \cdot \boldsymbol{\sigma} + \mathbf{f} = \rho \frac{\partial^2 \boldsymbol{u}}{\partial t^2}$$
(2.2)

where ρ and c are the mass density and specific heat, respectively, T is the temperature, q is the heat flux ($q = -k\nabla T$, where k is the thermal conductivity), Q is the energy per volume contributed by all heat sources, σ is the Cauchy stress, \mathbf{f} is the body force, and \mathbf{u} is the displacement tensor. For linear elastic deformation, $\sigma = \mathbf{C} : \boldsymbol{\varepsilon}$, where \mathbf{C} and $\boldsymbol{\varepsilon}$ are the stiffness matrix and infinitesimal strain tensor, respectively.

To describe the thermal deformation in the head, the strain can be obtained by the temperature difference between the current temperature and the reference temperature. Eqs. (2.1) and (2.2) are coupled through the relation

$$\varepsilon = \alpha (T - T_{\rm ref}) \tag{2.3}$$

where α is the thermal expansion coefficient and T_{ref} is the reference temperature, set equal to 293.15 K (20 °C) in the present analysis.

The resistive heating and eddy current heating in the write coil should be obtained from the EM analysis. A constant-frequency write current yields a time-harmonic physical process that obeys Maxwell's equations, given by

$$\nabla \times \boldsymbol{H} = \boldsymbol{J} + j\omega\varepsilon_0\varepsilon_r\boldsymbol{E} \tag{2.4}$$

$$\nabla \times \boldsymbol{E} = -j\omega\mu_0\mu_r\boldsymbol{H} \tag{2.5}$$

$$\nabla \cdot \boldsymbol{E} = \rho_{\nu} / \varepsilon_0 \varepsilon_r \tag{2.6}$$

$$\nabla \cdot \boldsymbol{H} = 0 \tag{2.7}$$

where **H** is the magnetic field intensity, **J** is the current density, ω is the angular frequency of the write current, ε_0 and ε_r are the permittivity in vacuum and the relative permittivity of the material, respectively, **E** is the electric field intensity, μ_0 and μ_r are the permeability in vacuum and the relative permeability of the material, respectively, and ρ_v is the charge density. Eqs. (2.4) - (2.7) are solved to obtain the spatial distribution of the eddy current density, which was then used to compute the power dissipated due to eddy current heating using Joule's law.

2.1.2 Thermo-plasmonics simulation

In the laser energy transmission process of HAMR, laser propagation also follows Maxwell's equations written in a different form as following:

$$\nabla \times \boldsymbol{H} = \boldsymbol{J} + \frac{\partial \boldsymbol{D}}{\partial t} \tag{2.8}$$

$$\nabla \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t} \tag{2.9}$$

$$\nabla \cdot \boldsymbol{D} = \rho_{\boldsymbol{v}} \tag{2.10}$$

$$\nabla \cdot \boldsymbol{B} = 0 \tag{2.11}$$

where **H** is the magnetic field strength in vacuum, **J** is the electric current density, **D** is the electric displacement field, **E** is the electric field strength, **B** is the total magnetic field (magnetic induction), and ρ_v is the electric charge density. For optically isotropic materials, $\mathbf{B} = \mu \mathbf{H}$ and $\mathbf{D} = \varepsilon \mathbf{E}$, where μ and ε are the permeability and permittivity of the material, respectively.

The electric field obtained from solving Eqs. (2.4) causes heat generation, which is given by [1]

$$Q = \frac{1}{2} \operatorname{Re}(\sigma) |\boldsymbol{E}|^2 = \frac{1}{2} \varepsilon_0 \omega \operatorname{Im}(\varepsilon_r) |\boldsymbol{E}|^2$$
(2.12)

where Q is the dissipated power density, σ is the conductivity, and ε_0 and ε_r are the vacuum permittivity and relative permittivity, respectively, which are related by [2]

$$\varepsilon_r = 1 + j \frac{\sigma}{\varepsilon_0 \omega} \tag{2.13}$$

where ω is the angular frequency of laser.

The heat transfer in this simulation also obeys Eq. (2.1).

All of the simulations are performed with the Comsol Multiphysics software, a commercial FEA code.

2.2 Molecular dynamics

MD simulation is a technique for computing the equilibrium and transport properties of a classical many-body system. The initial idea is that the atoms in a MD simulation are treated as spherical rigid balls and the motion of atoms obeys Newton's law of motion, where the forces are represented by an empirical interatomic potential energy. Therefore, the most vital task in the development of the MD method is to find the empirical interatomic potential work that is appropriate for the modeled material system. The interatomic potentials used in this dissertation and their evolution are discussed in this section.

2.2.1 Tersoff potential

Significant efforts have been made to develop empirical potentials for a wide range of chemical elements. The first empirical potential that can effectively describe a covalent system was developed for silicon by Tersoff in 1988 [3] and it was soon re-parameterized for a carbon-silicon system in the same year [4]. The advantage of the Tersoff potential is that it replaced the unpractical N-body (N>3) potential by a two-body pair potential whose strength depends on the local environment, i.e., the number of neighboring atoms, which can account for multi-body correlations. The Tersoff potential energy of a system is expressed as

$$E = \sum_{i} E_{i} = \frac{1}{2} \sum_{i \neq j} V_{ij}$$
 (2.14)

$$V_{ij} = f_{C}(r_{ij}) [f_{R}(r_{ij}) + b_{ij} f_{A}(r_{ij})]$$
(2.15)

where E_i is the potential energy of atom *i*, V_{ij} is the bonding energy between atoms *i* and *j*, r_{ij} is the distance between atoms *i* and *j*, f_C is a smooth cutoff function used to generate a gradual energy decrease to zero with increasing atomic distance, f_R and f_A are repulsive and attractive two-body potentials, respectively, and b_{ij} is termed the bond order and represents the bond strength in the local environment, i.e., the bond strength of atoms having more neighboring atoms is characterized by a lower potential energy. The terms in Eq. (2.15) are given by

$$f_R(r) = A \exp(-\lambda_1 r) \tag{2.16}$$

$$f_A(r) = -B \exp(-\lambda_2 r) \tag{2.17}$$

 $f_{C}(r) = \begin{cases} 1, & r < R - D \\ \frac{1}{2} - \frac{1}{2} sin \left[\frac{\frac{\pi}{2}(r - R)}{D} \right], & R - D < r < R + D \\ 0, & r > R + D \end{cases}$ (2.18)

$$b_{ij} = \left[1 + \beta^n \zeta_{ij}^n\right]^{-1/2n}$$
(2.19)

$$\zeta_{ij} = \sum_{k \neq i,j} f_C(r_{ik}) g(\theta_{ijk}) \exp\left[\lambda_3^m (r_{ij} - r_{ik})^m\right]$$
(2.20)

$$g(\theta) = \gamma_{ijk} \left(1 + \frac{c^2}{d^2} - \frac{c^2}{[d^2 + (\cos\theta - \cos\theta_0)^2]} \right)$$
(2.21)

2.2.2 Reactive empirical bond order potential

Although the Tersoff potential is used for the covalent system of carbon and silicon, the significant difference between silicon and carbon is that silicon cannot form multiple bonds due to weak π - π interaction, thus making the Tersoff potential unable to describe π and conjugate bonds. The Tersoff potential only accounts for the nearest neighbor interactions, overestimating the binding energy for intermediate bonding configurations. An improved potential for hydrocarbon was introduced in 1990 by Brenner that overcomes the binding energy problem with then Tersoff potential, wherein a bond order function is used to deal with conjugate bonds or many-body interactions [5]. The bond order function b_{ij} in the Tersoff potential is replaced by \overline{B}_{ij} , given by

$$\bar{B}_{ij} = \frac{B_{ij} + B_{ji}}{2} + F_{ij}(N_i^{(t)}, N_j^{(c)}, N_{ij}^{conj})$$

$$B_{ij} = \left(1 + H_{ij}(N_i^H, N_i^C) + \sum_{k \neq i,j} f_C(r_{ik})g(\theta_{ijk})\exp\left\{\alpha_{ijk}\left[\left(r_{ij} - R_{ij}^e\right) - \left(r_{ik} - R_{ik}^e\right)\right\}\right)^{-\delta_i}$$

$$(2.22)$$

where N_i^H and N_i^C are the number of hydrogen and carbon atoms bonded to atom *i*, respectively, $N_i^{(t)}$ is the total number of neighbors of atom *i*, and N_{ij}^{conj} depends on whether a bond between carbon atoms *i* and *j* is part of a conjugate system. The other parameters are detailed in ref. [5].

The Brenner potential was further modified in 2002 to model the formation and breaking of covalent bonds and the new version is called second generation reactive empirical bond order (REBO) potential [6]. The Brenner potential was also upgraded to the so-

called adaptive intermolecular reactive empirical bond order (AIREBO) in 2000 by Stuart to include van der Waals force and torsional potential from dihedral angles with single bonds [7].

The Tersoff and AIREBO potentials are used in the simulations of deposition, annealing and sliding contact presented in Chapters 4 and 5.

2.2.3 Reactive force field

Classical interatomic potentials are well developed for nonreactive systems; however, they are not capable of modeling chemical reactions where bond formation and breaking occur. The REBO and AIREBO potentials consider non-bonded forces, such as the van der Waals force that is important in many systems involving chemical reactions and can describe certain hydrocarbon chemical reactions [8]; nevertheless, fundamental problems relevant to dissociation and reactive potential curves still exist.

Interatomic potentials including atom connectivity-dependent terms, called reactive force field (ReaxFF) potential, have also been proposed. The ReaxFF potential takes into account electronic interactions that can drive chemical bonding, making it possible to model complex processes involving multi-phase chemical reactions. Nowadays, roughly half of the elements in the periodic table can be described by ReaxFF potentials [9] and the potentials used to model numerous reactions can be categorized in two major groups: oxidation/combustion/explosion and chemical/biological reactions in aqueous solutions [10-14].

The ReaxFF potential also employs a bond-order function and applies bond order correction for local overcoordination. van der Waals and Coulomb forces are included for non-bonding interactions. The energy contributions in the ReaxFF potential are listed as following [9]:

$$E_{system} = E_{bond} + E_{over} + E_{angle} + E_{tors} + E_{vdWaals} + E_{Coulomb} + E_{specific}$$
(2.24)

where E_{bond} describes the energy correlated with bond formation, E_{over} is the overcoordination correction, E_{angle} and E_{tors} are the energies correlated with three-body valence angle strain energy and four-body torsional angle strain energy, and $E_{specific}$ is used in some cases that require specific system properties, such as hydrogen binding and conjugation.

The ReaxFF potential was used in the *a*-C oxidation simulations presented in Chapter 5.

2.3 Film deposition techniques

This dissertation employed physical vapor deposition (PVD) in the experimental studies. PVD is characterized by a process where the source material in condensed phase from a target undergoes vaporization and the vaporized source material returns to the condensed phase in the form of a film at substrate surface. The two film deposition techniques used in this dissertation, RF sputtering and FCVA, are introduced in this section.

2.3.1 Radiofrequency (RF) sputtering

In a typical RF sputtering process in inert atmosphere, Ar plasma is ignited and accelerated towards a negatively biased target. The target material vaporized to atoms or clusters of atoms by the bombarding Ar^+ ions is deposited onto the substrate surface as a film, which can be further densified by the impinging Ar^+ ions when a negative bias voltage is applied to the substrate.

In this dissertation, a variant of RF sputtering, namely reactive RF sputtering, was used to nitrogenate a silicon substrate to obtain a SiN_x diffusion layer between the *a*-C film and silicon substrate. These experiments were carried out with a low-pressure sputtering system (Perkin-Elmer, Randex-2400 model), shown in Fig. 2.1, consisting of three key subsystems: (1) a cylindrical chamber in which three target holders with diameters equal to 20 cm are placed 7 cm above the substrate holder, (2) an RF coupling coil and capacitive tuning network above the chamber cap to excite and maintain the plasma, and (3) a control system underneath the chamber used to adjust the deposition time, RF power, and working pressure. In the nitrogenation process, nitrogen gas rather than Ar gas is introduced into the chamber through a throttle at a controlled flow rate. After the ignition of the plasma, the ionized nitrogen gas penetrates the silicon substrate and chemically reacts with the silicon to form a SiN_x layer.

2.3.2 Filtered cathodic vacuum arc (FCVA)

A schematic of the customized FCVA system used in this dissertation is shown in Fig. 2.2. In FCVA deposition, a target material is vaporized by a high-current/low-voltage electric arc ignited in a vacuum environment between the grounded anode and the cathode target. The arc produces a highly energy emitting area, known as cathode spot, typically with a size of 1-10 μ m and an intense current density of 10⁶ -10⁸ A/cm² [15]. The extremely high current density and the resultant localized high temperature (~ 15.000 K) result in high-velocity ejection of target material in the form of plasma containing neutral particles, multiple charged ions, atom clusters, and macroparticles (droplets). To eliminate the undesired neutral particles and droplets that negatively affect carbon hybridization and are detrimental to the film's continuity and smoothness, the plasma is filtered by an S-shaped magnetic filter duct. The toroidal currents in the guiding solenoids produce a magnetic field intensity of about 0.1 T along the axis of the duct. The magnetic field causes the electrons to follow a spiral trajectory about the filter axis and the electrostatic field generated by this electron motion navigates the positive ions to move along the duct axis. By filtering the undesired microparticles, the ionization of the plasma is increased from 30% to nearly 100%. Finally, only single C⁺ ions leave the filter duct and arrive at the substrate surface where they deposit to form a continuous, smooth, conformal ultrathin film.

Various process parameters have been investigated to tune the structure of FCVAdeposited *a*-C films. The pulsed substrate bias voltage and the C⁺ ion incidence angle have been found to greatly affect the film thickness, morphology, and sp^3 content [16-19]. Using an optimal process window, i.e., 80-100 V pulsed substrate bias, 65% bias duty cycle, and 10-30° incidence angle, results in the growth of ultrathin *a*-C films with up to 87.5% *sp*³ content [17-20]. The cryopump and mechanical pumps shown in Fig. 2.2 are used to maintain the base chamber pressure below 5×10^{-7} Torr. The magnitude, frequency, and duty cycle of the pulsed substrate bias voltage are controlled by a DC voltage source and an electrical chopper (Spark-le V, Advanced Energy Industries). Water cooling is also applied to maintain near room temperature at the target and the substrate.

2.4 Film characterization techniques

2.4.1 High resolution transmission electron microscopy (HRTEM)

HRTEM is a phase contrast imaging technique. Different from conventional TEM that is based on transmitted electrons, HRTEM can render images with resolution of <1 Å by taking advantage of the interference of transmitted electrons and the scattered electrons passing through the specimen. In the experimental studies described in Chapters 3 and 6, an FEI F20 UT Tecnai microscopy was used to obtain high resolution images and electron energy loss spectra (EELS) of the specimen materials. The microscope was operated at 200 kV and was equipped with a spherical and chromatic aberration of 0.5 mm and 1.1 mm, respectively. EELS can provide information about the nanostructure of materials in high spatial and energy resolution. Electron energy loss is mainly due to inelastic interactions between incoming electrons and inner shell electrons of the specimen material. For example, the characteristic peaks of carbon are at 284 eV (π peak) and 290 eV (σ peak) and represent K-shell electron transfer into empty π^* states representing sp^2 bonding and transition into the σ^* states in both sp^2 and sp^3 bonding, respectively. Since the energy resolution of EELS is ~ 0.5 eV, it is sufficient to distinguish sp^2 from sp^3 bonding because their bandgaps differ by 0.8–0.9 eV. This feature allows quantitatively analysis of the fractions of sp^2 and sp^3 bonding using EELS. The sp^3 depth profiles of ultrathin *a*-C films shown in Chapter 3 were calculated from the carbon π and σ peaks.

Cross-sectional TEM specimens were fabricated in order to obtain high-resolution images and EELS depth profiles of the thin-film samples. The preparation of a cross-sectional specimen comprised a series of operations including glue bonding, surface finishing, and ion milling. A thin-film sample was coated with a ~25 nm-thick Cr capping layer by ion beam deposition before glue bonding. Then, a sample stack was prepared by gluing the surfaces of two samples face-to-face with M-bond 610 epoxy, allowing them to cure at ~180 °C for 2 h, and then sectioning it into 1-mm-thick stack slices with a diamond blade. The stack slice was then thinned down in an Allied Multiprep Polishing system by polishing each side of the stack slice using sequentially smaller diamond grits of size equal to 30, 15, 6, 3, 1, and 0.5 µm until the thickness decreased to 100 µm. Then, the stack slice was tilted to introduce a 1° wedge and thinned down to $\sim 20 \,\mu m$ (measured at the thick side of the wedge). When the tip region of the wedge slice became transparent to transmitted light, the wedge slice was attached to a 3-mm-diameter Molybdenum ring using M-bond 610 epoxy to fit the size of the TEM sample holder. A schematic of the sample thinning from a 1-mm-thick stack slice to a ring/wedge combination is shown in Fig. 2.3. Finally, Ar⁺ ion milling using a Gatan PIPS 2 system was performed to further reduce the thickness of the edge and remove the contaminants. This wedge-polishing method creates a stack slice of a trapezoidal shape which contains an electron transparent region at the edge of the wedge. This method is proven to be much less laborious than the flat polishing/dimpling method.

2.4.2 Scanning electron microscopy (SEM)

SEM utilizes a focused electron beam to scan a sample surface and extracts surface morphology images based on the secondary electrons emitted by the sample atoms excited by the electron beam. The number of secondary electrons, i.e., the image signal intensity, depends on the sample surface topography and composition. In Chapter 6, the *a*-C/NiFe/Si stacks were examined with an FEI Quanta 3D FEG SEM before and after annealing to investigate the morphology of the formed graphene, the metal segregation, and the formation mechanism of graphene. Before SEM imaging, the samples were coated with a thin (~10 Å) gold layer to improve surface conductance.

2.4.3 Raman spectroscopy

Raman spectroscopy is a non-destructive chemical analysis technique that provides information about the chemical structure, phase, crystallinity, and molecular interactions. It relies on the inelastic scattering of photons due to the interactions between a laser beam and the vibrations, phonons or other excitations in the system, resulting in laser photon energy shift. The energy shift represents the vibration modes in the tested materials and hence their structures.

A visible Raman spectroscope with a 532-nm laser was used to examine the carbon-based materials in Chapter 6. The common features of carbon in the 800-2000 cm⁻¹ spectrum range are the D peak at ~1360 cm⁻¹ and the G peak at ~1560 cm⁻¹. Both the G and D peaks arise from vibrations of *sp*²-hybridized carbon atoms. The G peak corresponds to optical E_{2g} phonons at the Brillouin zone center, whereas the D peak is caused by A_{1g} breathing-like vibration mode and requires a defect for its activation. Graphene can be distinguished by a fingerprint 2D peak centered at ~2680 cm⁻¹ that is due to the second-order overtone of the D peak. Thus, Raman spectroscopy is an effective method to investigate the transformation from *a*-C to a crystalline graphitic structure.

2.4.4 X-ray photon spectroscopy (XPS)

The XPS is also a non-destructive surface-sensitive characterization technique that is based on the photoelectric effect. In XPS, photoelectrons excited from the specimen surface by X-ray irradiation are emitted to the free space. The composition and bonding structure of the specimen can be determined from the binding energy of the electrons in a particular shell (usually the core shell in XPS) for an atom or ion. The binding energy $E_{binding}$ can be determined using the following photoelectric effect equation

$$E_{binding} = E_{photon} - E_{kinetic} - \phi \tag{2.25}$$

where E_{photon} is the photon energy of the X-ray, $E_{kinetic}$ is the kinetic energy of the emitted photoelectron measured by the instrument, and ϕ is the work function of the instrument, treated as an energy correction term that is rarely adjusted in practice.
In Chapter 6, XPS analysis of the carbon-based material was performed using a PHI 5400 XPS spectrometer that uses a monochromatic Al K α radiation source of energy equal to 1486.6 eV and a work function of 5.7 eV. The C1s core-level spectra in the range of 280-292 eV were acquired to investigate the composition and determine the *sp*³ content. The spectra can be deconvoluted to multiple peaks correlated with certain chemical states with different characteristic biding energies, i.e., *sp*² (284.4 eV), *sp*³ (285.6 eV), C-O (286.6 eV), and O-C=O (288.5 eV) peaks. The atomic percentage can be obtained by calculating the area fraction of the corresponding peak.

2.5 References

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Figure 2.1 Perkin-Elmer Randex-2400 sputtering system: (a) picture of the sputtering system and (b) schematic of the chamber design.



Figure 2.2 Schematics of the FCVA system: (a) front view, (b) top view, and (c) schematic demonstrating the deposition process in the FCVA system.



Figure 2.3 Preparation procedure of the cross-sectional specimen using a wedge polishing method. The electron transparent region is enclosed by a red circle.

Chapter 3. Thermomechanical and electromagnetic analysis of heat-assisted magnetic recording devices

3.1 Analysis of near-field heat transfer in a heat-assisted magnetic recording head

3.1.1 Introduction

Heat-assisted magnetic recording (HAMR) was introduced in response to increasing demands for data storage densities of 1 Tb/in² and beyond. The high areal data density of contemporary hard-disk drives (HDDs) has been largely due to the decrease of the head-disk physical spacing and the development of fine-grained magnetic media [1,2]. However, a further increase in HDD areal density has been halted by fundamental problems, such as the superparamagnetic limit [3]. When the grain volume of a magnetic material becomes sufficiently small, the intrinsic thermal energy of the grain may destabilize the bit [4,5]. HAMR technology aims to circumvent this problem by using laser heating to instantaneously lower the coercivity of high-magnetic-anisotropy media to enable data recording by the electromagnetic transducer embedded in the trailing edge of the slider body.

A typical HAMR device is designed to include several critical components, such as laser diode, waveguide, and near-field transducer (NFT) [6]. The laser diode sends an incident beam to the waveguide, transferring laser energy to the NFT. The role of the NFT is to increase the laser energy density by focusing the incident laser beam to a tiny spot (~50 nm) [7]. During the write process, the head flies over the fast rotating disk at a height of a few nanometers, while the NFT heats the magnetic medium of the hard disk above its Curie temperature, lowering its high coercivity and, in turn, allowing the transducer at the trailing edge of the head to write (store) data in the form of closely packed bits.

Because the head is flying only a few nanometers (typically 4–5 nm) above the hard disk, the near-field heat transfer coefficient can be several orders of magnitude higher than the far-field heat transfer coefficient [8]. As the gap distance across the head-disk-interface (HDI) decreases, the heat transfer mechanism gradually changes from thermal radiation to phonon heat conduction [9]. Thus, a single heat transfer mechanism, such as classical heat conduction or radiation, cannot describe heat transfer across nanoscale gaps. Several models based on fluctuating electrodynamics continuum theory [10], non-equilibrium Green's function [11], extension of Planck's law of thermal radiation [12], and lattice dynamics [9] have been used to study near-field thermal energy transfer.

The elevated operating temperature of several hundred degrees Celsius of a HAMR HDD may significantly affect the device performance, resulting in working instabilities and short lifetime [13-15]. Therefore, knowledge of the temperature distribution and the development of thermal protrusion on a HAMR head are critical to the reliability of these devices. According to fluctuating electrodynamics continuum theory, the apparent heat transfer coefficient at the nanoscale due to near-field radiation heat transfer is inversely proportional to the square of the gap size d [10]. With the decrease of gap size, the

apparent heat transfer coefficient will deviate from this relation due to gradual involvement of phonon tunneling heat transfer [9]. The objective of this study was to perform a near-field heat transfer analysis of a HAMR head with changing gap size and provide insight into the surface temperature distribution and evolution of thermal protrusion on the magnetic head in the light of electromagnetic-thermomechanical simulation results obtained for various heat sources and read/write conditions.

3.1.2 Simulation model

3.1.2.1 Electromagnetic Analysis

An electromagnetic (EM) analysis of a HAMR head was performed with the Comsol Multiphysics (version 5.2) to study heat generation due to a high frequency write current applied during the write process. A high frequency write current produces resistive heating and eddy current heating. In a conductor, eddy current is observed as electrical current loops generated by the changing magnetic field. The eddy current flows through the conductor causing Joule heating. When a high frequency write current is applied to the coil of a HAMR head to generate an alternating write magnetic field, an eddy current is generated in the nearby write pole. The resistive heating in the coil and eddy current heating in the poles act as heat sources that raise the temperature resulting in thermal deformation of the head. The governing equations of this process are Maxwell's equations as listed in Eqs. (2.4)-(2.7).

Eqs. (2.4) - (2.7) were solved to obtain the spatial distribution of the eddy current density, which was then used to compute the power dissipated due to eddy current heating using Joule's law. The EM analysis provided input conditions to the thermomechanical analysis described below. A three-dimensional HAMR head model that includes all key components, i.e., waveguide, antenna-based near-field transducer (NFT), write pole, return pole, write coil, photoresist insulator, heater, upper and lower read-shields, and read pole, was used in the analysis. The role of the heater is to maintain the read pole in proximity with the disk during data reading when there is no write current. All of the aforementioned components were included in the model of the trailing edge of the slider body. To reduce the computational time, only the trailing edge of the head was used in the analysis. Fig 3.1(a) and 3.1(b) show side and front views of the $100 \times 100 \times 25 \ \mu\text{m}^3$ HAMR head model, respectively. For clarity, the end of the trailing edge and the photoresist insulator surrounding the write coil are not shown in Fig 3.1. A write current of 50 mA peak-to-peak magnitude and 2 GHz frequency was applied to the write coil in all simulations. The materials of the HAMR head components, listed in Table 3.1, are typical of those reported in other studies [16-18].

3.1.2.2 Thermomechanical Analysis

Using the EM simulation results as input conditions, a thermomechanical analysis of the HAMR head (Fig. 3.1) was performed to determine the temperature distribution at the head surface and the formation of thermal protrusion. This analysis was based on the governing equations of heat transfer and linear elastic deformation as listed in Eqs. (2.1) - (2.2). As mentioned in section 2.1.1, to describe the thermal deformation, thermal expansion needs to be considered using Eq. (2.3). The heat sources in the HAMR head

include resistive heating in the coil and heater as well as eddy current heating in the write and return poles. The heat power of the coil and the poles was obtained from the EM analysis. The power needed to heat a magnetic recording bit to the Curie temperature is ~0.5 mW [19]. For a well-designed NFT, the power efficiency (defined as the ratio of the power absorbed by the disk to the power incident to the NFT) is ~5% and the absorption rate (defined as the ratio of the power absorbed by the NFT to the power incident to the NFT) is 10% [20]. Thus, the heating power (adsorbed power) of the NFT was set equal to 1 mW.

Thermal boundary conditions were prescribed to all surfaces. Specifically, at the bottom surface of the head, termed the air bearing surface (ABS), the occurrence of near-field heat transfer due to the nanoscale gap makes the heat transfer coefficient a function of the HDI gap. Considering radiation and phonon heat conduction in a nanoscale space, the contributions of associated heat transfer mechanisms can be included in an equivalent heat transfer coefficient that is a function of gap size. The thermal boundary conditions at other surfaces were set as following. The heat transfer coefficient at the top surface of the head was set at 2000 W/(m² K), which is a reasonable value considering the high heat capacity of the metal suspension. Because only heat sources due to the coil, poles, and NFT are considered in the analysis, it is reasonable to presume that the slider body does not experience significant temperature rise because of its much larger size compared to that of the trailing edge. Therefore, the temperature at the surface in contact with the slider body was set at 298 K. The heat transfer at all other non-ABS surfaces was modelled as natural air convection with a heat transfer coefficient (predicted from boundary layer theory) equal to 100 W/(m^2 K) [21,22]. All the degrees of freedom (DOF) of the nodes in contact with the slider body were fully constrained. The finite element model consists of 1,729,196 quadratic (10-node) tetrahedron elements consisting of ~2.3 million nodes (~7.3 million DOFs including temperature and x-, y-, and z-displacements). The smallest elements used to mesh the tip of the write pole and the NFT have a size equal to 18 nm.

Because the heat transfer coefficient at the ABS depends on the gap size, the profile of the thermal protrusion was determined by an iterative procedure. In these simulations, a function of the ABS equivalent heat transfer coefficient versus gap size was obtained by fitting the heat conductance-gap size data reported elsewhere [9]. Each simulation comprised the following sequential steps. First, an initial heat transfer coefficient (corresponding to a gap distance of 5 nm) was assigned to all the ABS nodes and an initial temperature distribution and thermal protrusion profile were obtained. Then, the derived empirical equation of the ABS equivalent heat transfer coefficient was used to compute a new heat transfer coefficient for each ABS node, taking into account the effect of the protrusion profile on the local gap distance. The new surface temperature distribution and thermal protrusion were then calculated using the new heat transfer coefficients. This procedure was repeated until changes in the thermal protrusion profile between successive iterations decreased below 0.1 nm.

3.1.3 Results and discussion

Fig. 3.2(a) shows heat power dissipation results for a 2-GHz write current in the range of 0-200 mA. The red and blue curves represent the power dissipated due to resistive heating of the coil and eddy current heating of the write and return poles, respectively. The black curve represents the total power dissipated due to resistive and eddy current heating. The coil is surrounded by high-resistance polydimethylsiloxane (PDMS) and the write current is confined into the coil. Because the permeability of the pole material is 4-5 orders of magnitude higher than that of all other materials, the eddy current in all other components is negligible compared to that in the poles; thus, power dissipation in all other components can be neglected as secondary. The increase in power due to coil resistive heating from 0 to 100 mW due to the increase of write current from 0 to 200 mA matches the dependence of power due to resistive heating on current squared. The power due to eddy current heating in the write and return poles increases from 0 to 21 mW with the increase of write current from 0 to 200 mA, also showing a square relation of the power with write current. Regardless of the write current, coil resistive heating generates 83% of the dissipated total heat power, whereas eddy current heating in the poles generates another 17%. The fraction of power due to eddy current heating in the poles remains constant with increasing write current. This is because the eddy current is proportional to the strength of the magnetic field and the rate that the magnetic field changes due to the alternating write current. In these simulations, the strength of the magnetic field generated by the alternating write current is proportional to the write current, whereas the rate that the magnetic field changes is constant because the write current frequency is set at 2 GHz. This is why the fraction of power due to eddy current heating remains constant and equal to 17%.

Fig. 3.2(b) shows heat power dissipation results for a 50-mA write current in the frequency range of 0-3 GHz. When the write current frequency increases in the Gigahertz range, the penetration depth of the write current is much smaller than the coil cross-section because of the skin effect. Consequently, the increase in coil resistance generates more heat. This explains the increasing trend of the coil heat power in Fig. 3.2(b). The pole heat power also shows a dependence on the write current frequency; however, it increases faster than the coil heat power. The fraction of the pole heat power increases from 0 to 30% with the increase of write current frequency from 0 to 3 GHz. This indicates a more significant effect of eddy current heating at higher current frequencies. Therefore, as the writing speed increases, it is important to consider the effects of pole heat power and thermal deformation on the HDD design.

Fig. 3.3 shows results of the surface profile and surface temperature distribution along the ABS centerline in the vicinity of the NFT and the write, return, and read poles obtained with and without the previously mentioned iterative procedure. Because this analysis is for the writing process, the heater was deactivated in these simulations. In Fig. 3.3 and subsequent Figs, the left boundary of the return pole (region 3) is labelled as the zero position. The simulation results show the effect of near-field heat transfer on the head surface profile and temperature rise. The largest thermal protrusion and highest temperature occur at the NFT, which has the highest power density among all head components. The maximum protrusion at the NFT predicted with and without the iterative procedure is 3.8 and 4 nm, respectively. While both methods yield similar trends, the iterative method predicts less thermal expansion and slightly lower surface

temperature. This is attributed to the more intense heat transfer conditions (compared to the non-iterative method) arising as the temperature increases and the thermal protrusion develops. The more pronounced heat transfer in the iterative method decreases the temperature at the ABS, resulting in the formation of a smaller thermal protrusion. Eventually, heat generation and heat transfer reach equilibrium and the evolution of the surface temperature and growth of the thermal protrusion stabilizes. Although the maximum temperature difference between the two methods is only 5 K, the 0.2 nm protrusion difference is significant considering the extremely small HDI gap in typical HDD devices (~2 nm) and high magnetic field gradient near the poles (~10 mT/nm [23]).

The NFT is a vital component of a HAMR head. It receives laser energy from the waveguide and transfers a fraction of it to the hard disk to enable data writing by the magnetic field of the write pole. Because of the very low efficiency of the NFT, only 5% of laser energy is transferred to the disk [20]. A large fraction of laser energy is dissipated in the NFT in the form of heat. Thus, the effect of the heat power dissipated by the NFT on the formation of the thermal protrusion and the evolution of surface temperature is of critical importance. Fig. 3.4 shows simulation results of the surface profile and surface temperature distribution along the ABS centerline for an NFT heat power equal to 0.5, 0.75, and 1.0 mW and a write current of 50 mA. The increase of the NFT heat power from 0.5 to 1.0 mW yields an increase in NFT protrusion from 2.9 to 3.8 nm and a peak temperature rise from 373 to 440 K. The temperature rise at other surface regions, especially the read pole, is insignificant. This suggests that the NFT mainly acts as a concentrated heat source. Considering the small size and high power density of the NFT, a small increase in NFT power can dramatically affect the thermal protrusion and temperature at the NFT, consequently, increasing the likelihood of intermittent contact at the HDI.

The effectiveness of the read/write data process strongly depends on achieving the smallest possible gap at the HDI, which is critical to achieving a high signal-to-noise ratio. Write current heating produces a small gap during data writing; however, there is no current in the coil during data reading. The solution is to energize the heater during the read process. It is important that the gap distance is fixed because sudden changes in gap size may cause contact at the HDI or unstable data writing/reading. This problem can be partially overcome by combining electromechanical control and heater activation. Therefore, during the read and write processes the protrusion size must closely follow the fluctuations in gap size. Fig. 3.5 shows the surface profile and temperature distribution along the ABS centerline for both write and read process conditions. In the simulation of the read process, the heater was activated by power of 8 mW. A comparison of the simulation results shown in Fig. 3.5(a) indicates that the heater produces similar local protrusions at the NFT and the write pole during data writing and reading. This is desirable for stabilizing the protrusion during read-write alternations. The ~3 nm protrusion at the read pole provides proximity between the read pole and the disk during data reading. It is also noted that the NFT still has a small local protrusion during reading. This is due to the low power (0.4 mW) applied to the NFT for the purpose of further decreasing the protrusion difference between the read and write process conditions. Fig. 3.5(b) shows that the temperature in the vicinity of the heater does not increase significantly during the read process, apparently due to the large size of the heater. While the NFT acts as a localized heat source, the large heater acts as a global heat source, producing a thermal protrusion and a temperature increase over a larger area of the head. Clearly, the heater position affects the evolution of the thermal protrusion and surface temperature distribution to a large extent. If the distance of the heater from the ABS is increased, the heater will mainly heat the trailing edge of the slider body that has a low thermal conductivity. In this case, the heat will be confined in the vicinity of the heater, producing a smaller but more widely distributed protrusion at the ABS.

3.1.4 Conclusions

A near-field heat transfer analysis of a HAMR head was performed based on a model that includes all key elements. In the EM analysis, the ABS heat transfer coefficient was varied with the local gap distance to account for near-field heat transfer due to near-field radiation and photon conduction. Simulation results showed that most of dissipated heat power is predominantly due to coil resistive heating, while eddy current heating becomes significant at high write current frequencies. The NFT acts as a local heat source, causing significant local changes in both the thermal protrusion profile and the surface temperature distribution. Different from the NFT, the heater acts as a global heat source, with resulting thermal protrusion and elevated temperature affecting a larger area of the head. While the focus in this study was on near-field heat transfer of HAMR heads, the air bearing cooling effect can easily be included in the analysis by simply adding the air bearing heat transfer coefficient to the near-field heat transfer coefficient.

3.1.5 References

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	Material	Mechanical properties		Thermal properties		
Component		Elastic modulus (GPa)	Poisson's ratio	Specific heat (J/kg K)	Thermal conductivity (W/m K)	Thermal expansion coefficient $(\times 10^{-6}/K)$
Trailing edge body	Al_2O_3	200	0.25	760	1.5	7.5
Write/return pole and shields	NiFe	207	0.3	470	35	12.2
Waveguide core layer	Ta ₂ O ₅	136	0.31	260	33	5.7
Waveguide cladding layer	SiO ₂	70	0.17	730	1.4	0.5
NFT	Au	70	0.44	129	317	14.2
Coil	Cu	120	0.34	384	401	16.5
Photoresist	PDMS	0.00075	0.49	1460	0.16	300
Heater	NiCr	165	0.3	450	93.9	2
Read pole	Multilayer*	220	0.29	384	18	13.6

Table 3.1 Material properties used in the HAMR head model.

*Assumed to consist of FeCo.



Figure 3.1 Schematic of HAMR head model: (a) side view and (b) front view.



Figure 3.2 Heat power versus (a) magnitude of a 2-GHz write current and (b) frequency of a 50-mA write current.



Figure 3.3 Comparison of simulation results obtained with and without an iterative procedure: (a) surface profile and (b) surface temperature distribution along the ABS centerline of the HAMR head. The shaded regions 1, 2, 3, and 4 indicate the positions of the NFT and the write, return, and read poles, respectively.



Figure 3.4 Comparison of simulation results for an NFT heat power of 0.5, 0.75, and 1.0 mW: (a) surface profile and (b) surface temperature distribution along the ABS centerline of the HAMR head. The shaded regions 1, 2, 3, and 4 indicate the positions of the NFT and the write, return, and read poles, respectively.



Figure 3.5 Comparison of simulation results for the write and read processes: (a) surface profile and (b) surface temperature distribution along the ABS centerline of the HAMR head. During the read process, the heater was activated by a power of 8 mW. The shaded regions 1, 2, 3, and 4 indicate the positions of the NFT and the write, return, and read poles, respectively.

3.2 Effect of material optical properties on thermo-plasmonics of heat-assisted magnetic recording devices

3.2.1 Introduction

Plasmonics is the field concerned with the collective oscillations of free electrons in a metal excited by the electric component of light. Plasmonic devices can confine electromagnetic oscillations at optical frequencies to volumes significantly smaller in size than the wavelength generated in free space at that frequency. This allows the generation of light from devices much smaller than the wavelength of incident light and the evolution of extremely intense, concentrated electromagnetic fields at optical frequencies. The high confinement and intensity of light beyond normal optical limits, such as the diffraction limit, has been exploited in many application areas, including lithography, near-field optical microscopy, single-molecule spectroscopy (e.g., surface-enhanced Raman spectroscopy), plasmon-enhanced fluorescence, bio-imaging, and more recently, heat-assisted magnetic recording (HAMR). The data storage density in current magnetic recording technologies, such as perpendicular or shingled magnetic recording, is limited to about 900 Gbit/in² due to the superparamagnetic effect [1]. The HAMR technology has the potential to overcome this fundamental limit through the implementation of a plasmonic near-field transducer (NFT) that produces localized surface plasmons, which can heat a sub-diffraction-limit spot on the recording medium [2]. This increases the local temperature above the Curie temperature of the "hard" magnetic medium, enabling the write pole of the head to write data in the laser-heated magnetic nanodomain (bit). To achieve the desired temperature in a given bit without erasing data stored in neighboring bits, the laser light generated by the NFT must possess sufficiently high energy density over a tiny cross-sectional area. Thus, understanding the thermo-plasmonic characteristics of the NFT is of paramount importance.

Plasmons are quanta of surface-charge-density oscillations [3]. Because a plasmon results from the quantization of plasma oscillations, it may be considered as a quasiparticle, just like phonons are quantizations of mechanical vibrations. Plasmon excitation by the electric field of an electromagnetic wave does not occur in the bulk of metals because the dimensions exceed the metal skin depth [4]. However, specific plasmon modes can be excited by the electric field of external electromagnetic waves at the interfaces of different materials [4], a phenomenon known as surface plasmons, which are only sustainable at optical frequencies [5]. For a tiny NFT of several hundred nanometers in size, which is comparable to the skin depth in metals, the electric field of an external electromagnetic wave generates surface plasmons confined within the surface nanostructure of the metal; therefore, these surface plasmons are referred to as localized surface plasmons. In a HAMR device, an optical laser is incident to a dielectric waveguide. As the laser light travels through the dielectric waveguide, it excites localized surface plasmons, coupling the incident laser energy to the media stack of the hard disk. Devices that utilize surface plasmons, such as NFT, quantum dots, and optical nanocircuits [6], are collectively called plasmonic devices. Localized surface plasmons and energy transport in plasmonic devices are affected by several factors, including structure size and shape, surrounding environment, and optical properties of structural

layers [7-9]. Therefore understanding how the performance of HAMR hard-disk drives depends on the optical properties of various stack layers is critical to the optimal functionality of the device.

The optical properties of a material can be characterized by its complex refractive index $\underline{n} = n + jk$, where the real part *n* is the refractive index that describes the phase velocity of light in the material, and the imaginary part *k* is the extinction coefficient, which controls the attenuation of light propagating through the material [10]. Because metals possess a large extinction coefficient, light penetration is limited to a very small depth, resulting in very strong attenuation. The laser energy absorbed by the media stack and the temperature rise in the magnetic medium show a strong dependence on the complex refractive index of the NFT and the media stack. Using materials with unsuitable optical properties may cause a temperature rise in the magnetic medium below the Curie temperature hindering data storage, or intense NFT self-heating that may dramatically decrease the lifetime of the plasmonic device. Thus, knowledge of the effect of material optical properties on the performance of HAMR devices is of great importance.

Because of the sophisticated nanostructure, extreme operating conditions, and multiple interfaces of highly dissimilar materials, a HAMR device is characterized by unique physical phenomena. For example, near-field heat transfer at the head-disk-interface (HDI), high electric field density, and different material failure modes may be simultaneously encountered within a region of a HAMR device only a few tens of micrometers in size. Various experimental and analytical studies have been recently carried out to elucidate the complex physics of HAMR devices. For example, Zhao et al. used a physical model based on Green's functions and showed that near-field heat transfer at the HDI does not follow Planck's law of blackbody radiation [11]. Wu et al. and Ma et al. used simplified HDI experimental setups to study heat transfer in small gaps and observed a dependence of the near-field heat transfer coefficient on gap size [12,13]. Hu et al. and Wang and Komvopoulos used the finite element method (FEM) to investigate heat transfer and thermal deformation in HAMR devices due to near-field heat transfer [14,15]. In addition, studies have been devoted to investigating the thermoplasmonic performance of HAMR devices. For instance, Bhargava et al. used inverse electromagnetic design to optimize the NFT structure and demonstrated a 50% improvement in thermal performance [16], while Hu et al. presented simulations of the thermal and optical performance of the NFT and discussed the role of the NFT in the performance of HAMR devices [17]. The NFT plasmonic device has drawn significant attention because of its important role in focusing the laser light to a very small spot. However, Hu et al. and Xu et al. have reported that other HAMR components can also greatly affect the device performance [18,19]. Therefore, it is of great importance to investigate how the optical properties of various layers comprising a HAMR stack assembly affect the thermal performance of the device.

The objective of this study was to develop a comprehensive electromagnetic (EM)thermal analysis, which can provide results revealing the effect of material optical properties of a typical HAMR stack assembly on its thermal performance. EM simulation results of the electric field intensity and temperature distribution at the waveguide entrance, the NFT exit, and the top and bottom interfaces of the magnetic medium are presented for a typical incident laser power and fixed wavelength. The EM results are used as input in the thermal analysis of the HAMR device to obtain simulation results elucidating the effect of the optical properties of the NFT, magnetic medium, underlayer, and heat-sink sublayer materials on device power efficiency, maximum NFT temperature, and maximum temperature rise in the magnetic medium.

3.2.2 Simulation model

Fig. 3.6 shows schematics of a typical HAMR stack consisting of waveguide, NFT, head overcoat, air gap between the head and the disk surfaces, disk overcoat, magnetic medium, underlayer, heat-sink sublayer, and substrate. Since the design of key plasmonic devices (i.e., waveguide and NFT) has been discussed in earlier publications [20,21], only a brief description is given here. The waveguide consists of a Ta₂O₅ core of uniform rectangular cross-section and a SiO_2 cladding layer that surrounds the core (Fig. 3.6(a)). The NFT is an E-shaped antenna made of Au consisting of a body, two wings, and a tiny notch (Fig. 3.6(b)). The magnetic medium is a thin granular film consisting of $L1_0$ FePt (001), whose growth is controlled by an MgO seed layer, referred to as the underlayer [22]. Below the underlayer is a relatively thick heat-sink sublayer consisting of Au whose role is to facilitate fast heat conduction from the magnetic medium during data writing. The ultrathin amorphous carbon (a-C) overcoat on the head and disk surfaces provides protection against corrosion and mechanical wear at instances of intimate contact of the proximity head with the fast rotating hard disk. During the operation of a HAMR device, the incident laser at the waveguide entrance reaches the NFT after exiting the waveguide. To generate a strong plasmon at the antenna notch, the laser light is polarized in the direction parallel to the notch. The tiny notch induces plasmon intensification in a small volume by the lighting rod effect [23]. By focusing the incident laser to a small size, the disk is spontaneously heated to a temperature above the Curie temperature of the magnetic medium, simultaneously enabling data writing by the write pole on the head.

The propagation of laser light through the HAMR stack can be described by Maxwell's equations, as shown in Eqs. (2.8) - (2.11). Solving the Eqs. (2.8) - (2.11) produce electrical field in the HAMR stack which lead to heat generation described by Eq. (2.12) and (2.13). The heat generation is then used as heat source in the governing equations of heat transfer (Eq. (2.1)). The solution of Maxwell's equations with the FEM or the finite difference method has been common practice in HAMR studies [16,17,20,24]. In fact, simulation results of Stipe *et al.* for the temperature rise on the magnetic head of a HAMR design, which is the origin of the HAMR design used in the present study, were shown to be in agreement with temperature measurements obtained with a scanning thermal microscope, which provides indirect support to the present numerical approach [20]. The simulations of the present study were performed with the Comsol Multiphysics software (version 5.2), which is an FEM solver. The composition, thickness, and optical properties of each layer comprising the stack assembly are given in Table 3.2 and corresponding thermal properties are given in Table 3.3. All thickness and material property values listed in Tables 3.2 and 3.3 are typical of those reported in the literature [16,21,24,25], except the specific heat c and the thermal conductivity k of air and the a-C overcoat, which are polynomial functions of temperature (Table 3.3).

A complete simulation comprises an EM analysis coupled with a thermal simulation by Eq. (2.12). Although the waveguide length in a typical HAMR device can be as long as 200 µm, only a small portion (i.e., 5 µm) of the waveguide's length was modeled to minimize the computation time. An incident laser to the waveguide entrance of 830-nm wavelength and 12-mW power were used in all simulations. In view of the large in-plane model dimensions, all exterior surfaces were modeled as radiative boundaries, except the waveguide entrance and substrate bottom surface, which were modeled as non-reflective surfaces. Because of the low extinction coefficient of waveguide materials and the laser heating of only a tiny volume of magnetic medium, the region of elevated temperature in the model is very small compared to the whole model. For this reason, all exterior surfaces were modeled as constant-temperature (320 K) boundaries, which is reasonable considering the global temperature in a HAMR device is in the range of ~313-323 K [26,27]. The FEM model consists of 153,277 quadratic (10-node) tetrahedron elements and 41,532 quadratic (6-node) triangular elements. The total number of degrees of freedom (including temperature and electric field components in the x-, y-, and zdirection) is 1,017,012. The mesh of the overcoat on the head and disk surfaces has 5 nodes in the thickness direction. Due to the large temperature gradients in the vicinity of the NFT notch, the mesh was locally refined with 4-nm-size elements.

For a fixed incident laser power, an effective HAMR design yields minimal NFT selfheating, high temperature rise (above the Curie temperature) in the magnetic medium, and sufficient incident laser power transfer to the magnetic medium. In this context, the thermal performance may be characterized by the power efficiency e (defined as the fraction of incident laser power absorbed by a 100-nm-radius cylindrical throughthickness volume of magnetic medium), the NFT maximum temperature $T_{\text{NFT}}^{\text{max}}$, and the maximum temperature rise in the laser-heated magnetic medium $T_{\text{mag}}^{\text{max}}$. Simulation results of these thermal performance parameters are presented and discussed in terms of optical properties of various stacking layers in the following section.

3.2.3 Results and discussion

To capability of the NFT to enhance and confine the incident laser in the present HAMR stack model (Fig. 3.6) with material properties given in Tables 3.2 and 3.3 can be interpreted in the context of simulation results of the electric field intensity |E| and temperature T arising in different layers, shown in Fig. 3.7 and Fig. 3.8, respectively. A comparison of Fig. 3.7(a) and (b) shows an enhancement of the maximum electric field intensity at the NFT exit by about two orders of magnitude compared to the waveguide entrance. The electric field intensity at the top interface of the magnetic medium (Fig. 3.7(c)) is slightly less than that at the NFT exit (Fig. 3.7(b)), but still of the same order of magnitude. The electric field is confined within a sub-100-nm-diameter circular region at both the NFT exit (Fig. 3.7(b)) and through the thickness of the magnetic medium (Fig. 3.7(c) and (d)). These results demonstrate the effectiveness of the NFT to enhance and confine the power of incident laser light. Fig. 3.8 shows corresponding temperature distributions at the waveguide entrance, NFT exit, and top and bottom interfaces of magnetic medium after 1 ns of laser heating. The small variation in temperature across the waveguide cross-section (Fig. 3.8(a)) is attributed to the relatively low extinction coefficient (0.001) of the waveguide material (Ta_2O_5), which is almost transparent to the

incident laser light. The maximum temperature at the NFT exit is ~550 K (Fig. 3.8(b)), whereas the peak temperature at the top (Fig. 3.8(c)) and bottom (Fig. 3.8(d)) interfaces of the magnetic medium is ~616 and ~550 K, respectively. The electric field intensities and temperature distributions reported in this study, which are supported by experimental results reported by Zhou *et al.* [2] and Kinkhabwala *et al.* [28], demonstrate the capability of the present analysis to tackle thermo-plasmonic problems.

The materials selection can have a profound effect on the performance of a plasmonic device [29]. In HAMR, the data writing process and device lifetime greatly depend on the thermal performance of the plasmonic NFT. However, in addition to the NFT, the optical properties of the magnetic medium, underlayer, and heat-sink sublayer strongly affect the absorption of laser energy and the heat generation in the hard disk, which, in turn, influence the overall thermal performance of the HAMR device. Fig. 3.9 shows the effect of the NFT optical properties on the thermal performance of the HAMR device. Potential NFT materials include noble metals and metal nitrides. The selected ranges of the refractive index $(0.01 < n_{\rm NFT} < 2.0)$ and the extinction coefficient $(4.7 < k_{\rm NFT} < 8.0)$ are inclusive of various potential NFT materials [30-32]. As shown in Fig. 3.9(a), a maximum power efficiency e = 1.33% is obtained for $n_{\text{NFT}} \approx 0.01$ and $k_{\text{NFT}} \approx 5$. These values also yield a fairly low maximum NFT temperature of ~435 K (Fig. 3.9(b)) and the highest peak temperature of ~837 K in the magnetic medium (Fig. 3.9(c)). As indicated by Eq. (2.12), heat generation is proportional to the imaginary part of the relative permittivity $(\text{Im}(\varepsilon_r) = 2nk)$ [3]. This suggests a decrease of $\text{Im}(\varepsilon_r)$ with decreasing n_{NFT} and fixed $k_{\rm NFT}$, implying a decrease in NFT self-heating. Because a low Re(ε_r) indicates inadequate localization of incident laser light, the power efficiency decreases with the real part of the relative permittivity ($\operatorname{Re}(\varepsilon_r) = n^2 - k^2$) [3]. However, the simulation results shown in Fig. 3.9 indicate an optimum extinction coefficient $k_{\rm NFT} \approx 5$. The absorption and transfer of laser energy in the media stack depend not only on the material properties of a specific layer but also on the material property mismatch of adjacent layers. For instance, in the case of a significant mismatch between NFT and magnetic medium optical properties, strong laser reflection occurs at the top interface of the magnetic medium, dramatically decreasing the absorption of laser energy in the magnetic medium.

Fig. 3.10 shows the dependence of the thermal performance of the HAMR stack assembly on the optical properties of the magnetic medium. A maximum power efficiency e = 1.18% is obtained for $n_{mag} = 5$ and $k_{mag} \approx 2.5$ (Fig. 3.10(a)). These optical property values yield a maximum NFT temperature $T_{\text{NFT}}^{\max} \approx 559$ K (Fig. 3.10(b)) and a maximum temperature rise in the magnetic medium $T_{mag}^{\max} \approx 444$ K (Fig. 3.10(c)). While a temperature of 559 K might be detrimental to the NFT lifetime, a peak temperature and, therefore, will not enable data writing with the write pole. Although high values of n_{mag} and k_{mag} are conducive to strong heat generation in the magnetic medium, because they yield a high $\text{Im}(\varepsilon_r)$, the large mismatch between the NFT and magnetic medium optical properties (Table 3.2) intensifies the reflection of laser light at the top interface of the magnetic medium, yielding a moderate T_{mag}^{\max} . Therefore, determining an optimum set of n_{mag} and k_{mag} properties requires a compromise between laser energy absorption and laser light reflection. Fig. 3.10(b) and (c) show that both the lowest T_{NFT}^{\max} and the highest T_{mag}^{\max}

are obtained for $n_{\text{mag}} \approx 1.5$ and $k_{\text{mag}} \approx 1-2$, with a corresponding power efficiency $e \approx 0.74\%-0.80\%$. Thus, enhanced data writing, low NFT self-heating, and acceptable power efficiency can be obtained with magnetic media having $n_{\text{mag}} \approx 1.5$ and $k_{\text{mag}} \approx 1-2$. While this range of optical properties may not be possible to achieve with FePt [33],modified FePt media, such as nanocomposite thin films of FePt-C with n = 3 and k = 1.8 at a 830-nm wavelength laser light [34], may be considered as potential candidate materials of magnetic media for HAMR devices.

Fig. 3.11 shows the effect of underlayer optical properties on the thermal performance of the HAMR stack. The highest power efficiency $e \approx 0.99\%$ is obtained for $n_{ul} \approx 4$ and $k_{ul} \approx 1-2$ (Fig. 3.11(a)), the minimum $T_{NFT}^{max} = 479$ K occurs for $n_{ul} \approx 0.1-1.0$ and $k_{ul} \approx 0-0.5$ (Fig. 3.11(b)), and the maximum $T_{mag}^{max} = 621$ K is generated when $n_{ul} \approx 2$ and $k_{ul} \approx 0$ (Fig. 3.11(c)). Thus, the underlayer optical properties do not yield a consistent trend for all thermal performance parameters. While high n_{ul} and moderate k_{ul} are desirable for increasing the power efficiency, significantly low n_{ul} and k_{ul} are needed to achieve low T_{NFT}^{max} and high T_{mag}^{max} . Nevertheless, an underlayer material with $n_{ul} \approx 2$ and $k_{ul} \approx 0$ yields $e \approx 1\%$, high $T_{mag}^{max} \approx 560$ K, and $T_{NFT}^{max} \approx 621$ K, which could satisfy the requirements for acceptable data writability and NFT lifetime.

Fig. 3.12 shows the dependence of the device thermal performance on the optical properties of the heat-sink sublayer. In addition to the fast dissipation of heat by the magnetic medium, the heat-sink sublayer electromagnetically interacts with the NFT to increase the electric field intensity in the magnetic medium. The results shown in Fig. 3.12 illustrate the enhancement effect of the heat-sink material on the thermal performance of the device. A heat-sink sublayer consisting of a good electrical conductor material intensifies the laser interaction with the NFT, thus increasing the electric field strength in the NFT and the magnetic medium. For an electrically conductive material, the Im(ε_r)/Re(ε_r) ratio assumes a very large positive value [35]. Thus, low $n_{\rm hs}$ and high $k_{\rm hs}$ yield high electric field intensities both in the NFT and the magnetic medium. This explains the high $T_{\rm NFT}^{\rm max}$ and $T_{\rm mag}^{\rm max}$ for $n_{\rm hs} \approx 0$ and $k_{\rm hs} \approx 5$ seen in Fig. 3.12(b) and (c), respectively. However, although this is desirable for raising the maximum temperature in the magnetic medium, the simultaneous increase of the NFT temperature could be detrimental to its lifetime. Thus, the identification of the optimum optical properties of the heat-sink material is challenging.

From the foregoing discussion it is apparent that the optical properties of each stack layer can significantly affect the device thermal performance. However, stack layer thickness effects also play an important role. In particular, the relatively thick (15 nm) underlayer exhibits a high thermal resistance, which tempers the cooling effect of the heat-sink sublayer. In addition, a thick underlayer weakens the electromagnetic interaction between the NFT and the heat-sink sublayer, because it increases their relative distance. Therefore, a decrease in underlayer thickness is beneficial to increasing the temperature rise in the magnetic medium. However, a thin underlayer also increases the electric field intensity in the NFT that promotes NFT self-heating, which is detrimental to the lifetime of the plasmonic device. Clearly, a tradeoff between the maximum temperature rise in the magnetic medium and NFT self-heating must be considered when seeking the optimum underlayer thickness.

The simulation results and interpretations given above provide insight into the thermoplasmonic performance of a typical HAMR device, specifically illustrating how the thermal performance of the device is affected by the resulting electrical field and temperature increase. The developed analytical/numerical treatment is amenable to variations in plasmonic device geometry and dimensions as well as changes in the optical properties of comprising structural layers. Thus, the present study provides a computational framework for designing and optimizing thermo-plasmonic devices with more complex geometries and more degrees of freedom.

3.2.4 Conclusions

An EM-thermal analysis of a typical HAMR stack assembly was performed to elucidate the effect of optical properties of various stacking layers on the device thermal performance. The selection of suitable optical properties of the NFT, magnetic medium, underlayer, and heat-sink sublayer to enhance the thermal performance was interpreted in the context of simulation results. It was shown that preferred NFT materials are characterized by a small refractive index and an extinction coefficient of ~5, while regarding the magnetic medium, the preferred refractive index and extinction coefficient are in the range of 1-2. Due to its low thermal conductivity, the underlayer acts as a thermal barrier. For the preferred optical properties of the underlayer material (i.e., a refractive index of ~2 and a very low extinction coefficient), selecting an appropriate underlayer thickness requires a compromise between NFT self-heating (lifetime) and maximum temperature rise in the magnetic medium (writability). To enhance the electromagnetic interaction with the NFT, the heat-sink sublayer material must exhibit good electrical conductivity. The present analysis provides a general framework for investigating the effect of optical properties of structural layers on the thermal performance of various plasmonic devices.

3.2.5 References

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Commente	Thickness	Refractive index		
Component	(nm)	п	k	
Waveguide core (Ta ₂ O ₅)	5000	2.096	0.001	
Waveguide cladding (SiO ₂)	5036	1.4	0	
NFT (Au)	100	0.154	5.31	
Head overcoat (a-C)	2	1.6	0	
Head-disk gap (air)	2.5	1.0	0	
Disk overcoat (a-C)	2	1.6	0	
Magnetic medium (FePt)	10	2.9	1.5	
Underlayer (MgO)	15	1.7	0	
Heat-sink sublayer (Au)	80	0.26	5.28	
Disk substrate (SiO ₂)	semi-infinite	1.5	0	

Table 3.2 Thicknesses and optical properties of the HAMR stack assembly

Table 3.3 Thermal properties of the HAMR stack assembly

Component	Specific heat c (J/kg⋅K)	Thermal conductivity k (W/m·K)
Waveguide core (Ta ₂ O ₅)	260	33
Waveguide cladding (SiO ₂)	730	1.4
NFT (Au)	129	317
Head overcoat $(a-C)^{a}$	$c_{a-\mathrm{C}}(T)$	$k_{a-\mathrm{C}}(T)$
Head-disk gap (air) ^{b)}	$c_{\rm air}(T)$	$k_{\rm air}(T)$
Disk overcoat $(a-C)^{a}$	$c_{a-\mathrm{C}}(T)$	$k_{a-\mathrm{C}}(T)$
Magnetic medium (FePt)	333	5 (in-plane) 50 (out-of-plane)
Underlayer (MgO)	15	1.7
Heat-sink sublayer (Au)	129	317
Disk substrate (SiO ₂)	703	1.38

^{a)} The thermal properties of the *a*-C overcoat are functions of temperature.
^{b)} The thermal properties of air are functions of temperature.



Figure 3.6 Schematics of the HAMR model examined in the present study: (a) lateral cross-section of waveguide, (b) lateral cross-section of NFT, and (c) vertical cross-section of the HAMR stack assembly. (The schematics shown in (a) and (b) are reproduced from Ref. 11.)



Figure 3.7 Electric field intensity |E| distribution at different lateral cross-sections of the HAMR stack assembly: (a) waveguide entrance, (b) NFT exit, (c) top interface of the magnetic medium, and (d) bottom interface of the magnetic medium.



Figure 3.8 Temperature T distribution at different lateral cross-sections of the HAMR stack assembly obtained after 1 ns of heating by a 12-mW laser beam: (a) waveguide entrance, (b) NFT exit, (c) top interface of the magnetic medium, and (d) bottom interface of the magnetic medium.



Figure 3.9 Effect of refractive index $n_{\rm NFT}$ and extinction coefficient $k_{\rm NFT}$ of the NFT material on (a) power efficiency e, (b) maximum NFT temperature $T_{\rm NFT}^{\rm max}$, and (c) maximum temperature in the magnetic medium $T_{\rm mag}^{\rm max}$.



Figure 3.10 Effect of refractive index n_{mag} and extinction coefficient k_{mag} of the magnetic medium on (a) power efficiency e, (b) maximum NFT temperature $T_{\text{NFT}}^{\text{max}}$, and (c) maximum temperature in the magnetic medium $T_{\text{mag}}^{\text{max}}$.



Figure 3.11 Effect of refractive index $n_{\rm ul}$ and extinction coefficient $k_{\rm ul}$ of the underlayer material on (a) power efficiency e, (b) maximum NFT temperature $T_{\rm NFT}^{\rm max}$, and (c) maximum temperature in the magnetic medium $T_{\rm mag}^{\rm max}$.



Figure 3.12 Effect of refractive index $n_{\rm hs}$ and extinction coefficient $k_{\rm hs}$ of the heat-sink sublayer material on (a) power efficiency e, (b) maximum NFT temperature $T_{\rm NFT}^{\rm max}$, and (c) maximum temperature in the magnetic medium $T_{\rm mag}^{\rm max}$.

Chapter 4. Evolution of ultrathin amorphous carbon films during deposition and thermal annealing

4.1 Thermal stability and diffusion of ultrathin amorphous carbon films synthesized by filtered cathodic vacuum arc deposition

4.1.1 Introduction

Amorphous carbon (a-C) films are used as protective overcoats in various applications, predominantly because of their unique physical properties, such as chemical inertness, thermal stability. optoelectrical characteristics. tribomechanical properties. biocompatibility, and corrosion resistance [1-4]. With the exception of the optoelectrical characteristics, all of the foregoing properties of *a*-C films are linked to a high fraction of tetrahedral (sp^3) carbon atom hybridization. Among various techniques of *a*-C film deposition [5-8], the most commonly used methods are plasma-enhanced chemical vapor deposition, ion beam deposition, radiofrequency (RF) and magnetron sputtering, pulsed laser deposition, and filtered cathodic vacuum arc (FCVA). Particularly, the former technique has been proven to be one of the most effective methods for synthesizing ultrathin a-C films with high sp^3 contents. The growth of sp^3 -rich a-C films with the FCVA method is attributed to several intrinsic process features, such as low-temperature film growth, swift plasma manipulation, effective macroparticle filtering, pulsed substrate biasing, and stable plasma arcing [9]. These advantages have made FCVA the prime process of a-C film deposition in several thin-film technology sectors, including magnetic storage devices, laser photonics, microelectromechanical systems, and biomedical implants [2,4,10-12].

It is well established that a-C films grown by deposition methods wherein the film precursors are energetic particles, such as C⁺ ions in carbon film deposition with the FCVA method, exhibit a multilayered structure consisting of three main layers, namely intermixing, bulk, and surface layer [13], of which the intermediate sp^3 -rich bulk layer is mainly responsible for the high hardness, excellent tribomechanical properties, and good thermal stability demonstrated by FCVA-deposited a-C films [14]. The substrate bias voltage controls the energy of the C^+ ions impinging onto the substrate and film surfaces. The implantation of energetic C^+ ions into the film/substrate system, a process known as subplantation [15], leads to the formation of an intermixing layer consisting of film and substrate atoms, the densification of the growing film, and the development of an sp^3 -rich bulk layer in the core of the *a*-C film. The thickness of the intermixing layer depends on the penetration range of incident C^+ ions, which is controlled by the substrate bias voltage, whereas the thickness of the predominantly sp^3 -hybridized bulk layer is affected by the *a*-C film thickness. The formation of a relatively low density, principally triangularly hybridized (sp^2) surface layer is due to the limited ion bombardment of the carbon material deposited onto the film surface in the final stage of the deposition process.

In concurrence with the synthesis of ultrathin a-C films, specialized characterization methods were also developed in response to high demands for imaging techniques that
can elucidate the composition and structure of films with thicknesses in the low nanometer range. Deciphering the local nanostructure and ascertaining the chemical composition at the nanoscale have enabled more accurate estimation of the sp^2 and sp^3 fractions and thicknesses of the layers comprising the structure of ultrathin *a*-C films [13,16-20]. The overall sp^3 content of *a*-C films is of paramount importance because it directly affects the thermal, structural, and tribomechanical properties of the film and also the magnitude of the intrinsic compressive stress [14,21], which is conducive to sp^3 hybridization.

Alongside with current trends for device miniaturization, the thickness of protective films has been constantly decreasing, raising concerns about preserving the physical properties that characterize the protective capability of the films, such as uniformity, density, wear and corrosion resistance, and thermal stability. For example, the thickness of a-C films used as protective overcoats in contemporary data storage hard-disk drives is in the range of 2-4 nm [20,22]. It has been reported that a-C film thinning to only a few nanometers leads to the predominant decrease of the thickness and sp^3 content of the bulk layer, whereas the effect on the thickness and hybridization state of the intermixing and surface layers is significantly less pronounced [17]. Accordingly, excessive film thinning may compromise the film's protective capability. This problem is further exacerbated in elevated-temperature applications, such as laser photonics and heat-assisted magnetic recording (HAMR). However, despite significant insight into the structure of ultrathin a-C films exposed to ambient conditions derived from previous studies [16-20,23,24], relatively less is known about the structural stability of ultrathin a-C films at elevated temperatures. Because several technologies rely on effective device operation at elevated temperatures, maintaining the mechanical integrity of a-C films in hot environments is critical. For example, a-C films used to protect vital head components of HAMR harddisk drives, such as the near-field transducer and write pole, must demonstrate structural stability at temperatures in the range of 100-300 °C [25]. Transient thermal spikes and prolonged heating may destabilize an ultrathin a-C film [26]. To this end, thermal annealing studies were performed to illuminate temperature-induced changes of the structure, composition, and thickness of the intermixing, bulk, and surface layers of ultrathin *a*-C films [27,28]. In addition, oxidation, delamination, $sp^3 \rightarrow sp^2$ rehybridization (graphitization), and carbon diffusion into the substrate may occur at elevated temperatures, compromising the reliability of data storage devices. Accordingly, an underlayer can be extremely beneficial not only for preventing carbon diffusion, especially if the intermixing layer of the *a*-C film cannot fulfil the role of a diffusion barrier, but also for acting as an adhesive layer that can effectively bond the a-C film to the substrate, as demonstrated in previous studies [23,24,29].

In the light of the aforementioned challenges, the present study was undertaken with the main objective being to explore the efficacy of an ultrathin SiN_x underlayer to prevent carbon diffusion into the substrate, while preserving the thermal stability of ultrathin *a*-C films synthesized under optimal DCVA deposition conditions. Rapid thermal annealing (RTA) experiments were performed at an elevated temperature for prolonged durations to gauge two phenomena, i.e., the ability of the SiN_x underlayer to prevent carbon diffusion into the substrate and the thermal stability of the sub-5-nm-thick *a*-C film. High-resolution transmission electron microscopy (HRTEM) and electron energy loss

spectroscopy (EELS) were used to evaluate the continuity, thickness, and hybridization state of various layers comprising the multilayered *a*-C/Si and *a*-C/SiN_x/Si stacks ant through-thickness structure of the intermixing, bulk, and surface layers comprising the *a*-C film before and after RTA. Results from the HRTEM and EELS studies of the *a*-C/Si and *a*-C/SiN_x/Si stacks are contrasted to assess the aforementioned competencies of the SiN_x underlayer and elucidate its effect on the thermal stability of the *a*-C film.

4.1.2 Experimental procedure

4.1.2.1 Film deposition

A Si(100) wafer was cut in $5 \times 5 \text{ mm}^2$ substrates, which were then cleaned with acetone for 10-15 min. After drying the substrates in air, they were placed inside the chamber of an RF sputtering system (Perkin-Elmer, Randex 2400 model) and the chamber was outgassed at a vacuum pressure of ~10⁻⁶ Torr to remove any residual gasses adsorbed onto the chamber walls. Subsequently, Ar gas was introduced into the chamber at a flow rate of 20 sccm, while the pressure was maintained at 3 mTorr, and the Si substrates were sputter-cleaned by bombarding with Ar⁺ ions under conditions of 250 W RF forward power, 3 mTorr chamber pressure, and zero substrate bias voltage. The chamber was then pumped down again to remove any traces of Ar and N₂ gas. After filling the chamber with N₂ gas, ionization was instigated and the substrates were bombarded with N⁺ ions under conditions of 750 W RF forward power, 3 mTorr chamber pressure, 20 sccm N₂ gas flow rate, and zero substrate bias for a duration of 3 min. Because of their small size, the energetic N⁺ ions were implanted into the near-surface region of the Si substrate forming a SiN_x layer.

Ultrathin *a*-C films were deposited on Si(100) substrates (with and without a SiN_x layer) using a custom-made FCVA system described in detail elsewhere [8,9]. After pumping down the system to 10^{-7} Torr to remove any residual gasses adsorbed on the chamber walls, plasma arcing was initiated by striking the high purity (99.99%) graphite cathode with a mechanical striker. Plasma arcing was stabilized by a special cusp-configuration magnetic field generated in the vicinity of the cathode [9]. An electromagnetic coil with an out-of-plane S configuration was used to collect any macroparticles expelled from the cathode during arcing on the walls of the S-shaped filtering duct before reaching the substrate. The C^+ ions traveling through the applied magnetic field were imparted a certain radius of curvature (controlled by the ion mass and charge) by the Lorentz force acting perpendicular to both the C⁺ ion velocity and the direction of the magnetic field. During the deposition process, the current in the auxiliary, upstream, and downstream coils was set at 32 A and the arc current was fixed at 80 A. Under these process conditions, only C^+ ions reached the substrate surface. The deposition of *a*-C films on Si and SiN_x-coated Si substrates was performed under optimal FCVA process conditions of -80 V substrate bias voltage, 10° ion incidence angle (measured from the normal to the substrate surface), and 65% duty cycle of substrate pulse biasing [16,19,20]. To obtain ultrathin a-C films, the duration of each deposition was fixed at 6 s. During the deposition, the substrate holder was rotated at 60 RPM to enhance the film uniformity.

4.1.2.2 Rapid thermal annealing

Samples of the *a*-C/Si and *a*-C/SiN_x/Si stacks were placed in the chamber of a heating system (AccuThermo, AW610 RTP) for RTA treatment. The process comprised heating from room temperature to 250 °C in 60 s, maintaining the temperature at 250 °C for either 30 or 90 min, and, lastly, allowing the samples to cool down to the ambient temperature. To prevent oxidation during the heating/cooling cycle, a constant flow of Ar gas was sustained from the instant the samples were loaded onto the heating system until their removal. The FCVA and RTA process steps used to fabricate and thermally treat the *a*-C/Si and *a*-C/SiN_x/Si stacks are depicted schematically in Fig. 4.1.

4.1.2.3 Microanalysis techniques

Cross-sectional TEM specimens were prepared using the method in Section 2.4.1. Highquality HRTEM images and EELS spectra were obtained with a 200-kV FEI monochromatic (Tecnai, F20 UT) microscope (the microscope was operated without the monochromator in this study) quipped with a standard field emission gun. A 150- μ mdiameter condenser aperture (C2) with a 9.3-mrad semi-angle and a 16.3-mrad collection semi-angle were used to acquire the EELS spectra. Using the full width at half maximum of the zero-loss peak, the energy resolution achieved in the EELS measurements was in the range of 0.5-0.6 eV. A line scan starting from the Si substrate at the bottom of the stack, passing through the SiN_x underlayer and the *a*-C film, and terminating at the Cr capping layer at the top of the stack was used to collect sequential EELS spectra with a step size of ~0.2 nm. A beam current of 80 pA and an acquisition time of 0.5 s were used for each spectra line scan. Two sets of EELS spectra were collected, i.e., a full survey spectrum of all the elements existing in the cross-sectional sample and a spectrum specific to carbon bonding.

The EELS technique is appropriate for analyzing the elemental composition and obtaining a better insight into the multilayered structure of the sample stacks. In this technique, incident electrons inelastically scatter inside the material, causing the electrons to lose energy and to change travel paths. By gauging this energy loss with an electron spectrometer, the ionizations of inner shells are used to determine the elemental components of the material. The ionization edge of carbon is at 285 eV and can be fitted with π^* and σ^* peaks in the range of 285-305 eV. Using the EELS spectra, the sp^2 and sp^3 hybridization fractions were determined by a method introduced in a previous study [13], which uses the π^*/σ^* ratio of the sample material calibrated by the π^*/σ^* ratio of a standard material. The standard specimen used to obtain reference spectra was graphitized evaporated carbon consisting of 100% sp^2 .

4.1.3 Results and discussion

Fig. 4.2 shows representative cross-sectional HRTEM images of the *a*-C/Si and *a*-C/SiN_x/Si stacks obtained before and after RTA for 30 and 90 min. While the crystalline Si substrate exhibits long-range atomic order, the *a*-C film and the SiN_x underlayer are both amorphous. Therefore, distinguishing them based on contrast differences is difficult, especially because they are adjacent layers in the stack. Thus, a SiN_x/Si sample was used to measure the nominal thickness of the SiN_x underlayer. Cross-sectional HRTEM images revealed that the nominal thickness of the *a*-C film in the *a*-C/Si and *a*-C/SiN_x/Si stacks was equal to 4.8 ± 0.8 and 2.7 ± 0.3 nm, respectively, whereas that of the SiN_x

underlayer in the *a*-C/SiN_x/Si stack was equal to 5.0 ± 0.2 nm. The different thickness of the *a*-C film in the two stacks is partly attributed to differences in the sticking coefficient of C on Si and SiN_x as well as the subplantation effect. Because the layer thickness measurements obtained from the HRTEM images were based on qualitative visual contrast differences, they represent nominal thickness estimates. Consequently, accurate thickness measurements (i.e., Si, N, and C) in the EELS spectra that are chemical fingerprints of Si, SiN_x, and *a*-C. Therefore, the main observation from the HRTEM images is that the *a*-C films are continuous, uniform, and demonstrate desired surface morphology attributes, such as high surface smoothness. In addition, the films are devoid of macroparticles, illustrative of the efficiency of the present FCVA setup to effectively filter out any macroparticles expelled from the graphite cathode during arcing.

Fig. 4.3 shows the normalized carbon intensity and the sp^3 fraction estimated from C Kedge EELS spectra of the a-C/Si and a-C/SiN_x/Si stacks before and after RTA for 30 and 90 min. The carbon atom hybridization fractions are of paramount importance because the sp^2 correlates with the optical and electrical properties, whereas the sp^3 controls the hardness, tribological properties, and thermal stability of the a-C film. In addition, the EELS spectra provide an effective means of determining the layer interfaces in the stacks with a previously developed method [22], consequently enabling an accurate estimation of the thickness of the a-C film and the SiN_x underlayer. Specifically, the interface delineating the intermixing layer was assigned a normalized carbon intensity of <0.15 in tandem with a sharply increasing sp^3 fraction, the interface of the intermixing layer with the bulk layer was determined by a normalized carbon intensity of 0.9-1.0 and approximately constant sp^3 fraction, whereas the interface of the bulk layer with the surface layer was defined by a normalized carbon intensity of 0.85-0.95 in conjunction with the sharp decrease of the sp^3 fraction. Finally, the interface between the surface layer and the capping layer was identified as the location having a normalized carbon intensity of 0.3-0.4 and very low and constant sp^3 fraction, attributed to adventitious carbon seeping into the matrix of the capping layer. Representative C K-edge EELS spectra of the untreated (as-fabricated) and thermally annealed a-C/Si and a-C/SiN_x/Si stacks are respectively shown in Fig. 4.4. These spectra were collected by incremental advancement from the Si substrate or the SiN_x underlayer toward the Cr capping layer.

Synthesizing ultrathin *a*-C films by deposition methods that use energetic particles as film precursors, such as the FCVA process, is challenging because reducing the film thickness leads to preferential thinning of the sp^3 -rich bulk layer, which controls almost all the aforementioned desirable attributes of the *a*-C film. This problem becomes even more acute when the film is exposed to an elevated temperature that may activate $sp^3 \rightarrow sp^2$ rehybridization and destabilize the structure of the film. Hence, a challenging task is to decrease the *a*-C film thickness without compromising its physical properties and structural integrity. A comparison of the EELS profiles shown in Fig. 4.3 reveals only a slight decrease of the sp^3 content due to RTA. In particular, for the *a*-C/Si stack (Figs. 4.3(a) and 4.3(c)), the sp^3 content of the bulk layer decreased by 4.5% and 7.5% after RTA for 30 and 90 min, respectively, whereas for the *a*-C/SiN_x/Si stack, the decrease of the sp^3 content of the bulk layer of thermally treated *a*-C films,

providing evidence of the thermal stability of the *a*-C film deposited on Si and SiN_x under the selected FCVA process conditions.

Fig. 4.5 shows the thickness of the intermixing layer, measured from individual EELS scans acquired along the cross section of the a-C/Si and a-C/SiN_x/Si stacks before and after RTA for 30 and 90 min. EELS scanning was instigated at the crystalline Si substrate where only the L_{2.3}-major edge peak was observed at 99 eV. By scanning across the stack cross section, the interface of the Si substrate with the SiN_x underlayer was revealed by the first appearance of the N K-major edge peak at 401 eV, that is, the SiN_x underlayer was identified by the firstly observed coexistence of the Si and N peaks in the EELS spectrum. Similarly, the interface of the SiN_x underlayer with the *a*-C film was determined by the first appearance of the C K-major edge peak at 284 eV, also designating the start of the intermixing layer up until the point that both the Si and N peaks disappeared from the EELS spectrum. Finally, the a-C film surface was determined by the last point where the C K-major edge peak was detected, accordingly enabling the precise calculation of the total film thickness, i.e., the sum of the thicknesses of the intermixing, bulk, and surface layers. Beyond this point, only the Cr L_{2,3}-major edge peak, attributed to the capping layer, could be detected in the range of 575 - 584 eV of the EELS spectrum. This procedure was used to compute the thicknesses of the a-C film and the SiN_x underlayer (Table 4.1) and the thickness of the intermixing layer in the *a*-C/Si and a-C/SiN_x/Si stacks (Fig. 4.5). The determination of the thickness of each layer with the foregoing method is preferred from that based on visual inspection of the HRTEM images because it uses fingerprint elements of each material rather than contrast differences. Moreover, it was not possible to detect any changes in the thickness of the intermixing, bulk, and surface layers of the *a*-C film due to carbon migration instigated by RTA using the HRTEM images. Thus, all of the thickness measurements in this study were deduced from the EELS spectra, while the HRTEM images were used to estimate the nominal thickness of the SiN_x underlayer and the *a*-C film (not including the intermixing layer, which was not discernible in the images) and to obtain an overall assessment of the cross-sectional structure of the *a*-C/Si and *a*-C/SiN_x/Si stacks.

The role of the SiN_x underlayer is to enhance the adhesive strength of the *a*-C film to the substrate and to preserve the structure and composition of the substrate by inhibiting alloying due to carbon implantation during film deposition and/or diffusion at elevated temperatures. Fig. 4.5 reveals that the SiN_x underlayer satisfied the latter objective. Indeed, a thinner intermixing layer fully confined within the SiN_x underlayer was obtained even after heating for 90 min. However, even though the RTA effect on the thickness of the intermixing layer in the *a*-C/Si stack was insignificant, the thickness of the intermixing layer in the a-C/SiN_x/Si stack increased with the RTA time. This can be explained by considering that the SiN_x underlayer was produced by nitrogenation of the Si substrate. The implanted N⁺ ions generated pathways for the C atoms to move through the SiN_x underlayer during the RTA treatment. Moreover, the valence electrons of most Si atoms interacted with implanted N atoms during the formation of the intermixing layer in the *a*-C/SiN_x/Si stack, leaving significantly fewer sites for C atoms to bond during the *a*-C film growth, consequently enabling C implantation deeper into the SiN_x underlayer. Compared to the *a*-C/SiN_x/Si stack, the C atoms in the intermixing layer of the *a*-C/Si stack had significantly more Si atoms to bond with during direct and recoil implantation.

Although this increased the thickness of the intermixing layer, it also inhibited C atom migration into the substrate during the RTA, which explains the secondary effect of RTA on the thickness of the intermixing layer in the *a*-C/Si stack. The thickness change of the *a*-C film, SiN_x underlayer, and intermixing layer reported herein are consistent with the findings of previous studies [22,25,26].

In traditional physical and chemical vapor deposition processes, intermixing of the film with the substrate either does not occur or is very limited. As a consequence, there is a high probability of film delamination under the effect of thermomechanical loadings, particularly for film/substrate systems characterized by a significant lattice mismatch and different elastic properties and thermal expansion coefficients. This major shortfall can be offset by a post-deposition thermal treatment that can promote element interdiffusion or, more effectively, by a deposition process like the FCVA that integrates the film with the substrate in the same process step through the formation of an intermixing layer. Because of the charged film precursors (e.g., C^+ ions for *a*-C film growth), applying an optimal substrate bias voltage in FCVA deposition [14,18] leads to the formation of an intermixing layer of thickness in the range of about 0.5-3 nm [17,19,20] by the subplantation process [15]. This enhances the adhesive strength of the film to the substrate, while preserving the structure and composition of the substrate and suppressing the development of large strain gradients at the film/substrate interface. Therefore, the SiN_x underlayer not only augments the interfacial adhesive strength [23,24,29,30] but, as shown in this study, can also prevent carbon migration into the substrate at elevated temperatures. Thus, the SiN_x underlayer effectively functions both as an adhesion layer and a diffusion barrier.

4.1.4 Conclusions

The thermal stability and diffusion characteristics of ultrathin a-C films grown on crystalline and nitrogenated Si with the FCVA method were investigated by HRTEM/STEM and EELS. The nitrogenation of the Si substrate by RF sputtering with N^+ plasma resulted in the formation of a 5-nm-thick SiN_x underlayer that prevented the migration of carbon atoms into the Si substrate, while preserving the thermal stability of the a-C film. Cross-sectional HRTEM images revealed the growth of sub-5-nm-thick a-C films demonstrating desirable morphology and structure attributes, whereas the EELS spectra ascertained the respective sp^3 fractions in the multilayered structure of the a-C films. The thermal stability of the a-C films in the a-C/Si and a-C/SiN_x/Si stacks was confirmed by the marginal decrease in sp^3 content of the bulk layer even after prolonged RTA. While the RTA effect on the thickness of the intermixing layer in the *a*-C/Si stack was secondary, an increase of the intermixing layer thickness in the a-C/SiN_x/Si stack was found with increasing RTA time. This discrepancy is probably due to structural differences between the intermixing layers of the two stacks. The subplantation process that is intrinsic to film growth by the FCVA method and the formation of the SiN_x underlayer by nitrogenation that created pathways for carbon atom migration in the underlayer but not in the substrate are the main physical processes responsible for the observed diffusion characteristics of the two stacks. The results of this study elucidate the important role of an ultrathin underlayer in heated multilayered media and provide an effective experimental framework for accurately assessing the thermal stability and elemental diffusion in ultrathin multilayered microstructures exposed to elevated temperatures.

4.1.5 References

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Substrate	Layer composition		Layer thickness (nm)					
			Before annealing		After 30 min annealing		After 90 min annealing	
	Layer 1	Layer 2	Layer 1	Layer 2	Layer 1	Layer 2	Layer 1	Layer 2
Si	_	a-C	_	5.6±1.0	_	6.6±0.4	_	7.0±1.0
Si	SiN _x	a-C	6.9±0.4	3.4±0.3	6.8±0.2	4.0±0.3	6.9±0.4	5.4±0.4

Table 4.1 Stack configurations and layer thickness estimated from EELS spectra acquired before and after RTA at 250 °C in Ar atmosphere for 30 and 90 min.



Figure 4.1 Schematic illustration of film synthesis by FCVA and RF sputtering deposition methods and heat treatment by RTA: (a) *a*-C film deposition on a Si substrate by FCVA followed by RTA and (b) SiN_x film formation on a Si substrate by RF sputtering with N⁺ plasma followed by *a*-C film deposition by FCVA and subsequent RTA under the same conditions as in (a).



Figure 4.2 Cross-sectional HRTEM images of (a–c) *a*-C/Si and (d–f) *a*-C/SiN_x/Si stacks obtained before (a, d) and after RTA at 250 °C in Ar atmosphere for (b, e) 30 min and (c, f) 90 min. All scale bars are equal to 2 nm.



Figure 4.3 Depth profiles of normalized carbon intensity (black curves) and sp^3 fraction (red curves) obtained from the C K-edge EELS spectrum of *a*-C films in (a-c) *a*-C/Si and (d-f) *a*-C/SiN_x/Si stacks obtained before RTA (a, d) and after RTA at 250 °C in Ar atmosphere for (b, e) 30 min and (c, f) 90 min. The EELS profiles reveal a multilayered cross-sectional structure consisting of (i) substrate, (ii) intermixing layer, (iii) bulk layer, (iv) surface layer, and (v) capping layer.



Figure 4.4 Carbon K-edge EELS spectra. For *a*-C/Si stacks: (a) untreated and (b, c) thermally annealed at 250 °C in Ar atmosphere for (b) 30 min and (c) 90 min. For *a*-C/SiN_x/Si stacks: (d) untreated and (e, f) thermally annealed at 250 °C in Ar atmosphere for (b) 30 min and (c) 90 min. Representative spectra of the intermixing, bulk, and surface layers of the *a*-C film were obtained by advancing from the bottom spectra (blue color) of the Si substrate to the top spectra (dark red color) of the Cr capping layer in 0.2-nm increments.



Figure 4.5 Intermixing layer thickness in *a*-C/Si and *a*-C/SiN_x/Si stacks measured before and after RTA at 250 °C in Ar atmosphere for 30 and 90 min.

4.2 Structure evolution during deposition and thermal annealing of amorphous carbon ultrathin films investigated by molecular dynamics simulations

4.2.1 Introduction

Amorphous carbon (*a*-C) is a solid consisting of multiple types of bonding configurations that lack long-range ordered structures and may exhibit deviations in interatomic distances and bond angles due to the presence of a high concentration of dangling bonds [1]. In principle, carbon atoms can form three different bonding configurations, i.e., sp^3 , sp^2 , and sp^1 atomic carbon hybridizations [2]. Thus, most *a*-C films contain graphite-like (sp^2) and diamond-like (sp^3) carbon crystals. Various studies have shown that the physical properties of *a*-C films, such as hardness, friction, and thermal stability, are mainly determined by the fraction of sp^3 bonding [3-10].

The development of thin-film deposition techniques during the late 20th century accelerated the use of carbon films in applications requiring protective coatings with excellent tribomechanical properties and coatings with exceptional optical and electrical properties [11,12]. For example, in contemporary hard-disk drives (HDDs) an ultrathin (~20 Å thick) a-C film is used to protect the magnetic head and the hard disk against corrosion and surface damage caused by intermittent asperity contact that may lead to mechanical wear and seizure. In addition to outstanding tribomechanical properties, the a-C films may be required to exhibit good thermal stability if the device operates at an elevated temperature. An example is heat-assisted magnetic recording (HAMR), a contemporary data storage technology that promises to provide extremely high areal storage densities, in which intensive laser heating is applied to both the head and disk media to enable data to be written in the magnetic medium of the hard disk; thus, the thermal stability of the protective a-C film is vital to the functionality and longevity of these HDDs that operate under intense thermal conditions [13,14]. Earlier studies were focused on the investigation of the structure of a-C films deposited under various process conditions (e.g., incidence angle, substrate bias voltage and duty cycle, and deposition time) using high-resolution transmission electron microscopy and electron energy loss spectroscopy [15-19]. These studies have revealed a strong dependence of deposition parameters on *a*-C film structure and the deposition conditions for synthesizing *a*-C films with a high sp^3 content. The thermal stability of ultrathin *a*-C films deposited on various substrates has also been assessed in the light of annealing experiments [6,20].

Despite important insight into the growth and thermal stability of ultrathin *a*-C films derived from aforementioned investigations, knowledge of the structure evolution of these ultrathin films during deposition and thermal annealing is mostly empirical, presumably due to the lack of high-resolution instruments for real-time probing of structural changes at the atomic and molecular levels. Molecular dynamics (MD) is a powerful computational method that promises to bridge the knowledge gap of atomic-scale structural changes instigated in nanometer-thick films during deposition and heating. MD simulations of carbon deposition on diamond performed with the Tersoff or adaptive intermolecular reactive empirical bond order potential have elucidated the effect of

deposition parameters on the *a*-C film structure [21-23]. Graphitization of *a*-C films because of thermal annealing or ion bombardment has also been investigated in MD studies that used the modified Brenner and Tersoff potentials to model atomic interaction [24-26]. The former studies have provided important information about the growth and graphitization of ultrathin *a*-C films, which is difficult, if not impossible, to obtain experimentally. The multi-layer structure of *a*-C films synthesized by energetic deposition processes, such as filtered cathodic vacuum arc [17], makes the experimental study of structural changes in these films even more challenging, especially for nanometer-thick films.

The evolution of the structure of *a*-C films during thermal annealing strongly influences the continuity, permeability, and nanomechanical/tribological properties of these films. However, the majority of previous MD studies only considered spatial changes in the multi-layer structure of ultrathin a-C films before and after annealing at different temperatures, lacking critical time-dependent information about spatial changes in film structure. Knowledge of time-dependent changes in *a*-C film structure during deposition and thermal annealing is critical to the fundamental understanding of the film-growth process and the development of thermally-induced damaging processes, such as graphitization and oxidation. Consequently, the objective of this investigation was to perform a comprehensive MD analysis of ultrathin a-C film deposition on silicon followed by thermal annealing, using the Tersoff potential to model carbon-carbon, silicon-silicon, and carbon-silicon atomic interactions. The analysis comprised two simulation phases. First, carbon atom deposition on a silicon substrate was simulated and the evolution of the a-C film structure under deposition conditions of various atom carbon kinetic energies was investigated. Second, thermal annealing of a-C films with the highest sp^3 content was simulated at various temperatures to illuminate transient changes in the film structure. The MD simulations of this study confirm the multi-layer structure of ultrathin a-C films and reveal spatiotemporal variations in the film structure at different annealing temperatures, providing insight into the structural stability of a-C films under application conditions where thermal effects are significant.

4.2.2 Analytical methodology

4.2.2.1 Interatomic potential energy

In all MD analyses, atomic motion in multi-atom systems in which interatomic forces are described by a potential energy function is determined by solving a set of differential equations of motion. Commonly used interatomic potential energy functions, such as one-, two-, and three-body potentials, provide a description of the atom positions. However, these interatomic potentials may fail to describe the different bonding states of atoms, such as carbon and silicon. This inadequacy can be remedied by a bond order potential that couples a two-body potential with a multi-atom correlation [27]. Using the so-called Tersoff potential, the total energy E of an atomic system can be expressed as

$$E = \sum_{i} E_{i} = \frac{1}{2} \sum_{i \neq j} V_{ij}$$
 (4.1)

$$V_{ij} = f_{C}(r_{ij}) [f_{R}(r_{ij}) + b_{ij} f_{A}(r_{ij})]$$
(4.2)

where E_i is the potential energy of atom *i*, V_{ij} is the bonding energy between atoms *i* and *j*, r_{ij} is the distance between atoms *i* and *j*, f_c is a smooth cutoff function used to generate a gradual energy decrease to zero with increasing atomic distance, f_R and f_A are repulsive and attractive two-body potentials, respectively, and b_{ij} is termed the bond order and represents the bond strength in the local environment, i.e., the bond strength of atoms having more neighboring atoms is characterized by a lower potential energy. The potential parameters are obtained by theoretical and experimental fits of the cohesive energy of element configurations. The first two elements to be fit with the Tersoff potential are carbon and silicon [27,28]. More details about the Tersoff potential can be found elsewhere [29,30].

4.2.2.2 Simulation procedure

As mentioned earlier, the MD simulations of the present study comprise two phases: (1) *a*-C film growth on a Si(100) substrate for various carbon atom kinetic energies and (2) thermal annealing at various temperatures. Film growth was simulated on a $23 \times 23 \times 59.7$ Å silicon substrate consisting of 1620 atoms (Fig. 4.6). To model an infinitely large deposition area, periodic boundary conditions were applied to the lateral sides of the substrate. The silicon substrate atoms are classified in three categories shown by different colors in Fig. 4.6. To simulate a semi-infinite substrate, the two lattice layers at the bottom of the MD model consisting of yellow atoms were fixed. The hollow prism made of red atoms is a Berendsen heat bath that controls the temperature during the simulation process [31]. The green atoms inside the hollow prism of red silicon atoms are free to interact with the incident carbon atoms. This model dissipates the internal energy rise caused by incident carbon atoms and maintains the substrate temperature at the desired level.

Before initiating carbon atom deposition, the silicon substrate was allowed to relax so that to minimize both the energy and internal stress in the system. This was accomplished by increasing the temperature from 300 to 800 K, maintaining the temperature at 800 K for 5 ps, and finally cooling to 300 K. Thermal relaxation prevented the development of high internal stresses due to the effect of surface tension. After the relaxation of the silicon substrate, 2000 carbon atoms were randomly introduced one at a time from a height of 57 Å above the substrate surface and with velocity normal to the substrate surface. Using a time interval of 2 ps between sequential carbon atom injections allowed the system to relax and reach equilibrium via the Berendsen heat bath using a damping constant of 100 fs. Considering that the thermal spikes generated by bombarding energetic particles of kinetic energy less than 100 eV typically last for less than 0.5 ps [32], using a time interval of 2 ps was adequate for simulating film growth for a particle kinetic energy of less than 120 eV. In all the deposition simulations, the time step was fixed at 0.5 fs and the heat bath temperature was set at 300 K.

In the thermal annealing simulations, the *a*-C film formed in the deposition phase of the simulation was kept at a constant temperate for 50 ns. The temperature was controlled by the Berendsen heat bath using a damping constant of 100 fs. In all the annealing simulations, the time step was fixed at 0.1 fs. All the MD simulations were performed with the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) using a node with a 20-core Intel Xeon E5-2670 CPU.

4.2.2.3 Model validation

To validate the MD model, several simulations were performed to determine the time step and model dimensions that did not affect the results. Representative results from these simulations are shown in Fig. 4.7. To investigate the effect of the substrate dimensions on the simulation results, four substrates with in-plane dimensions 7.68 \times 7.68, 15.36×15.36 , 23.04×23.04 , and 30.72×30.72 Å were used to simulate carbon film growth for an atom kinetic energy of 80 eV. In all four models, the substrate size in the z-direction was fixed at 59.74 Å, which is sufficiently large for modeling a half-space substrate, and the time step was set at 0.5 fs. Fig. 4.7(a) shows sp^3 depth profile for each substrate size. The 23.04 \times 23.04 and 30.72 \times 30.72 Å substrate sizes yield very similar results, while for smaller substrate sizes the sp^3 depth profile exhibits significant variation. It is noted that the total number of carbon atoms introduced into the MD system was adjusted according to the substrate size to yield films of similar thickness. For example, while 2000 carbon atoms were deposited onto the 23.04×23.04 Å substrate, only 889 carbon atoms were deposited onto the 15.36×15.36 Å substrate, i.e., ~3.8 atoms/Å² in both cases. In view of the results shown in Fig. 4.7(a), the substrate dimensions in the MD model were selected to be $23.04 \times 23.04 \times 59.74$ Å.

The effect of the time step was examined by performing simulations of *a*-C film growth at an atom kinetic energy of 80 eV on a $23.04 \times 23.04 \times 59.74$ Å substrate for a time step equal to 0.25, 0.5, 1, and 2 fs. Fig. 4.7(b) shows similar sp^3 depth profiles for 0.25 and 0.5 fs time step, whereas the sp^3 depth profile for 1 fs demonstrates more pronounced fluctuations. The simulation with a 2 fs time step resulted in all atoms escaping from the simulation box during post-deposition relaxation because the large time step produced overlapping atoms that encountered very large repulsive forces, leading to model failure. Therefore, a time step of 0.5 fs rather than 0.25 fs was used in the MD simulations to reduce the computational time. The slight difference in the range of the sp^3 depth profiles is due to the random number generator used in the LAMMPS code to generate the incident carbon atoms impinging onto the growing film surface at randomly selected surface positions.

4.2.3 Results and discussion

4.2.3.1 Film growth

Fig. 4.8 shows *a*-C film growth on a silicon substrate for a carbon atom kinetic energy in the range of 1-120 eV. Silicon and carbon atoms are shown in green and yellow colors, respectively. The bombardment of carbon atoms changes the crystalline structure of the silicon substrate, leading to the formation of an amorphous layer at the surface, hereafter referred to as the intermixing layer. The atoms in the intermixing layer comprise various silicon components bonded to neighboring silicon or carbon atoms. The intermixing layer acts as an adhesion layer that bonds the *a*-C film to the silicon substrate. The thicknesses of the intermixing layer and the *a*-C film strongly depend on the kinetic energy of the incident carbon atoms. The carbon atoms with a high kinetic energy can penetrate deeper into the substrate, producing a thicker intermixing layer. The intense bombardment of high energy (i.e., \geq 80 eV) carbon atoms also causes a small fraction of silicon atoms to migrate into the *a*-C film.

The coordination number of carbon atoms affects the structure and properties of the a-C film significantly. This number is defined as the number of nearest neighbor atoms and is indicative of the hybridization state, i.e., a coordination number equal to 4, 3, and 2 implies sp^3 (tetrahedral, diamond-like), sp^2 (trigonal, graphite-like), and sp^1 (linear) hybridization, respectively. The coordination number of an atom depends on the cutoff distance of the nearest neighbor atoms. The position of the minimum between the first peak (r_1) and the second peak (r_2) of the radial distribution function is a plausible choice for the cutoff distance. Typical values of r_1 and r_2 for C-C bonds are 1.45 and 2.55 Å, whereas for C-Si bonds r_1 and r_2 are equal to 1.85 and 2.85 Å, respectively. In the present study, the cutoff distance for C-C bonds was set at 1.9 Å, while that for C-Si bonds was set at 2.0 Å, which is close to the 2.1 Å cutoff distance used in previous works [33,34]. Because carbon atoms can form bonds with both carbon and silicon atoms, the sp^2 and sp³ contents reported here include both C-C and C-Si bonds. Although over- and undercoordinated carbon atoms may co-exist, they represent a very small fraction. Specifically, very few (0.7%) under-coordinated carbon atoms (coordination number = 1) were found at the film surface, which are attributed to the limited atomic bombardment of the outermost atomic plane and the effect of surface relaxation. A very small amount (3.9%) of over-coordinated carbon atoms (coordination number = 5) was found in the asdeposited film structure. Within a very short time from the inception of thermal annealing, all the over-coordinated atoms attained a more stable state corresponding to a coordination number of 2, 3, or 4. Consequently, the effect of under- and overcoordinated carbon atoms on the film structure was secondary. Fig. 4.9(a) shows the sp^3 . sp^2 , and sp^1 hybridization contents and the relative density of the *a*-C film (defined as the ratio of the film density to that of diamond) versus the deposition energy of carbon atoms. Low deposition energy (e.g., 1 eV) yields a low-density and mostly sp^2 -hybridized a-C film forming by carbon atom physisorption. A graphite-like film structure ($\sim 72\% sp^2$) is produced because the low kinetic energy of impinging carbon atoms is not effective in breaking the thermodynamically stable sp^2 and sp^1 carbon-carbon bonds. The increase of the carbon atom energy enhances carbon-silicon intermixing and sp^3 hybridization in the a-C film, resulting in a thicker intermixing layer (Fig. 4.8) and a thinner, denser, and more sp^3 -hybridized film structure (Fig. 4.9(a)). Energetic incident carbon atoms can break existing carbon-carbon bonds (mainly the relatively weaker sp^1 and sp^2 bonds) and cause resputtering and/or recoil implantation, increasing the film density and promoting sp^3 hybridization. The highest sp^3 content (~48%) and relative density (~0.84) correspond to carbon atom deposition energy equal to 80 eV. Increasing further the deposition energy (e.g., 120 eV) decreases both the sp^3 fraction and the relative density of the film. This is attributed to localized relaxation prompted by thermal spikes and the greater prospect of sp^3 bond breakage and resputtering of deposited carbon material resulting from the intense atomic bombardment. All of the foregoing effects are conducive to graphitization. The similar variations of the sp^3 content and the relative density of the *a*-C film with the increase of deposition energy (Fig. 4.9(a)) reveal a close dependence of film density on sp^3 content.

It is well-known that *a*-C films synthesized by energetic particle bombardment exhibit a multi-layer structure consisting of intermixing, bulk, and surface layers characterized by significantly different hybridizations [17,35,36]. The bulk layer possesses a much higher sp^3 content than the other two layers. The sp^3 content of the intermixing layer increases

gradually from the substrate toward the interface with the bulk layer, while that of the surface layer decreases sharply from the interface with the bulk layer toward the film surface. To examine whether the MD model can simulate the multi-layer structure of a-C films, sp^3 depth profiles were computed by averaging the sp^3 content of 1-Å-thick slices through the film thickness. Fig. 4.9(b) shows the effect of carbon deposition energy on the sp^3 depth profile of simulated a-C films. All cases reveal a sharply increasing sp^3 content at the film's interface with the silicon substrate (intermixing layer), a high sp^3 content in the middle region (bulk layer), and a sharply decreasing sp^3 content in the region adjacent to the film surface (surface layer). For very low deposition energy of 1 eV, the sp^3 depth profile is fairly flat, the sp^3 content is below 20%, and the intermixing layer is very thin, indicating the formation of a graphite-like *a*-C film that is slightly integrated with the substrate. Increasing the deposition energy to 80 eV not only enhances carbon-silicon intermixing, which is critical to the bond strength of the film to the substrate, but also decreases the film thickness and increases significantly the sp^3 content in the bulk layer, which controls the overall properties of the *a*-C film. However, the sp^3 content in the bulk layer decreases with the increase of the deposition energy to 120 eV, indicating the existence of an energy threshold for achieving the highest sp^3 content, in agreement with the experimental evidence [19]. Interestingly, all simulation cases show the formation of a surface layer with sp^3 content sharply decreasing toward the film surface, also in agreement with the results of a previous experimental study [15]. The formation of a graphite-like surface layer is attributed to less atomic bombardment than the bulk layer (because it forms at the end of the deposition) and surface relaxation resulting in a minimum energy state. During surface relaxation, the carbon atoms adjacent to the film surface migrate to lower energy sites where it is easier for them to become sp^2 hybridized and the decrease of the intrinsic compressive stress promotes $sp^3 \rightarrow sp^2$ rehybridization.

The above simulation results and analysis suggest a film-growth process characterized by the sequential main phases depicted in Figs. 4.9(c)-(f). During the initial deposition phase, carbon atom physisorption and/or implantation are the dominant physical mechanisms, depending on the kinetic energy of the carbon atoms, which control the formation of an ultrathin carbon layer on top of the intermixing layer. Newly arriving carbon atoms collide with previously deposited carbon atoms, knocking them deeper into the substrate (recoil implantation) and contributing to the formation of the intermixing layer (Fig. 4.9(d)). This deposition phase ends when the substrate becomes fully saturated with carbon atoms and carbon-silicon atom interaction diminishes. Next, the incident carbon atoms impinging onto the formed carbon atom planes lead to the growth of the bulk layer (Fig. 4.9(e)). The densification of the bulk layer and the evolution of high compressive stresses that are conducive to sp^3 hybridization and $sp^2 \rightarrow sp^3$ rehybridization are encountered under deposition conditions of energetic atom bombardment (e.g., deposition energy of 80 eV). In the final deposition phase, the resputtering of weakly bonded carbon atoms decreases and the development of high compressive stresses for sp^3 hybridization diminishes due to less atomic bombardment of the topmost carbon planes. These effects together with surface relaxation are responsible for the formation of a surface layer rich in sp^2 hybridization (Fig. 4.9(f)).

Table 4.2 shows the effect of the deposition energy of carbon atoms on the thickness of the intermixing, bulk, and surface layers. The boundaries of these layers were determined by computing the number of carbon atoms N_c in each 1-Å-thick slice. The N_c of the surface layer showed a sharp decrease, whereas that of the bulk layer remained fairly constant. The thickness of each layer was consequently determined from its known boundaries with other layers. For low deposition energy (e.g., ≤ 20 eV), penetration of the crystalline silicon structure by impinging carbon atoms is minimal; thus, the thickness of the intermixing layer is very small (2-3 Å). The increase of deposition energy (e.g., ≥ 80 eV) enhances carbon atom penetration, direct implantation, and recoil implantation in the silicon substrate, producing a significantly thicker intermixing layer. Indeed, for deposition energy equal to 80 and 120 eV, the thickness of the intermixing layer is 12 and 15 Å, respectively, corresponding to about 2.2 and 2.8 times the silicon lattice constant (5.431 Å). In contrast to the intermixing layer thickness, the bulk layer thickness decreases with increasing deposition energy because carbon atoms with a higher kinetic energy are implanted into the silicon substrate, contributing to the formation of a thicker intermixing layer than the growth of a thicker bulk layer. Nevertheless, the effect of carbon atom deposition energy on the surface layer thickness is secondary. This is attributed to less pronounced atomic bombardment of the surface layer in the last deposition phase and the effect of surface relaxation, as explained above.

4.2.3.2 Thermal annealing

MD simulations of thermal annealing were performed for the *a*-C film with the highest (48%) sp^3 content, corresponding to carbon atom deposition energy of 80 eV. To examine the thermal stability of this film, simulations of thermal annealing were performed for a temperature between 150 and 450 °C. As stated earlier, the thermal stability of ultrathin *a*-C films is critical to the performance of devices operating at elevated temperatures, such as the HDDs designed for HAMR. Thus, the selected range of annealing temperatures is typical of the temperature range of *a*-C films used as protective overcoats of HAMR media.

Fig. 4.10 shows the overall sp^3 film content (computed as the average of the sp^3 contents of the intermixing, bulk, and surface layers) versus annealing time in the temperature range of 150-450 °C. The film's structural stability is determined by the minimum temperature that causes the sp^3 fraction to decrease sharply, resulting in $sp^3 \rightarrow sp^2$ rehybridization. Annealing at 150 and 200 °C decreases the sp^3 fraction by only ~2%, whereas annealing at 250, 300, 350, and 450 °C decreases significantly the sp^3 fraction by 9%, 11%, 15%, and 17%, respectively. These predictions are in agreement with experimental results showing that annealing at 350 °C causes a decrease of the sp^3 content of a-C films deposited on various substrates by 4-16% [20]. For annealing at 300, 350, and 450 °C, the sp^3 content reaches a steady state in a very short time, indicating that rehybridization is a very rapid process. The increase of the annealing temperature decreases the time for the sp^3 fraction to reach a steady state. Table 4.3 shows the effect of annealing temperature on the thickness of the intermixing, bulk, and surface layers. The thickness of the surface layer increases with the temperature at the expense of the bulk layer thickness, while the thickness of the intermixing layer remains constant. The latter is in agreement with electron energy loss spectroscopy results of a previous study

showing that annealing at 350 °C yields minor changes of the intermixing layer thickness of *a*-C films deposited on Au, SiN, NiCr, TaO_x, and FeCo substrates [20].

Although Fig. 4.10 shows the evolution of the *a*-C film structure due to heating, i.e., $sp^3 \rightarrow sp^2$ rehybridization, it does not provide insight into spatiotemporal changes of the film structure. Thus, to investigate localized changes in the film structure in the course of annealing, the variation of the sp^3 fraction through the film thickness with the annealing time and temperature was examined. As shown in Figs. 4.11(a) and (b), the effect of annealing at 150 and 200 °C on the spatial and temporal variation of the sp^3 fraction is practically insignificant, consistent with the invariance of the overall sp^3 content at these temperatures (Fig. 4.10). However, annealing at 250 °C causes a discernible decrease in the sp^3 content of the bulk layer (Fig. 4.11(c)), with the effect intensifying as the temperature is further increased (Figs. 4.11(d)-(f)). Different from the profound heating effect on the structure of the bulk layer, the effect of annealing on the structure of the intermixing and surface layers is much less pronounced, although a similar decreasing trend of the sp^3 content of these layers is also observed with increasing temperature. For instance, annealing at 250 °C causes overall sp^3 content to decrease by 9%, with a 12% decrease in sp^3 content sustained by the bulk layer, while the change of the sp^3 content of the intermixing and surface layers is relatively insignificant. Annealing at a temperature above 250 °C intensified the rehybridization process in the bulk layer, which controls the overall sp^3 content of the *a*-C film. Specifically, annealing at 300, 350, and 450 °C resulted in the decrease of the overall sp^3 film content and the bulk layer sp^3 content by 11% and 17%, 15% and 20%, and 17% and 25%, respectively. As with the overall sp^3 content, the sp^3 content at each depth also reached a steady state within a very short annealing time.

Additional insight into the evolution of the film structure was obtained by examining the spatial distribution of carbon atoms in sp^1 , sp^2 , and sp^3 hybridizations. This was accomplished by slicing the *a*-C film with 48% overall sp^3 content (Table 4.2) into ten 4-Å-thick horizontal (x-y) slices, as shown in Fig. 4.12. The spatial distributions of carbon atoms with different hybridizations reveal a multi-layer film structure. The first slice (z =18 Å), representing the surface layer of the *a*-C film, contains a few carbon atoms that are mostly sp^2 hybridized. Thus, it may be inferred that the surface layer of the *a*-C film possesses a graphite-like porous structure of relatively low density. The slices corresponding to the bulk layer (2 Å $\leq z \leq 14$ Å) contain roughly the same number of carbon atoms, which is significantly higher than that of the surface layer. These slices show a gradual increase in sp³ hybridization with increasing depth in the range 6 Å $\leq z \leq$ 14 Å, followed by a slight decrease in sp^3 hybridization at a depth z = 2 Å, which is adjacent to the interface of the bulk layer with the intermixing layer. The slices assigned to the intermixing layer (z < 0) show a sharp decrease in sp^3 hybridization and carbon atom density with increasing depth. The foregoing variation of the sp^3 content of the surface, bulk, and intermixing layers is consistent with the sp^3 depth profile corresponding to a carbon atom deposition energy equal to 80 eV and in qualitative agreement with experimental findings [19].

The data shown in Fig. 4.12 provide a reference for the annealing simulations. Fig. 4.13 shows the number of carbon atoms in different hybridizations at various depths through the film thickness before and after thermal annealing in the temperature range of 150-

450 °C. Figs. 4.13(a) and (b) show that annealing at 150 and 200 °C, respectively, does not change significantly the carbon atom density and the hybridization state. However, as evidenced from Figs. 4.13(c)-(f), annealing at a temperature above 200 °C changes significantly the number of carbon atoms in each slice and also triggers an $sp^3 \rightarrow sp^2$ rehybridization, more notably in the bulk layer ($0 \le z \le 13$ Å). For instance, while annealing at 250 °C increases the number of carbon atoms in the surface layer (13 Å $\leq z \leq$ 18 Å) by 29 (46%) and decreases those in the bulk layer (0 Å $\leq z \leq 13$ Å) by 32 (2.3%), annealing at 450 °C causes the carbon atoms in the surface layer to sharply increase by 84 (140%) and those in the bulk layer to decrease by 78 (5.5%). Carbon atom rehybridization induced by annealing decreases the sp^3 content of the bulk layer by 9% at 250 °C and by 16.7% at 450 °C. Compared to the bulk layer and the surface layer, the intermixing layer exhibits insignificant changes in carbon atom number at all temperatures. The carbon atom changes in the surface layer and the intermixing layer indicate atom migration during annealing attributed to stress relaxation of the bulk layer. The increase of carbon atoms and the insignificant hybridization changes in the surface layer indicate the development of a thicker surface layer as a result of annealing at an elevated temperature (i.e., >250 °C). The decrease of the number of carbon atoms and the sp^3 content of the bulk layer due to annealing in the temperature range 250-450 °C suggests the development of a thinner, lower density, and partially graphitized bulk layer.

In addition to the distributions and hybridizations of carbon atoms in horizontal slices through the film thickness, carbon atom hybridization in 4-Å-thick vertical (*y-z*) slices was also examined to identify any changes in the as-deposited film structure due to annealing at planes perpendicular to the film surface. Fig. 4.14 shows sp^1 , sp^2 , and sp^3 hybridized carbon and silicon atoms in vertical slices before and after annealing at 450 °C. The simulations reveal two important results. First, only changes in hybridization can be observed after thermal annealing, whereas differences in the number of carbon atoms in each vertical slice are insignificant. In the light of this result and the periodic boundary conditions, it may be inferred that the film possesses a fairly uniform structure. Second, a comparison of carbon atom hybridizations in each slice before and after annealing shows a uniform trend for $sp^3 \rightarrow sp^2$ rehybridization throughout the film structure, especially in the bulk layer.

In some elevated-temperature applications, the decrease of the sp^3 content of the protective *a*-C film as a result of heating may enhance its chemical reactivity, especially in an oxidizing atmosphere. The evolution of the *a*-C structure in a hot, oxidizing atmosphere could be more complex than that simulated for inert thermal annealing conditions. Thermal annealing in an oxidizing atmosphere may accelerate oxidation and material loss at the film surface, with the thermally excited oxocarbon molecules entering the oxidizing gaseous environment. The reaction of an oxidizing gas with the film in conjunction with the development of mechanical traction due to surface contact may promote or even accelerate carbon oxidation at elevated temperatures, thus degrading the structural integrity of the *a*-C film and, in turn, its protective effectiveness. The detrimental effect of oxidizing gas diffusion on the film's structural stability may be more pronounced than that of $sp^3 \rightarrow sp^2$ rehybridization propelled by thermal effects. An MD analysis of ultrathin *a*-C films rich in sp^3 hybridization exposed to an elevated temperature in an oxidizing atmosphere will be present in Chapter 5.

4.2.4 Conclusions

A comprehensive MD analysis of energetic carbon atom deposition on silicon was performed to elucidate the growth process of ultrathin *a*-C films and identify the structural changes induced by thermal annealing. The MD simulations confirmed the multi-layer structure of *a*-C films synthesized by energetic particle deposition methods. The study of the effect of carbon deposition energy on the film growth characteristics revealed a deposition energy threshold for synthesizing *a*-C films of maximum density and sp^3 hybridization. Increasing the deposition energy toward the deposition energy threshold, the intensifying carbon atom bombardment promotes direct and recoil implantation and the development of high compressive stresses, which are conducive to film/substrate intermixing, preferential resputtering of weakly bonded atoms, sp^3 hybridization, and $sp^2 \rightarrow sp^3$ rehybridization. However, for deposition energy above the deposition energy threshold, the intense bombardment of the growing film promotes resputtering and, presumably, the development of thermal spikes, which reduce the film density and high compressive stresses, favoring sp^2 hybridization and $sp^3 \rightarrow sp^2$ rehybridization.

The MD simulations of thermal annealing of the *a*-C film with the highest sp^3 content (48%) in this study demonstrated insignificant structural changes for temperatures up to 200 °C, with progressively intensifying carbon atom migration in the intermixing and surface layers and $sp^3 \rightarrow sp^2$ rehybridization in the bulk layer with the temperature increasing from 250 to 450 °C. While annealing increases the thickness of the surface layer, it decreases the thickness of the intermixing layer and the density of the bulk layer. An important finding is that $sp^3 \rightarrow sp^2$ rehybridization at an elevated temperature is a very rapid process. Annealing at a relatively high temperature (e.g., 450 °C) may also have a negative effect on the film's permeability because it may create potential oxidizing gas diffusion sites.

The results of this study provide new insight into the dependence of the growth and structure of a-C films on deposition process conditions and annealing at various temperatures. The knowledge derived from the present MD simulations has direct implications on the physical properties of ultrathin a-C films used as protective overcoats of devices operating at elevated temperatures. The good agreement between the simulation trends and results of this study and experimental findings of earlier investigations validate the present MD model and employed analytical methodology. This work provides impetus for using the present MD modeling approach to guide the selection of appropriate film deposition and annealing conditions and to perform parametric studies aimed at tuning the multi-layer structure of a-C films according to specific application requirements.

4.2.5 References

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Deposition	Thickness (Å)				
energy (eV)	Intermixing layer	Bulk layer	Surface layer		
1	2	33	6		
20	3	22	3		
80	12	13	4		
120	15	11	3		

Table 4.2 Thickness of intermixing, bulk, and surface layers comprising the multi-layer structure of *a*-C films versus carbon atom deposition energy.

Table 4.3 Thickness of intermixing, bulk, and surface layers comprising the multi-layer structure of *a*-C film with 48% sp^3 overall content obtained after annealing versus annealing temperature.

Annealing	Thickness (Å)				
temperature (°C)	Intermixing layer	Bulk layer	Surface layer		
150	12	13	4		
200	12	13	4		
250	12	13	5		
300	12	12	5		
350	12	12	6		
450	12	12	6		



Figure 4.6 The MD model of the crystalline Si(100) substrate. The yellow atoms at the bottom of the model are fixed to simulate a semi-infinite bulk substrate. The red atoms comprise a Berendsen heat bath that is used to control the temperature of the whole model. The green atoms that are fully surrounded by the thermostat atoms can freely interact with incoming carbon atoms.



Figure 4.7 Simulated *a*-C film growth on a crystalline Si(100) substrate for a carbon atom deposition energy equal to 80 eV using different models: (a) sp^3 depth profiles for in-plane substrate size equal to 7.68×7.68 , 15.36×15.36 , 23.04×23.04 , and 30.72×30.72 Å and 0.5 fs time step and (b) sp^3 depth profiles for in-plane substrate size equal to 23.04×23.04 Å and time step equal to 0.25, 0.5, and 1 fs.



Figure 4.8 Simulated *a*-C film growth on a crystalline Si(100) substrate for carbon atom deposition energy equal to (a) 1, (b) 20, (c) 80, and (d) 120 eV. Silicon and carbon atoms are shown in green and yellow colors, respectively.



Figure 4.9 (a) Variation of sp^1 , sp^2 , and sp^3 contents and relative density (normalized by the density of diamond) of *a*-C films with the carbon atom deposition energy, (b) sp^3 depth profiles of *a*-C films for carbon atom deposition energy equal to 1, 20, 80, and 120 eV (negative depth values correspond to the silicon substrate), (c) silicon substrate after relaxation, (d) carbon-silicon intermixing during the initial deposition phase resulting in the formation of an intermixing layer, (e) main deposition phase involving the growth of a bulk layer, and (f) formation of a surface layer during the end of the deposition process. Silicon and carbon atoms are shown in green and yellow colors, respectively.



Figure 4.10 Variation of the overall sp^3 content of *a*-C film with 48% sp^3 content versus annealing time and temperature in the range of 150-450 °C.



Figure 4.11 Depth profiles of sp^3 fraction of *a*-C film with 48% sp^3 content versus annealing time and temperature equal to (a) 150 °C, (b) 200 °C, (c) 250 °C, (d) 300 °C, (e) 350 °C, and (f) 450 °C. Negative depth values correspond to the silicon substrate.



Figure 4.12 Carbon atoms of different hybridizations in 4-Å-thick horizontal (x-y) slices of *a*-C film with 48% sp^3 content. The exploded view on the left shows the depth of each slice. Negative depth values correspond to the silicon substrate. Silicon atoms are not shown for clarity.


Figure 4.13 Number of carbon atoms of different hybridizations in 4-Å-thick horizontal (*x-y*) slices of *a*-C film with 48% sp^3 content before and after thermal annealing at a temperature of (a) 150 °C, (b) 200 °C, (c) 250 °C, (d) 300 °C, (e) 350 °C, and (f) 450 °C.



Figure 4.14 Carbon atoms of different hybridizations in adjacent 4-Å-thick vertical (*y*-*z*) slices of *a*-C film with 48% sp^3 content before and after annealing at 450 °C. The region below each dashed line is the silicon substrate.

4.3 Internal stress evolution in ultrathin amorphous carbon films subjected to thermal annealing investigated by molecular dynamics simulations

4.3.1 Introduction

The growth of ultrathin amorphous carbon (*a*-C) films possessing significant fractions of tetrahedral (sp^3) atomic carbon hybridization has been the objective of many studies, mainly because of the well-established correlation between the physical properties and sp^3 content of *a*-C films. In particular, *a*-C films with high sp^3 fractions, also known as diamondlike-carbon films, have been proven to exhibit high hardness, low friction, excellent chemical inertness, and good thermal stability [1-5]. The combination of these desirable properties led to the usage of thin *a*-C films as protective overcoats in a wide range of applications, including automobile and aerospace components, orthopedic implants, optoelectronics, laser lenses, microelectromechanical devices, and hard-disk drives [6-9].

Despite the unprecedented industrial applications of *a*-C films, fundamental studies are still ongoing, principally because establishing correlations between the hybridization state and internal stress is challenging for films with thickness only a few nanometers. Elucidating such correlations is important because the internal stress can affect the film structure, mechanical integrity, and functionality under various industrial settings [10,11]. According to the generally accepted subplantation theory [12,13], the implantation of energetic particles (film precursors) increases the local density, causing the development of compressive stress that is conducive to sp^3 hybridization. Because the internal stress depends on the process conditions [14], film growth by techniques encompassing intense particle bombardment, such as ion implantation, reactive sputtering, and filtered cathodic vacuum arc, usually generates a high compressive stress in the film caused by localized structural incompatibilities introduced by the impinging energetic particles. However, for a large internal stress to be sustained without negatively affecting the adhesive strength at the film/substrate interface, it may be necessary to decrease the film thickness significantly. Several studies have been performed to determine the dependence of internal stress in a-C films on various factors, such as film structure and composition, substrate bias voltage (energy of incident particles), deposition temperature, and postdeposition heat treatment (e.g., thermal annealing) [10,15-19]. Although these studies have provided important guidance for tuning the stress in *a*-C films by controlling the process conditions, changing the deposition conditions is not always feasible and/or it may alter the film structure and properties. Therefore, a post-deposition heat treatment may be required to relieve a high film stress. Furthermore, in applications involving frictional heating or operation at elevated temperatures, such as high-load bearing components, laser lenses, and heat-assisted magnetic recording devices, changes in film stress may negatively impact the film structure, such as sp^3 to trigonal (sp^2) rehybridization.

Traditionally, film stress has been measured by techniques based on the curvature method [14-19]. However, such techniques cannot provide high-resolution, real-time stress

measurements, especially for nanometer-thick films. Molecular dynamics (MD) provides an effective alternative for overcoming this experimental scarcity and obtaining insight into the evolution of stress at the atomic and molecular levels. For instance, MD analysis has been used to find the stress field in a metallic substrate indented by a hard ball or a diamond tool [20,21], to explore the evolution of dislocations in a Lennard-Jones solid due to a penetrating atom [22], to identify size, shape, and orientation effects of a diamond tip on sliding friction [23], to obtain the subsurface stress field in a facecentered-cubic semi-infinite medium indented by a rigid flat punch [24], and to determine the optimal incident energy range for synthesizing diamondlike-carbon films with desirable structures and properties [25]. The foregoing studies reveal the potential of MD simulations to elucidate the evolution of structure and internal stress in nanometer-thick films during deposition and heating. Consequently, the objective of this study was to perform a comprehensive MD analysis of the growth and development of internal stress in ultrathin a-C films and explore the effect of thermal annealing on the film structure and internal stress. The spatiotemporal evolution of the structure and internal stress in a-C films during growth and thermal annealing are examined in the context of MD simulation results obtained for a wide range of deposition energy and annealing temperature.

4.3.2 Molecular dynamics model

The MD model and the simulation procedure, as well as the Tersoff potential, in Section 4.2.2.2 were employed in this section. For the sake of brevity, details of the simulation will not be explicitly presented here.

The film stress was calculated as a per-atom-based stress tensor σ_{ab} that includes virial and kinetic energy contributions due to interatomic interactions [26]:

$$\sigma_{ab}^{i} = -\frac{1}{V^{i}} \left[\sum_{j} F_{ij}^{a} r_{ij}^{b} + m_{i} v_{i}^{a} v_{i}^{b} \right]$$
(4.3)

where σ_{ab}^{i} are components of the stress tensor of atom *i*, V^{i} is the atomic volume assigned to atom *i*, F_{ij} is the force acting on atom *i* due to atom *j*, m_i is the mass of atom *i*, and v_i is the velocity of atom *i*. For ultrathin films, the out-of-plane normal stress σ_{zz} is negligibly small compared to the in-plane stresses σ_{xx} and σ_{yy} . The magnitude of the hydrostatic (or mean) stress can be associated with the hybridization state. Specifically, a high compressive hydrostatic stress correlates to high sp^3 content, whereas a tensile hydrostatic stress favors sp^2 hybridization and may also promote film delamination. Thus, the in-plane and hydrostatic stresses not only affect the *a*-C film microstructure but may also impact the mechanical integrity of the film. Consequently, these stresses were used in the present analysis to quantify the effects of deposition energy and annealing temperature on film internal stress. Using Eq. (4.3), the hydrostatic stress σ_h and in-plane stress σ_p were computed using the following definitions

$$\sigma_h = \frac{\sigma_{xx} + \sigma_{yy} + \sigma_{zz}}{3\mathcal{V}} \tag{4.4}$$

$$\sigma_p = \frac{\sigma_{xx} + \sigma_{yy}}{2\mathcal{V}} \tag{4.5}$$

where \mathcal{V} is the volume of a given domain and σ_{kk} (k = x, y, z) represents the summation of the corresponding tensor components of all atoms in the particular domain. The hydrostatic and in-plane stresses were calculated by averaging the atomic stresses in 1-Åthick horizontal slices at various depths. The slice volume was computed by multiplying the horizontal cross-sectional area of the model (23 Å × 23 Å) with the slice thickness (1 Å).

4.3.3 Results and discussion

The a-C films grown under conditions of various deposition energies demonstrated significant differences in both the morphology and structure (hybridization state), as illustrated in Fig. 4.15. Deposition energy of 1 eV is typical of gas-phase film-growth processes, such as evaporation and physical/chemical vapor deposition, whereas deposition energy in the range of 20-120 eV is typical of film-growth processes that use energetic particles as film precursors, such as ion implantation and filtered cathodic vacuum arc. The hybridization state can be quantified by the atomic coordination number of an atom, defined as the number of its nearest neighbor atoms. A coordination number equal to 4, 3, and 2 indicates sp^3 , sp^2 , and sp^1 (linear) hybridization, respectively. An extremely small number of under-coordinated atoms with coordination number equal to 1 may also exist at the film surface because of the limited atom bombardment. Very low deposition energy (1 eV) produced a relatively thick a-C film dominated by sp^2 hybridization (Fig. 4.15(a)). Alternatively, a thinner, denser, and significantly rich in sp^3 hybridization a-C film was grown when the deposition energy was increased to 80 eV (Fig. 4.15(c)), while the films synthesized under conditions of moderate (20 eV) or high (120 eV) deposition energy, Figs. 4.15(b) and (d), respectively, were characterized by medium levels of sp^3 hybridization. A comparison of the simulation results shown in Fig. 4.15 indicates that the *a*-C film with the highest sp^3 content corresponds to deposition energy of 80 eV. From the analysis of the MD data, the sp^3 content of the *a*-C films grown under simulated conditions of deposition energy equal to 1, 20, 80, and 120 eV was found equal to 11%, 22%, 48%, and 32%, respectively. The implantation of energetic carbon atoms in the silicon substrate resulted in the formation of an intermixing layer acting as an adhesive layer between the film and the substrate. Fig. 4.15 also shows that the thickness of the intermixing layer increased with the deposition energy. This is an intrinsic characteristic of deposition processes wherein the film precursors are energetic particles. The deposition energy of 80 eV that yielded the higher sp^3 content is within the experimental deposition energy range (60 - 100 eV) of a-C films possessing maximum sp^3 contents [27]. The latter provides supporting evidence of the appropriateness of the present MD model for studying the *a*-C/Si system.

Fig. 4.16 shows the effect of deposition energy on the distribution of the hydrostatic and in-plane stresses through the film thickness. The zero depth position corresponds to the substrate surface; thus, all depth positions mentioned hereafter are measured from the substrate surface. A tensile stress field exists throughout the *a*-C film grown under conditions of deposition energy equal to 1 eV. At higher deposition energy, however, only the near-surface region of the *a*-C film is under tension (surface tension effect),

whereas the bulk and intermixing layers are under compression. The effect of deposition energy on the type of film stress can be explained by considering its effect on film densification and hybridization. Specifically, because low deposition energy (1 eV) does not cause energetic atom bombardment, which is a precursor to densification and the development of a compressive stress, the film structure is dominated by sp^2 hybridization and is under a tensile stress state. Alternatively, higher deposition energy (≥ 20 eV) promotes densification and, in turn, the evolution of a compressive stress state that favors sp^3 hybridization. Moreover, because energetic atom bombardment of the last atomic layers of the growing film is limited, densification at the film surface is reduced and the film surface is predominantly sp^2 hybridized and under a tensile stress. The highest compressive stresses developed for deposition energy of 80 eV. The evolution of a dominant compressive stress field is a consequence of the bombarding effect of energetic carbon atoms. For deposition energy of 80 eV, the maximum hydrostatic and in-plane stresses are equal to -14.2 and -21.3 GPa, respectively, and occur at a depth of 6 Å above the substrate surface. Nevertheless, both hydrostatic and in-plane stresses decrease with the increase of the deposition energy to 120 eV, showing the same dependence on deposition energy as the sp^3 content. The internal stress predicted by the MD model is consistent with the experimental results of a previous study [28], where the internal stress of a-C films with 50% sp³ content was found to be equal to ~16 GPa. It is known that energetic carbon atom bombardment produces a multilayered film structure consisting of intermixing, bulk, and surface layers [29]. In the present study, the boundaries of each layer were determined from the sp^3 depth distribution through the film thickness. Specifically, the boundaries of the intermixing and surface layers with the bulk layer existing in the middle region of the film and possessing the highest sp^3 content where identified by the instigation of a sharp decrease in sp^3 content. The formation of Si-C bonds in the intermixing layer and the short bombardment of the structure of the surface layer are responsible for the lower sp^3 content of these layers [30]. The stress distributions for deposition energy in the range of 20-120 eV shown in Figs. 4.16(b) - (d), demonstrate a through-thickness variation similar to that of the sp^3 content, indicating the existence of a correlation between local stress and local sp^3 content.

Although the simulation results shown in Fig. 4.16 provide insight into the effect of deposition energy on the development of film stress, they do not reveal how the film stress and structure evolve during film growth. An advantage of the MD analysis is that it can capture the progression of the structure and internal stress in the modeled system. Consequently, spatiotemporal distributions of the foregoing quantities were obtained by using 1-Å-thick horizontal slices to compute the average in-plane stress, sp^3 content, and number of carbon atoms at various depth positions during film growth. Fig. 4.17 shows simulation results revealing changes in in-plane stress, structure, and number of carbon atoms versus time at depth locations in the *a*-C film of 3, 6, and 9 Å above the substrate surface for deposition energy of 80 eV. Considering the film-growth simulation comprised the sequential deposition of 2000 carbon atoms, the 0.4 ns time scale in the plots shown in Fig. 4.17 is equivalent to 200 new incident carbon atoms, whereas the time range of >4 ns represents post-growth relaxation. Fig. 4.17(a) and (b) show similar temporal variations of the in-plane stress and sp^3 content; however, the time for the average sp^3 content at each depth position to stabilize appears to be longer than that for the average number of carbon atoms to stabilize at corresponding locations (Fig. 4.17(c)).

For instance, the average number of carbon atoms at a depth position of 3 Å stabilized after ~2 ns, whereas the average sp^3 content at the same location stabilized after ~3.2 ns. The stabilized average number of carbon atoms at a given location indicates local carbon saturation. However, the former was not conducive to high sp^3 hybridization at a specific location because of the inadequate constraint provided by material from above that did not effectively constrained stress relaxation as carbon atom deposition was still ongoing. This is evidenced from Figs. 4.17(b) and (c) that show a maximum sp^3 content at the 3 Å depth position only after the instigation of carbon atom saturation at the 6 Å depth position. Further insight into the deposition process can be obtained by considering the temporal variation of the average number of new incident carbon atoms at various depth positions (Fig. 4.17(d)). From Figs. 4.17(b) and (d), it may be inferred that the sp^3 content at the 3 Å depth position reached a maximum after 3.2 ns when virtually no more incident carbon atoms arrived at that location. Nevertheless, the sp^3 content at the 9 Å depth position continued to increase because there were still new incident carbon atoms arriving at this location even after 4 ns. Consequently, it may be inferred that the new incident carbon atoms formed new sp^3 sites when a spatial constraint was imposed by atoms depositing above the particular location, rendering higher compressive stress and higher sp^3 content at deeper film regions.

As mentioned earlier, a-C films with sp^3 -rich structures are desirable protective overcoats. For this reason, the structural stability of *a*-C films in elevated-temperature environments is of high importance. Consequently, thermal annealing simulations of the *a*-C film with 48% sp^3 hybridization grown under conditions of deposition energy equal to 80 eV were performed to investigate thermally-induced effects on the internal compressive stress, which is a requirement for the formation and stability of sp^3 -hybridized domains. Table 4.4 shows that both the average in-plane stress and sp^3 content of this a-C film sharply decreased with the increase of the temperature at 250 °C and beyond, indicating that the critical temperature that defines the thermal stability of this a-C film is close to 250 °C. Fig. 4.18 shows in-plane stress distributions through the thickness of the *a*-C film with overall 48% sp^3 hybridization (deposition energy = 80 eV) obtained before and after thermal annealing at 150 and 450 °C. The vertical dashed lines show the boundaries between the intermixing, bulk, and surface layers comprising the *a*-C film. It can be seen that heating resulted in stress relief, especially at 450 °C. In particular, the maximum compressive in-plane stress of -21.3 GPa at the ~6 Å depth position decreased to -18.2and -16 GPa after heating at 150 and 450 °C, respectively. The stress relief is more pronounced in the sp^3 -rich bulk layer of the *a*-C film. Because the in-plane stress correlates with the hybridization state of the a-C film, with compressive and tensile stresses favoring sp^3 and sp^2 hybridization, respectively [31], the decrease of the compressive in-plane stress due to thermal annealing can be associated with the simultaneous decrease of the sp^3 content. This explains the trend of the in-plane stress and sp^3 content with increasing temperature revealed by the data given in Table 4.4. The thermally-induced decreasing trend of the sp^3 content observed in the present simulations is consistent with the findings of a thermal annealing study of *a*-C films [32].

Further insight into the effect of thermal annealing on the film stress can be obtained in the light of the simulation results of stress change shown in Fig. 4.19 for the *a*-C film with 48% sp^3 content (deposition energy = 80 eV). The change in average (through-

thickness) stress versus annealing temperature (Fig. 4.19(a)) reveals the existence of a critical temperature for stress relief of ~250 °C, consistent with the data given in Table 4.4. The different critical temperature ranges of stress relief (250-300 °C) and sp³ drop (200-250 °C) are attributed to the increase of the thermal stress with annealing temperature and the simultaneous decrease of the intrinsic stress due to thermallyinduced $sp^3 \rightarrow sp^2$ rehybridization, leading to the decrease of the internal stress at a slightly higher temperature range compared to the sp^3 drop. The change of the compressive in-plane and hydrostatic stresses with increasing temperature follows a similar trend, characterized by a sharp decrease between 250 and 300 °C. In the temperature range of 300-450 °C, the change in average in-plane and hydrostatic stress is in the range of 12.7-16.8% and 9.4-16.7%, respectively. Fig. 4.19(b) shows the average in-plane stress change in each layer of the *a*-C film versus temperature. The in-plane stress in the sp^2 -dominated structure of the intermixing and surface layers shows insignificant changes due to the temperature variation compared to the sp^3 -rich bulk layer. Specifically, the average in-plane stress in the bulk layer decreased by 3.7, 3.6, and 4.5 GPa (i.e., by 15.6%, 15.0%, and 22.0%) after heating at 300, 350, and 450 °C, respectively. These results indicate that, although the stress changed throughout the film thickness, the stress relief was more pronounced in the bulk layer. Because a high compressive stress is a prerequisite for sp^3 hybridization, as confirmed by a previous experimental study [33], it may be inferred that the decrease of the compressive in-plane stress in each layer of the *a*-C film reveals a corresponding decrease in sp^3 content.

As mentioned earlier, a major advantage of the MD analysis is that it can provide insight into the spatiotemporal variations of the internal stress and structure of the modelled system. Fig. 4.20 shows the average in-plane stress in the surface, bulk, and intermixing layers of the *a*-C film with 48% sp^3 content (deposition energy = 80 eV) versus annealing time at various temperatures. The evolution of the in-plane stress in the three layers is consistent with the results shown in Fig. 4.19(b), illustrating significant stress changes in the bulk layer at 300, 350, and 450 °C. The stress relief during thermal annealing can be attributed to two simultaneously occurring processes, namely $sp^3 \rightarrow sp^2$ rehybridization and atomic migration. Although the volume of sp^2 sites is larger than that of sp^3 sites, the in-plane size of sp^2 sites is smaller due to the shorter bond length [28]. Consequently, the $sp^3 \rightarrow sp^2$ rehybridization contributes to the film stress relief from a volumetric change standpoint. The atomic rearrangement of sp^2 sites can lead to a volume decrease at the expense of a small reduction in sp^3 content [28,34]. The significant decrease of the sp^3 content after thermal annealing at a temperature of ≥ 250 °C revealed by the MD simulations of this study indicates that $sp^3 \rightarrow sp^2$ rehybridization is a major contributing factor to the stress relief in the *a*-C film. Nevertheless, the role of atomic rearrangement in thermally-induced stress relief needs further investigation.

The effects of the deposition energy and annealing temperature on the nanostructure and internal stress of the *a*-C films observed in the present analysis should be qualitatively valid for other substrate materials. Although the substrate may affect the nanostructure and properties of the intermixing layer, this effect on the bulk and surface layers of the *a*-C film is secondary in film growth by energetic atom bombardment. In addition, the findings regarding the optimum deposition energy for sp^3 -rich *a*-C film growth, the existence of a critical temperature range of film stress relief, and the variation of the film

stress with the annealing temperature, should also be applicable to different substrate materials, as shown by the existence of optimal deposition energy for *a*-C film deposition on diamond [25], for example.

It is well established that the development of a compressive stress in *a*-C films synthesized by deposition methods wherein the film precursors are energetic particles is a consequence of an intensive bombardment effect. An important contribution of this study is the elucidation of the underlying factors affecting the evolution of compressive stress in ultrathin films, the correlation of film stress with sp^3 hybridization, the dependence of the latter on local carbon atom saturation, and the stress relief above a critical temperature. The latter reveals the existence of an energy barrier that stabilizes the compressive stress in the *a*-C film, primarily in the sp^3 -dominant bulk layer. The role of thermal annealing in the stress relief process is to provide the energy needed to overcome the energy barrier for relaxing the compressive stress generated in the film during the deposition process [34].

4.3.4 Conclusions

The origins of internal stress in ultrathin a-C films synthesized by energetic particle bombardment processes and the effect of thermal annealing on stress relief were examined in the light of MD simulation results. It was shown that the high compressive stress generated in these films correlates with the amount of sp^3 hybridized atomic carbon, especially in the sp^3 -rich bulk layer of the multilayered *a*-C film structure. Importantly, a high compressive stress, which is a prerequisite for high sp^3 hybridization, emerges at a film location only when the incident carbon atoms at that location have been spatially constrained by the carbon-saturated atomic plane from above. For a-C films with 48% sp^3 hybridization, a significant stress relief was encountered after thermal annealing at a temperature of ≥ 250 °C. Simulations confirmed that the stress relief mainly commenced in the bulk layer of the a-C film and that the internal stress of the annealed a-C film decreased rapidly, suggesting that film stress relaxation is a very fast process. The two main mechanisms responsible for the stress relief during thermal annealing were found to be $sp^3 \rightarrow sp^2$ rehybridization and atomic migration. The results of this MD study provide insight into the spatiotemporal evolution of the internal stress in ultrathin a-C films and the underlying physics that correlate the distribution and magnitude of internal stress with structural changes activated by thermal annealing.

4.3.5 References

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Annealing temperature (°C)	Average film properties	
	In-plane stress (GPa)	sp^3 hybridization (%)
0	-14.3	48
150	-14.1	47
200	-14.6	46
250	-14.2	39
300	-12.5	37
350	-12.0	33
450	-11.8	31

Table 4.4 Average in-plane stress and sp^3 content of *a*-C film deposited at 80 eV obtained before and after thermal annealing in the temperature range of 150-450 °C.



Figure 4.15 Simulated *a*-C film growth on a Si(100) substrate for carbon atom deposition energy equal to (a) 1, (b) 20, (c) 80, and (d) 120 eV. The dark blue circles and the cyan circles represent silicon and carbon atoms with coordination number N = 1, respectively. The two black horizontal lines indicate the position of the substrate surface.



Figure 4.16 Depth distributions of the hydrostatic and in-plane stresses in a-C films for carbon atom deposition energy equal to (a) 1, (b) 20, (c) 80, and (d) 120 eV. The zero depth position represents the substrate surface.



Figure 4.17 Temporal variation of the average (a) in-plane stress, (b) sp^3 hybridization content, (c) number of carbon atoms, and (d) number of new incident carbon atoms at depth positions of 3, 6, and 9 Å above the substrate surface for carbon atom deposition energy equal to 80 eV.



Figure 4.18 Depth distribution of in-plane stress in the *a*-C film with 48% sp^3 hybridization content (carbon atom deposition energy = 80 eV) before and after annealing at 150 and 450 °C. The boundaries of the intermixing, bulk and surface layer are shown by vertical dashed lines.



Figure 4.19 Change of in-plane and hydrostatic stress in the *a*-C film with 48% sp^3 hybridization content (carbon atom deposition energy = 80 eV) versus annealing temperature: (a) through-thickness average stress change and (b) average in-plane stress change in the surface, bulk, and intermixing layers of the *a*-C film. A negative stress change indicates a decrease in compressive stress.



Figure 4.20 Average in-plane stress in the surface, bulk, and intermixing layers of the *a*-C film with 48% sp^3 hybridization content (carbon atom deposition energy = 80 eV) versus annealing time for temperature equal to (a) 150 °C, (b) 200 °C, (c) 250 °C, (d) 300 °C, (e) 350 °C, and (f) 450 °C.

Chapter 5. Oxidation mechanism, nanostructure evolution, and friction characteristics of ultrathin amorphous carbon films examined by molecular dynamics simulations

5.1 Introduction

The unique properties and microstructure of amorphous carbon (a-C) films have led to their usage in many applications requiring protective overcoats and thin-film structures demonstrating high strength, optical transparency in the visible and near-infrared wavelength range, thermal stability, chemical inertness, and biocompatibility [1-6]. In principle, carbon atom hybridization is characterized by three different atomic bonding configurations $(sp^3, sp^2, and sp^1)$, with most a-C films exhibiting predominantly either graphite-like (sp^2) or diamond-like (sp^3) carbon microstructures [7], depending on deposition conditions. The amorphous structure and most properties of a-C films are closely correlated to the fraction of sp^3 bonding, which can be tailored by adjusting the film growth conditions and doping with various elements, such as hydrogen, nitrogen, and metallic elements [8-11]. The superior tribomechanical properties (e.g., low friction and high hardness) of a-C films with significant sp^3 bonding fractions have led to their extensive use in a wide range of applications where preserving the substrate integrity and minimizing friction at contact interfaces are of critical importance to the reliability and operation efficiency of contact-mode electromechanical devices and mechanical components [12,13].

The performance of *a*-C films under various ambient conditions is another critical factor affecting their effectiveness as protective overcoats in harsh environments, where maintaining the thermal stability and chemical inertness of thin-film structures is challenging. The environmental response of *a*-C films can be generally characterized by changes in the morphology, microstructure, and properties, depending on the temperature, atmosphere, and type of dopant(s). For instance, the decrease of the optical gap and resistivity of *a*-C films due to thermal annealing has been correlated to the mobility of *sp*² sites and the growth of larger aromatic clusters [14].

The increasing interest to apply *a*-C films as protective, low-friction overcoats in many pioneering technologies has concentrated the attention of researchers on the structural stability, oxidation resistance, and tribological properties of a-C films under different environmental conditions, particularly for elevated-temperature applications. Characteristic application examples where the thermal stability of *a*-C films is of critical importance include optical data storage, heat-assisted magnetic recording, and low earth orbit spaceships, in which operation at high temperature, oxidation due to laser heating, and high-speed particle collision, respectively, can be detrimental to the endurance and functionality of the protective film [15-17]. Elevated temperatures may destabilize the microstructure and degrade the properties of a-C films by promoting sp^3 -to- sp^2 rehybridization, consequently lessening the film's ability to effectively protect the substrate material [18,19]. Experimental and computational studies have revealed the

existence of a threshold temperature in the range of 200-350 °C above which a-C films undergo significant structural changes [20-22]. Increasing the sp³ fraction and doping with certain elements, such as silicon, have been proven effective methods for enhancing the thermal stability of a-C films by stabilizing the carbon atoms in the sp^3 hybridization state and inhibiting sp^3 -to- sp^2 rehybridization at elevated temperatures [23-25]. The significant effect of environmental conditions (e.g., humidity) on the tribological properties of *a*-C films [26,27] impelled experimental studies to be performed in vacuum and various atmospheres, including ambient and dry air, or a pure gas, such as hydrogen, nitrogen, and carbon dioxide [28,29]. Macroscopically, a-C films exhibit lower friction in ambient air than dry air and even lower friction in hydrogen and carbon dioxide atmospheres, but significantly higher friction in vacuum and nitrogen environment. The low friction of a-C films has been attributed to surface passivation by gaseous species or functional groups from the atmosphere [30,31]. The termination of the free dangling bonds at the film surface by dissociated gaseous species or functional groups may significantly reduce the adhesive force at contact interfaces. These findings have shown that although adsorption and dissociation of hydrogen, oxygen, and water molecules can readily occur at the surface of *a*-C films, nitrogen dissociation is not favored.

Although the foregoing studies have provided valuable insight into the behavior of a-C films under various environmental conditions, the multiple types of carbon bonding configurations and vastly diverse operation conditions make thorough investigation of the underlying physicochemical processes expensive and often impossible. Therefore, insight into the structural changes and tribological behavior of ultrathin films exposed to different temperatures and environmental conditions requires atomic-scale approaches. The problem is further perplexed by the layered structure of a-C films grown by deposition methods that employ energetic particle bombardment [22]. In view of the challenges associated with structural characterization and quantification of the properties of films at the atomic level, atomistic computational methods have been developed to bridge the gap in fundamental knowledge about the effect of atmospheric conditions on the structural stability and tribological behavior of ultrathin films. Among various computational methods, molecular dynamics (MD) has been proven to be a particularly effective method for studying spatiotemporal structural changes in material systems at atomic and femtosecond scales. The supremacy of MD analysis over most experimental methods has enabled the procurement of basic insight into the environmental behavior of ultrathin a-C films. For example, MD simulations have shown that friction of a-C and a-C:H films is controlled by chemical reactions instigated between unsaturated carbon atoms in the film structure adjacent to the contact interface [32]. The mechanisms responsible for lowering friction via surface passivation by hydrogen, fluorine, carbon dioxide, nitrogen, and water have been studied by MD and quantum mechanics. The direct observation of bond formation and breakage and the calculation of interatomic energies in these studies have indicated that surface passivation is a consequence of the stress-induced activation and dissociation of the adsorbed molecules [28,29,33,34]. MD simulations of the tribochemical behavior of a-C films at the mesoscale have revealed tribo-emission of trace amounts of hydrocarbon molecules due to asperity contact interaction [35,36], which is difficult to track experimentally. The insight into the tribochemical characteristics of *a*-C films provided by the foregoing investigations and several others indicate that MD offers unique capabilities for examining structural and

tribochemical phenomena at the atomic level, which is the appropriate level for studying the behavior of films that are a few nanometers thick.

Despite the abundance of studies dealing with the structural stability and tribological behavior of a-C films under various environmental conditions, inclusive studies of the oxidation and tribo-oxidation processes encountered with ultrathin a-C films are sparse, despite the fact that such environmental conditions are typical in many leading-edge technologies. Therefore, the objective of this study was to perform comprehensive MD simulations of the oxidation and tribo-induced oxidation processes and the friction behavior of less than 2-nm-thick a-C films exposed to elevated temperature and oxidizing atmosphere. The MD simulations of this study comprised two phases. First, oxidation of ultrathin a-C films with low or high sp3 contents deposited on a diamond substrate was simulated to investigate the effect of the oxygen kinetic energy on the oxidation resistance of different film nanostructures. Second, normal and sliding contact of similar ultrathin a-C films with or without adsorbed oxygen was simulated for a range of surface interference (normal load) to elucidate the friction behavior and the effect of the sliding process on tribo-induced oxidation of the ultrathin a-C films. The simulation results presented below establish a computational framework that can be useful in guiding the development of low-friction and oxidation-resistant protective overcoats for elevatedtemperature and oxidizing environments.

5.2 Computational Procedure

5.2.1 Oxidation model

A $15.13 \times 15.13 \times 92$ Å simulation box with periodic *x*- and *y*-boundary conditions was used in the oxidation simulations. In the first phase of these simulations, ultrathin *a*-C films were grown on a $15.13 \times 15.13 \times 8$ Å diamond (100) substrate by the sequential deposition of single carbon atoms of various kinetic energies. Energetic carbon atom implantation resulted in crystalline-to-amorphous transformation of the top 5 Å of the diamond substrate. The subsequent carbon atom impingement onto the amorphized diamond sufface led to the growth of an *a*-C film. Thus, the MD model encompassed a three-layer architecture consisting of crystalline diamond substrate, amorphous diamond (intermixing) layer, and ultrathin *a*-C film. For simplicity, the amorphous diamond layer and the *a*-C film will be hereafter referred to as the amorphous carbon structure. The overall *sp*³ content of the *a*-C film was varied by changing the kinetic energy of the incident carbon atoms. The deposition procedure is quite similar with that in Section 4.2.2.2, beside the substrate material.

In the second phase of the oxidation simulations, 500 oxygen molecules were randomly generated in the space above the *a*-C film, as shown in Fig. 5.1. The bottom atoms of the diamond substrate were fixed to simulate a semi-infinite medium, whereas the remaining carbon atoms were allowed to move freely; however, they were also assigned to a Berendsen thermostat with a temperature damping constant of 10 fs to maintain the temperature in the film at 573 K during the simulation. The total number of particles in this MD model is ~1800, of which ~800 particles are carbon atoms. The oxidation process was simulated for 1000 ps using a time step of 0.2 fs. While the number of

carbon atoms involved in the oxidation process must be controlled to avoid excessive computation, the number of oxygen molecules must be sufficiently high to maintain a continuous carbon-oxygen interaction process and a realistic computation time. The kinetic energy of the oxygen molecules was varied in the range of 1-20 eV.

As stated in Section 2.2.3, an empirical reactive force-field method, termed ReaxFF, which allows for fully reactive atomistic scale MD simulations that encompass chemical reactions, was used in the present study [37]. The input parameters of the ReaxFF interatomic potential are usually obtained by fitting a training data set of both quantum mechanics and experimental data. The combination of energy accuracy and low computation cost makes the ReaxFF method suitable for chemically reactive systems. The input parameters of the ReaxFF potential used in this study were quoted from the literature [38].

5.2.2 Tribo-oxidation model

To investigate the normal and sliding contact behaviors of ultrathin *a*-C films in vacuum and oxygen atmosphere, a $15.13 \times 15.13 \times 65$ Å simulation box with periodic x- and yboundary conditions was used to simulate sliding between two similar a-C films (Fig. 5.2) that were grown in the same way as that described in the previous section. Similarly with the oxidation model, the bottom atoms of the lower film and the top atoms of the upper film were fully constrained to simulate semi-infinite media, whereas the remaining atoms were left unconstrained, but assigned to Berendsen thermostats with a temperature damping constant equal to 20 fs to maintain the film temperature at 573 K. Initially, the two films were placed apart by a distance of 5 Å. In the simulations of normal contact in vacuum, the upper film was displaced towards the stationary lower film at a constant speed of 40 m/s up to a maximum surface interference of 6.4 Å. After allowing the system to equilibrate for 10 ps at the maximum interference, the upper film was retracted at the same constant speed until it fully detached from the lower film. In the simulations of sliding contact in vacuum, the upper film was again displaced towards the lower film at a constant speed of 40 m/s to a maximum surface interference in the range of 1-6 Å and after equilibrating for 10 ps at the set interference it was traversed laterally at a constant speed of 20 m/s while keeping the interference fixed. After sliding for a total distance of 40 Å, i.e., more than two times the lateral dimension of the simulation box, the two films were fully separated by retracting the upper film at the same speed as for the loading. To simulate normal and sliding contact in an oxidizing environment, the upper and lower a-C films were initially kept in an oxygen atmosphere of 573 K that contained enough oxygen molecules until oxygen adsorption reached an equilibrium, then the excess free oxygen molecules were removed from the simulation box, and normal or sliding contact was simulated using the same parameters as in the vacuum simulations.

In the foregoing simulations, carbon-carbon interaction was described by the Tersoff potential whose parametrization is detailed elsewhere [39] and its ability to simulate *a*-C systems has been verified previously [22,40]. The carbon-oxygen and oxygen-oxygen interactions were described by the Lennard-Jones potential with parameters given elsewhere [41,42].

5.3 Results and discussion

5.3.1 Oxidation mechanism

Fig. 5.3 shows the carbon loss density and the adsorbed oxygen density versus oxygen kinetic energy for an a-C film with 66% sp^3 content. The carbon loss represents the carbon atoms removed from the film in the form of gaseous products, i.e., CO or CO₂, and may be inferred as being indicative of the depletion of the structural integrity and protection performance of the film. While both carbon loss and oxygen adsorption occurred with the onset of oxidation, they demonstrated distinctly different dependencies on oxidation time and oxygen kinetic energy. As shown in Fig. 5.3(a), the carbon loss density increased monotonically with time showing a strong dependence on oxygen kinetic energy. Specifically, for an oxygen kinetic energy of ≤ 7 eV, the carbon loss at the end of the simulation is less than 4% of the total carbon atoms comprising the film. In fact, the carbon loss for 1 and 3 eV is nearly zero throughout the oxidation process. For oxygen kinetic energies above 7 eV, however, the carbon loss at the end of the simulation increased proportionally with the oxygen kinetic energy; particularly, for oxygen kinetic energy equal to 10, 15, and 20 eV, the carbon atom loss is 8.0%, 20.9%, and 32.7% of the total number of carbon atoms, respectively. This reveals a critical kinetic energy of ~7 eV for continuous carbon loss due to oxidation. Fig. 5.3(b) shows that the adsorbed oxygen density reached rapidly a level at which it exhibited fluctuations that intensified with the increase of the oxygen kinetic energy. A remarkable increase of the oxygen adsorption density occurred due to the increase of the oxygen kinetic energy from 1 to 3 eV, revealing the existence of critical oxygen kinetic energy for significant oxygen adsorption. Indeed, all of the steady-state oxygen adsorption densities exhibited fluctuations in the range of 10-20 atoms/nm², except for 1 eV oxygen kinetic energy for which the steadystate oxygen adsorption density varied slightly at the 5 atoms/nm² level, implying surface saturation by adsorbing oxygen molecules independent of oxygen kinetic energy above ~ 1 eV. Importantly, oxygen surface adsorption was found to be dissociative in all simulation cases, suggesting that the oxygen bonds dissociated upon the adsorption of the oxygen molecules at the film surface. Hence, the rapid saturation of oxygen adsorption is attributed to the fixed density of dangling bonds at the film surface for oxygen atoms to attach and the dynamic equilibrium of oxygen adsorption at the simulated elevated film temperature. Since 1 eV is much less than the dissociation energy of the oxygen bond (5.15 eV) it may be inferred that the oxygen adsorption density at 1 eV was less than those at oxygen kinetic energy above 5 eV.

To examine the kinetics of the oxidation process, the carbon loss density versus time was graphed on a log-log plot, as shown in Fig. 5.4(a) for oxygen kinetic energy equal to 10, 15, and 20 eV. The parameters obtained from exponential fits to the data of each simulation are given in the inset of the figure. The plotted curves show that the coefficient A increases with the oxygen kinetic energy, whereas the exponent λ is fairly constant. Figure 5.4(b) shows sp^3 depth profiles for a 66% sp^3 film obtained before and after oxidation for 400 ps at various oxygen kinetic energies. The profiles were computed by averaging the sp^3 fraction of 1-Å-thick slices through the film thickness. The sp^3 depth profile before oxidation reveals a layered structure consisting of diamond substrate, bulk layer, and surface layer, which are characterized by nearly 100% sp^3 , roughly constant

and relatively high sp^3 , and sharply decreasing sp^3 , respectively, confirming the formation of a layered structure in the film-growth simulation phase, in agreement with experimental findings of a layered *a*-C film structure produced by deposition methods that use energetic particles as film precursors [43]. Notably, despite the decrease of the film thickness due to the significant loss of carbon after oxidation for 400 ps, the layered film structure was still preserved. The high sp^3 content of the bulk layer is a consequence of a highly compressive mechanical environment instigated by the intense carbon atom bombardment during film growth and the spatial constraint imposed by above-deposited atoms, whereas the low sp^3 content of the surface layer is due to the development of a tensile stress due to the effects of considerably less atomic bombardment compared to the bulk layer and surface relaxation due to the reduced spatial constraint of near-surface carbon atoms [40]. During the oxidation process, the energetic oxygen molecules dissociating at the film surface upon adsorption continuously consume the carbon atoms of the surface layer, causing the surface layer to become thinner. Because the latter weakens the spatial constraint on the bulk layer, it relaxes its top region, activating a phase transformation process characterized by sp^3 -to- sp^2 rehybridization, which converts the top region of the bulk layer to a new surface layer. Since this process maintains a fairly constant thickness of the surface layer, the high sp^3 hybridization in the rest of the bulk layer is preserved due to the constraint applied by the reforming surface layer. The foregoing process is revealed by the sp^3 depth profiles of the oxidized *a*-C film shown in Fig. 5.4(b).

It is widely accepted that a-C films with high sp^3 contents demonstrate a better protection performance because they exhibit improved mechanical properties. To examine the film structure effect on its oxidation resistance, simulations were performed with ultrathin a-C films with 39% and 66% sp³ contents for oxygen kinetic energy fixed at 20 eV. Henceforth, these two films will be referred as low and high sp^3 films, respectively, for simplicity. The sp³ depth profiles of the foregoing films obtained after oxidation, shown in Fig. 5.5(a), illustrate surface layers of similar thickness characterized by a sharply decreasing sp^3 content towards the film surface; however, the sp^3 content of the bulk layer of the high sp³ film is almost two times higher than that of the bulk layer of the low sp^3 film. Interestingly, the curves of the carbon loss density versus time, shown in Fig. 5.5(b), reveal that the rates of carbon loss of the two films are almost identical despite the vastly different overall and bulk layer sp^3 contents. These results suggest that the oxidation of ultrathin a-C films is confined within the surface layer. Because the formation of a surface layer with low *sp*³ content is inevitable due to the effects of surface relaxation and less intense bombardment by energetic atoms during film growth mentioned earlier, the results show that increasing the overall or bulk layer sp^3 contents will not necessarily enhance the film's oxidation resistance.

5.3.2 Friction characteristics and tribo-oxidation

Significant discrepancies in the friction behavior of a-C films are often encountered due to differences in structure and operation conditions. For instance, the coefficient of friction of various types of a-C films has been reported to vary in the wide range of 0.003-0.7 [44]. In particular, it is well established that the structure, testing method, and environmental conditions can strongly affect the tribochemical behavior of a-C films.

The combined effects of the aforementioned factors further perplex the tribochemical behavior when the film thickness is a few nanometers and structure changes and/or chemical reactions occur rapidly, making experimental tracking a formidable task. The MD simulation results of normal and sliding contact presented in this section provide insight into the spatiotemporal changes of the friction, nanostructure, and oxidation behavior of ultrathin *a*-C films in vacuum and oxygen atmosphere.

Fig. 5.6 shows the variation of the normal force with the surface interference for two similar *a*-C films having either low or high sp^3 contents brought into normal contact in vacuum and oxygen atmosphere. The results reveal significant differences and similarities of film interaction that cannot be easily captured experimentally. The hysteresis area between the loading (red) and unloading (blue) force paths indicates the commencement of irreversible deformation and, in turn, changes in the film nanostructure. The maximum positive (repulsive) normal force of the high sp^3 films is greater than that of the low sp^3 films in both vacuum and oxygen atmosphere simulation cases. This difference is attributed to the increase of the film stiffness and deformation resistance with increasing sp^3 content. The significant negative (attractive) normal forces encountered during unloading in the subzero surface interference range reveal the existence of strong attractive forces between the withdrawing films, attributed to their high affinity to bond to each other during loading. Henceforth, the maximum attractive force at which surface separation is instigated will be referred to as the adhesion force. Interfacial attractive forces may result from several types of bonding, including covalent bonds between free or dangling bonds at the film contact interface. This type of attractive force has been observed in the nanoindentation of *a*-C films by a diamond tip [45]. The film separation during unloading is a continuous process characterized by the gradual breakage of bonds at the film contact interface. The adhesion force drops rapidly to zero upon the full detachment of the low sp^3 films (Figs. 5.6(a) and 5.6(b)), due to the relatively abrupt instigation of bond breaking, whereas for the high sp^3 films the adhesion force decreases rather gradually (Figs. 5.6(c) and 5.6(d)) due to the progressive breakage of the bonds. The latter trend of the adhesion force may be attributed to a more extensive destruction of the surface layer of the high sp^3 films due to more carbon atom transfer during the retraction stage. In contrast to the vastly different maximum repulsive forces, the adhesive forces are almost identical in all four simulation cases, suggesting a high film reactivity due to a large amount of unsaturated carbon atoms at the film surfaces, even in the oxygen atmosphere. These unsaturated carbon atoms can easily form new bonds across the film contact interface during loading, regardless of the overall sp^3 film content. This is because both low and high sp^3 films possess similar sp^2 -dominted surface layers (Fig. 5.5(a)). It is further noted that the adhesion force of the high sp^3 films was encountered sooner during unloading compared to the low sp³ films, presumably due to the greater elastic strain energy release of the stiffer films with high sp^3 content. Another interesting observation is that oxygen adsorption does not appear to have an effect on the magnitude of the adhesion force. Different from hydrogen and water vapor, oxygen shows very diverse effects on the surface passivation of *a*-C films [46]. The dissociative oxygen adsorption due to the elevated temperature in the oxygen atmosphere simulations promoted oxygen adsorption at the film surface in the form of atomic oxygen. At equilibrium, the oxygen atoms adsorbed at each film surface were fewer than the surface carbon atoms due to the high temperature of the films, resulting in partial surface passivation. Thus, because of the dependence of the adhesion force on partial surface coverage and the larger van der Waals diameter of the oxygen atom than the carbon atom bond length, a similar adhesion force is encountered in vacuum and oxygen atmosphere [46,47].

The significantly more dynamic sliding process than normal contact makes experimental tracking of changes in the structure and tribological properties of ultrathin films even more challenging. The variations of the normal force, friction force, and friction coefficient with sliding distance in vacuum and oxygen atmosphere, shown in Figs. 5.7 and 5,8, respectively, provide insight into the contact behavior and the evolution of friction during sliding. In addition, the sliding simulation cases for low and high sp³ a-C films, 6 Å interference, and vacuum or oxygen atmosphere reveal the occurrence of atom intermixing and a continuous formation and breakage of bonds at the contact interface. As expected, the normal force increases with the surface interference in all simulations (Figs. 5.7(a) and 5.7(d), 5.8(a) and 5.8(d)). Alternatively, the friction force shows a twostage response in all cases, that is, an initial transient stage where the friction force increases rapidly up to a sliding distance of ~ 10 Å and a steady-state stage characterized by significant force fluctuations (Figs. 5.7(b) and 5.7(e), 5.8(b) and 5.8(e)). The intense surface atom interactions occurring during the transient stage of sliding due to the highly reactive surfaces lead to the repetitive formation and breakage of bonds and the rearrangement of surface atoms. In fact, the film contact interface was indistinguishable at the end of the transient stage of sliding due to the intermixing of the atoms of the surface layers of the sliding films. The rearrangement of the surface atoms also explains the decrease of the normal force with increasing sliding distance for the low sp^3 films at large interference (i.e., 4 and 6 Å in Figs. 5.7(a) and 5.8(a)). During sliding, the atoms in the less dense film surface migrate to lower energy sites, relaxing the normal force in the low sp^3 films at large interference. A relaxation of the normal force of the high sp^3 films (Figs. 5.7(d) and 5.8(d)) did not occur due to the considerably less free space for the rearrangement of surface atoms produced by the more intense compressive stress field generated in the stiffer nanostructures of these films.

Shear-induced breakage of interface bonds occurs during sliding as the shear surface traction overcomes the attractive forces. Thus, progressively more intense fluctuations of the friction force were instigated with increasing interference as new bonds were disrupted and formed during sliding. Because of the more pronounced fluctuations of the friction force than the normal force, the friction coefficient exhibited even more intense fluctuations after the initial transient stage of the friction force. The decrease of the average steady-state friction coefficient with increasing surface interference (normal force), shown in Figs. 5.7(c), 5.7(f), 5.8(c), and 5.8(f), reveals a nonlinear relation between normal and friction force. A nonlinear friction-normal force relation has also been observed in a previous study [48] and is indicative of the breakdown of Amontons' first law of friction at the atomic level. Moreover, a small variation of the friction force due to sliding of an active *a*-C film surface against a diamond surface has been reported for a wide range of the normal load [47].

The simulation results shown in Fig. 5.9 illuminate the effects of environment and sp^3 fraction on the dependence of the normal force on surface interference and the friction behavior on normal load. The monotonic increase of the normal force with the surface

interference (Figs. 5.9(a) and 5.9(d)) is attributed to a hardening effect due to the densification of the compressed films and the greater contribution of the stronger bulk layer to the penetration resistance that became more pronounced with the increase of the surface interference. The higher normal force of the high sp^3 films than the low sp^3 films at a given interference is attributed to the proliferation of the deformation resistance with sp^3 hybridization, in agreement with the loading paths of normal force shown in Fig. 5.6. The higher normal and friction forces in oxygen atmosphere than those in vacuum are ascribed to the force contributed by the adsorbed oxygen atoms. As mentioned earlier, the friction force undergoes more significant variations during sliding compared to the normal force (Figs. 5.7 and 5.8). The nonlinear relation between the normal and friction forces reflected by the nonlinear variation of the friction coefficient with the normal load (Figs. 5.9(c) and 5.9(f)) indicates a deviation of atomic-scale friction from the classical Amontons' friction theory according to which the friction force arising between two sliding macroscopic bodies is linearly proportional to the normal force due to the constancy of the friction coefficient [49]. However, power-law (Hertz theory) or sublinear (Maugis-Dugdale model) relations between friction and normal forces [50] have been presented in adhesion-based theories. The results shown in Figs. 5.9(b) and 5.9(e) for low and high sp^3 films sliding in vacuum and oxygen atmosphere, respectively, reveal a sublinear relation between normal and friction forces for a normal force less than 200 eV/Å, in agreement with the foregoing adhesion-based friction theory [50]. The existence of a sublinear force relation is also supported by the nonlinear decrease of the friction coefficient with normal force (Figs. 5.9(c) and 5.9(f)). The very high friction coefficients obtained for a low normal force are illustrative of the differences between macroscopic and atomic-scale friction, where long-range attractive forces contribute significantly to the magnitude of the applied normal force. The lower steady-state friction coefficients obtained in the low range of normal force for sliding in oxygen atmosphere than vacuum are attributed to adsorbed oxygen atoms that reduced the number of the stronger carbon-carbon bonds that readily formed in vacuum.

A significant oxidation effect on the nanostructure (hybridization state) of the a-C films was found under oxidizing conditions that did not involve surface contact (Fig. 5.4(b)). The shear traction generated by the sliding process may produce even more pronounced structural changes, especially for a large surface interference (high normal force). To investigate the progression of structural changes through the film thickness due to sliding, sp^3 depth profiles of both low and high sp^3 films were obtained at different stages of sliding in vacuum (to avoid complication from adsorbed oxygen atoms) and also after film separation for a surface interference equal to 1 and 6 Å, and the results are shown in Fig. 5.10. A significant difference between the sp^3 depth profiles of non-oxidized a-C films obtained before the films were brought into contact (Fig. 5.4(b)) with those of similar films brought into normal contact, i.e., zero sliding distance, (Figs. 5.10(c) and 5.10(d)) is that the latter films exhibited nonzero sp^3 fractions at their surfaces, indicating sp^3 hybridization of unsaturated surface carbon atoms under the compressive mechanical environment produced by the normal force. Sliding induced the formation and breakage of carbon atom bonds and the rearrangement and intermixing of carbon atoms in the proximity of the sliding contact interface. The intense atomic interactions affected not only the near-surface region of the films but also regions remote from the contact interface, especially for a relatively large surface interference (high normal force). Indeed,

a noticeable drop in sp^3 hybridization occurred in the depth range of 4-12 Å with increasing sliding distance and, more significantly, after film separation for a surface interference equal to 1 Å (Fig. 5.10(c)). A more dramatic decrease of the sp^3 fraction in the depth range of 4-9 Å occurred with the increase of the surface interference to 6 Å (Fig. 5.10(d)) after sliding for a distance of 20 Å. The significant structural changes remote from the contact interface reveal shear-induced sp^3 -to- sp^2 rehybridization in the bulk layer of the high sp^3 films (Figs. 5.10(c) and 5.10(d)). However, structural changes in the bulk layer of the low sp^3 films appeared to be minimal for both small and large surface interferences (Figs. 5.10(a) and 5.10(b)), presumably because sp^2 hybridization is energetically more stable than sp^3 hybridization. This is also evidenced by the similar sp^3 depth profiles of the high and low sp^3 films obtained after sliding for 40 Å (Figs. 5.10(d)) and 5.10(b), respectively). After film separation, all of the sp^3 depth profiles showed an increase in film thickness due to irreversible film stretching after the detachment of the films. Despite sliding-induced sp^3 -to- sp^2 rehybridization, the friction did not decrease because of the highly reactive film surfaces produced by the continuous breakage of surface bonds and the relatively short sliding distance for inducing extensive shearinduced surface graphitization [51].

Although oxygen surface adsorption did not produce a first-order effect on friction because of the incomplete film surface coverage (passivation), shear-induced chemical reactivity resulted in tribo-oxidation in the sliding simulations. This was demonstrated by the changes in the average oxygen coordination number of adsorbed oxygen atoms, calculated by averaging the numbers of nearest neighboring carbon atoms of all adsorbed oxygen atoms. Fig. 5.11 shows the average oxygen coordination number before and after sliding of low and high sp^3 films for a surface interference in the range of 0-6 Å. The increase of the average oxygen coordination number with surface interference indicates that film interpenetration during normal contact enhanced carbon-oxygen bond formation and, in turn, the oxidation of both low and high sp^3 films. The additional significant increase of the average oxygen coordination number caused by sliding illuminates the important role of shear traction in tribo-oxidation. For sliding of both low and high sp^3 films at a surface interference of 6 Å, the average oxygen coordination number is close to 2, implying chemical reaction of almost all oxygen atoms. These results confirm that tribo-oxidation reactions activated by persistent sliding in oxidizing environments can greatly modify the nanostructure and tribological properties of *a*-C films.

5.4 Conclusions

MD simulations were performed to elucidate the effects of nanostructure (hybridization state), surface interference (normal load), and oxygen adsorption (surface reactivity) on the oxidation behavior and friction characteristics of ultrathin *a*-C films. The MD analysis of film oxidation by energetic oxygen molecules revealed the existence of a critical oxygen kinetic energy below which carbon loss did not occur and that steady-state oxygen adsorption was independent of oxygen kinetic energy due to the saturation of the film surfaces by oxygen. Film oxidation comprised the removal of carbon atoms from the low sp^3 surface layer of the films as gaseous species. The relaxation of the surface layer by the oxidation process prompted sp^3 -to- sp^2 hybridization in the topmost region of

the bulk layer that replenished the surface layer. This oxidation mechanism perpetuated itself, resulting in an exponential relation of the carbon loss rate. These simulations confirmed that oxidation of ultrathin *a*-C films possessing a layered structure comprised of an sp^3 -rich bulk layer and an sp^2 -rich surface layer is a surface-dominated process controlled by the oxidation and removal of the surface layer and its progressive reformation via a phase transformation process involving sp^3 -to- sp^2 rehybridization that was instigated in the bulk layer adjacent to the interface with the surface layer.

The MD results of normal contact between identical *a*-C films revealed similar adhesion forces in vacuum and oxygen atmosphere due to the partial passivation of the contacting film surfaces by oxygen. Simulations of *a*-C films with similar nanostructures (hybridizations) sliding against each other in vacuum or oxygen atmosphere demonstrated intensifying normal and friction forces and decreasing friction coefficient with increasing surface interference, revealing a departure from Amontons' first friction law at the atomic scale. Atomic rearrangement and intermixing in conjunction with shearinduced sp^3 -to- sp^2 rehybridization occurred during sliding, especially for high sp^3 *a*-C films. Relatively higher friction coefficients were obtained for sliding in vacuum than oxygen atmosphere due to the formation of more carbon-carbon bonds compared to the partially oxygen-passivated film surfaces in oxygen atmosphere. Sliding (shear) traction enhanced film oxidation (tribo-oxidation) even in an oxygen lean environment. From a fundamental tribo-chemistry perspective, the present study provides a computational framework for investigating other thin-film systems exposed to various oxidizing and contact conditions and useful guidance for the design of tribo-oxidation experiments.

5.5 References

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Figure 5.1 The MD model of *a*-C film oxidation comprised of *a*-C film with $66\% sp^3$ (red and yellow atoms) and 500 oxygen molecules (white atoms). The red carbon atoms at the bottom of the film are fixed to simulate a semi-infinite diamond bulk substrate. The yellow atoms are unconstrained but are also assigned to a Berendsen thermostat to control the temperature. The kinetic energy of the oxygen molecules is controlled by a second Berendsen thermostat.



Figure 5.2 MD sliding models of two identical *a*-C films interacting in vacuum (left) and oxygen atmosphere (right). The green and red atoms at the bottom of the upper and lower films are fixed to simulate semi-infinite diamond substrates. The white and yellow atoms of the films are unconstrained, but they are also assigned to Berendsen thermostats to control the temperature during the simulation. The blue atoms are oxygen atoms adsorbed into the film surfaces during sliding in the oxygen atmosphere. The simulation comprises the sequential phases of indentation and sliding, involving the movement of the upper film in the *z*-direction and subsequent sliding in the *y*-direction, while the bottom film is kept stationary.



Figure 5.3 (a) Carbon loss density and (b) oxygen adsorption density versus oxidation time for an *a*-C film with 66% sp^3 and oxygen kinetic energy in the range of 1-20 eV. The carbon atoms leave the *a*-C film as CO and CO₂ gaseous products. The initial surface area density of the *a*-C film is 270 atoms/nm².


Figure 5.4 (a) Carbon loss density versus oxidation time and (b) depth profiles of sp^3 content of *a*-C film with 66% sp^3 before and after 400 ps of oxidation for oxygen kinetic energy equal to 10, 15, and 20 eV. The zero depth position in (b) corresponds to the bottom atomic plane of the film (the fixed red atoms in Fig. 5.1).



Figure 5.5 (a) Depth profiles of sp^3 content and (b) carbon atom loss density of *a*-C films with 39% and 66% sp^3 for an oxygen kinetic energy equal to 20 eV. The zero depth position in (a) corresponds to the bottom atomic plane of the film (fixed red atoms in Fig. 5.1).



Figure 5.6 Normal force versus surface interference for two identical *a*-C films with (a),(b) 39% sp^3 and (c),(d) 66% sp^3 interacting in vacuum and oxygen atmosphere. The negative force values represent the adhesion (attractive) force generated during the retraction phase of the simulation (1 eV/Å =1.6 nN).



Figure 5.7 Normal force, friction force, and coefficient of friction versus sliding distance and interference for two identical *a*-C films with (a)-(c) 39% sp^3 and (d)-(f) 66% sp^3 sliding against each other in vacuum (1 eV/Å =1.6 nN).



Figure 5.8 Normal force, friction force, and coefficient of friction versus sliding distance and interference for two identical *a*-C films with (a)-(c) 39% sp^3 and (d)-(f) 66% sp^3 sliding against each other in oxygen atmosphere (1 eV/Å =1.6 nN).



Figure 5.9 (a)&(d) Steady-state normal force versus interference and (b)&(e) friction force and (c)&(d) coefficient of friction versus normal force of two identical *a*-C films with 39% and 66% *sp*³ sliding against each other in vacuum and oxygen atmosphere (1 eV/Å = 1.6 nN).



Figure 5.10 Depth profiles of sp^3 content of two identical *a*-C films with 39% and 66% sp^3 sliding against each other in vacuum for surface interference equal to1 and 6 Å obtained after sliding for a distance equal to 0, 20, and 40 Å and after film separation.



Figure 5.11 Average coordination number of oxygen atoms adsorbed into the surfaces of two identical *a*-C films with 39% and 66% sp^3 versus surface interference. The increase of the coordination number with surface interference indicates an increase of oxygen-carbon bonds, implying an enhancement of film oxidation with intensifying film interaction instigated by the sliding process.

Chapter 6. Single-step metal-catalyzed synthesis of hybrid planar graphene–orbicular graphitic carbon structures using an amorphous carbon thin film as a precursor

6.1 Introduction

Carbon forms allotropes characterized by different shapes and bonds associated with various hybridizations. Among different carbon allotropes, graphene and amorphous carbon (a-C) synthesized by physical vapor deposition (PVD) exhibit unique optical, thermal, electrical, and mechanical properties. Graphene consists of carbon atoms arranged in a hexagonal lattice, can exist as a monolayer or few layers of graphite, and exhibits extraordinary physical properties, including high conductivity, transparency, and fracture strength. Because of its unmatchable properties, graphene has been used in numerous emerging technologies, such as electronics, photonics, sensors, and membrane structures [1]. The *a*-C lacks long-range order, comprises multiple types of bonding configurations, i.e., tetrahedral (sp^3) , trigonal (sp^2) , and linear (sp^1) , and its physical characteristics are principally controlled by both the dominant hybridization state and the existence of disorders, specifically the sp^2/sp^3 fraction and topological and/or structural disorders [2,3]. The combination of excellent tribomechanical properties and good thermal stability of a-C makes it an ideal material for applications requiring durable overcoats for protecting precious substrates against damage, mechanical wear, and corrosion, or a solid lubricant layer to minimize frictional traction [4-7].

Despite significant advances in *a*-C film deposition techniques, most of which utilize graphite as a precursor, the synthesis of graphene is characterized by completely dissimilar precursors (i.e., solid carbon like graphite, or carbon-containing gases like methane and acetylene) and different mechanisms. Numerous methods of graphene growth have been developed, including mechanical exfoliation and cleavage [8], anodic bonding [9], chemical exfoliation [10,11], chemical vapor deposition (CVD) [12], thermal decomposition of SiC [13], precipitation from single-crystal transition metals [14], and other less common methods [15]. Among various methods used to synthesize graphene, the transformation of non-graphitic to graphitic carbon structures has attracted significant attention because of its simplicity, low cost, and high efficiency [16-20]. In this transformation, metastable structures (e.g., *a*-C films and diamond nanoparticles) act as crystallization nuclei to instigate the growth of a graphitic structure under conditions of direct thermal annealing. However, the graphitization yield of this method is low and the extremely high annealing temperature (~3300 °C) and high pressure make it a high energy consuming process [21].

To overcome the limitations of direct thermal annealing, transition metals and alloys have been used as catalysts to enhance the growth and improve the crystallinity of graphitic structures, enabling the transformation from non-graphitic to graphitic carbon at a temperature as low as 600 °C [22]. This transformation process can be explained by the precipitation theory [23] according to which, carbon atoms diffuse into a metal layer at an elevated temperature and during cooling they precipitate out in the form of graphitic carbon as the solid solubility decreases [24,25]. However, the applicability of the precipitation theory to graphitic carbon transformation has been debated in recent years, principally because in the light of observed graphitic carbon nucleation under conditions of constant or even rising temperature, which dismisses the nucleation of graphitic carbon based on the core process of precipitation theory, that is, cooling-induced supersaturation [26,27]. Indeed, the nucleation and growth of graphitic carbon is a surface-catalyzed process for gaseous carbon sources, such as those usually used in CVD, or a bulk diffusion process for solid carbon sources, both of which do not rely on cooling [27,28]. The current perception is that the formation of graphitic carbon in the presence of transition metals is a consequence of metal-catalyzed crystallization. The nucleation and growth of graphene in the presence of a catalytically active transition metal has been studied by in-situ transmission electron microscopy (TEM) [27]. Although the nucleation and growth of graphene have been attributed to metal catalyzation, non-equilibrium precipitation of excess carbon also occurs during cooling, resulting in inhomogeneous graphene growth [28]. This suggests that the synthesis of graphitic carbon using transition metals may be a two-step process involving metal-catalyzed crystallization followed by precipitation-induced growth.

Graphitic carbon may comprise not only planar graphene but also molecules demonstrating different morphologies. For instance, carbon nanoribbons [29], nanotubes and fullerene [30], and 3D graphitic carbon architectures [31-34] can be synthesized by manipulating basic forms of carbon and/or controlling the growth conditions. In this study, we report a facile, one-step process of metal-catalyzed synthesis of a hybrid microstructure consisting of orbicular graphitic carbon (OGC) on top of planar graphene (PG). This microstructure was produced by thermal annealing, using a PVD-deposited *a*-C film as the carbon source and a film of a transition metal as the catalyst. The morphology of the grown graphitic carbon was characterized by scanning electron microscopy (SEM), high-resolution TEM, and electron energy loss spectroscopy (EELS), whereas the graphitic carbon structure was examined by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). A plausible mechanism of graphene growth is proposed in the context of the obtained experimental results and observations.

6.2 Experimental methods

6.2.1 Specimen fabrication

Films of a NiFe alloy with a thickness of ~20 nm were synthesized on Si(100) substrates in a radio-frequency (RF) sputter deposition apparatus (Perkin-Elmer, Randex 2400) using a hot-pressed, sintered Ni-rich (>90 wt% Ni) NiFe target with a diameter of 20 cm. The deposition conditions were 250 W RF forward power, 3 mTorr working pressure, 30 sccm Ar flow rate, and 0.4 min deposition time. Subsequently, 17-nm-thick *a*-C films were deposited onto the NiFe-coated Si samples in a custom-made filtered cathodic vacuum arc (FCVA) system using a high purity (99.99 wt%) graphite target with a diameter of 35 mm under working conditions of ~10⁻⁷ Torr base pressure, 1.483 × 10¹⁹ ions/m²·s ion flux and -80 V substrate bias voltage. These FCVA deposition conditions yielded a uniform *a*-C film that covered the whole NiFe surface [35]. Finally, the Si/NiFe/*a*-C stacks were placed in a rapid thermal annealer (AccuThermo AW610 RTP) and heated at 650 °C for 2.5 min in Ar atmosphere.

6.2.2 Microanalysis

Raman spectroscopy was performed with a 532-nm-wavelength laser to investigate *a*-C transformation to graphitic carbon. High-magnification SEM images obtained with an FEI Quanta 3D FEG microscope were used to identify changes in the surface morphology due to graphene formation and metal segregation during thermal annealing. XPS analysis was performed with a PHI 5400 XPS spectrometer using monochromatic Al K α radiation. TEM and EELS studies with cross-sectional stack samples were carried out with an FEI Tecnai F20 microscope operated at 200 kV equipped with an aberration-corrected condenser and a Gatan imaging filter. More information about the microanalysis instruments has been demonstrated in Section 2.4. The cross-sectional TEM samples were prepared using a wedge polishing method detailed elsewhere [36]. For the analysis of the Raman, XPS, and EELS spectra, multiple measurements were obtained from three different locations of each sample to ensure the repeatability of the results.

6.3 Results and discussion

Fig. 6.1(a) shows Raman spectra of *a*-C films obtained before and after thermal annealing that confirm the formation of graphitic carbon. The Raman spectrum of the as-grown a-C film exhibits a broad peak in the range of 1100–1800 cm⁻¹, which is indicative of the formation of a-C. The spectrum was fitted with two Gaussian distributions assigned to D and G peaks centered at 1409 and 1579 cm⁻¹, respectively (Fig. 6.1(b), top spectrum). The relatively low intensity of the D peak indicates the presence of few disordered sp^2 clusters in the as-grown film, which is a characteristic feature of sp^3 -rich *a*-C films [3,37]. A comparison of the Raman spectrum of the as-grown *a*-C film with those of *a*-C films deposited under similar conditions using the same FCVA system [38] indicated that the as-grown *a*-C film was rich in sp^3 hybridized carbon, in agreement with sp^3 estimates derived from EELS measurements [35]. The sharp apex of the G peak may be attributed to isolated sp^2 -bonded defects in the extended sp^3 matrix [39]. The Raman spectrum of the same *a*-C film obtained after thermal annealing (Fig. 6.1(a)) comprises four distinct peaks that were fitted with Lorentzian distributions. These peaks are referred to as the D (1362 cm^{-1}) , G (1589 cm^{-1}) , 2D (2696 cm^{-1}) , and D+D' $(\sim 2950 \text{ cm}^{-1})$ peaks (Fig. 6.1(b), bottom spectrum). The G and 2D peaks are characteristic of graphene. Because Raman spectroscopy is sensitive to sp^2 hybridization, the higher intensity and upward shift of the G peak in the Raman spectrum of the thermally annealed *a*-C film imply a carbon structure with increased sp^2 hybridization. This is evidence for the transformation from sp^3 -rich *a*-C to graphitic carbon. The D peak is usually due to a broken crystal symmetry and illuminates the existence of defects or grain boundaries in graphitic crystalline regions. The 2D peak is the second-order overtone of the D peak, may exist even in the absence of defects, and is considered to be a fingerprint of a graphitic structure. The peak centered at ~2950 cm⁻¹, referred to as the D+D' peak, is a combination of two vibrational modes of different momentum and its presence is also associated with defects in the graphitic structure [40].

The TEM images shown in Figs. 6.1(c) and 6.1(d) reveal that thermal annealing led to the formation of a hybrid film microstructure consisting of planar graphene (PG), orbicular graphitic carbon (OGC), and residual *a*-C. In particular, Fig. 6.1(c) shows PG comprised ~18 graphitic planes with a lamellar spacing of 0.368 nm, which matches that of a layered graphene structure, and residual *a*-C underneath. The in-plane size of PG was found to be several hundred nanometers (Fig. 6.2(a)). Figs. 6.1(c) and 6.2(a) show that some amorphous carbon did not transform to graphitic carbon, implying partial *a*-C to graphene transformation. The TEM image shown in Fig. 6.1(d) reveals the formation of OGC over PG, far from the Si substrate. The inset in Fig. 6.1(d) shows that the lamellar spacing of OGC is 0.370 nm. More evidence of PG growth on top of residual *a*-C and OGC formation above PG is provided by the TEM images shown Fig. 6.2(b).

Fig. 6.3 shows the deconvolution of the XPS C1s core-level spectrum of thermally annealed *a*-C film that comprises a carbon peak centered at ~284.4 eV with four Gaussian distributions, namely sp^2 C (graphitic carbon) at 284.4 eV, sp^3 C (diamondlike carbon) at 285.6 eV, C–O at 286.6 eV, and O–C=O at 288.5 eV. The profoundly higher intensity of the sp^2 peak indicates that thermal annealing led to the formation of a graphitic microstructure with an estimated sp^2 content (obtained as the $sp^2/(sp^2+sp^3)$) area fraction) equal to ~87.6%. The small sp^3 peak is attributed to diamondlike carbon embedded in residual *a*-C and the existence of sp^3 type defects in the graphitic carbon [41,42]. The minor C–O and O–C=O peaks indicate partial oxidation attributed to the sample exposure to the atmosphere during handling and transferring from the thermal annealer to the XPS. Thus, the XPS analysis provides further confirmation about the graphitization of the as-grown sp^3 -rich *a*-C film during thermal annealing.

The surface morphology of the sample provides further insight into graphitization and the role of the NiFe catalyst during thermal annealing. The smooth surface shown in Fig. 6.4(a) indicates a uniform coverage of the NiFe underlayer by the deposited a-C film. However, after thermal annealing the surface morphology exhibited roughening and dark islands surrounded by large bright areas (Fig. 6.4(b)). These changes in the surface morphology are attributed to NiFe agglomeration and Ostwald ripening, while the effect of the *a*-C film on metal agglomeration is believed to be secondary [27,43]. Fig. 6.4(c) shows high-magnification SEM images of the boxed area shown in Fig. 6.4(b), revealing a worm-like morphology for the bright area (A) and a textured morphology for the dark area (B) possessing tiny dark spots. From the carbon and metal characteristics observed under high-resolution SEM, it may be inferred that the dark and bright spots in area B are regions containing only carbon and metal agglomerates covered by carbon, respectively. The cross-sectional TEM images of Si/NiFe/a-C/Cr sample stacks obtained after thermal annealing (Figs. 6.4(d)-6.4(f)) provide evidence for the aforementioned structure changes responsible for the morphology characteristics seen in Figs. 6.4(b) and 6.4(c). Specifically, three cross-sectional structures characterize the annealed sample, i.e., pure carbon (Fig. 6.4(d)), carbon-covered NiFe (Fig. 6.4(e)), and pure NiFe agglomerate (Fig. 6.4(i)).

Raman spectroscopy produced additional evidence for a-C transformation to graphitic carbon and cross-sectional TEM images provided direct proof for the formation of OG and OGC in the thermally annealed a-C film. Insight into the role of the NiFe underlayer during the thermal annealing process is critical to understanding this transformation

process. The cross-sectional TEM images obtained after annealing (Figs. 6.1(c), 6.1(d), 6.2(a), and 6.4(d)) show the *a*-C film in direct contact with the Si substrate. Such crystallization of an amorphous structure may be explained by metal-induced layer exchange (MILE) theory. According to this theory, an amorphous film may exchange positions with a metal catalyst residing either on top or under the film, inducing amorphous-to-crystalline transformation in the film structure [44,45]. However, such layer exchange was not observed in the present study since no NiFe was found on top of the residual a-C or the graphene structures. Graphene growth parallel to the a-C/Ni interface has been attributed to an atomic level coherent match between metal and graphitic carbon [46]. However, the formation of PG in the *a*-C film remotely from the original *a*-C/NiFe interface (Fig. 6.4(d) and Fig. 6.2(a)) does not support the foregoing assertion. The rapid transformation process observed in the present study (e.g., formation of ~18 layers of graphene in only 0.5 min of thermal annealing) does not support the relatively slow transformation in the MILE process due to the low carbon solubility in transition metals, where the formation of a similar number of graphene layers is typically encountered after thermal annealing for 10-60 min at a higher temperature [44,46].

Fig. 6.5 shows cross-sectional TEM images and elemental maps of annealed Si/NiFe/a-C/Cr sample stacks elucidating the role of the NiFe underlayer and the formation of PG and OGC in the a-C film. Thermal annealing disrupted the continuity of the FeNi underlayer, resulting in the formation of metal agglomerates much thicker than its thickness (Fig. 6.5(a)). Elemental maps indicated that segregation produced Ni-rich agglomerates encased by an Fe-rich surface layer (see insets of Fig. 6.5(a)). The retraction of the NiFe underlayer explains the direct contact of the residual *a*-C film with the Si substrate (Figs. 6.4(d) and 6.2(a)). An inspection of the boundary between a metal agglomerate and residual a-C (Fig. 6.5(b)) suggests that the NiFe underlayer played a dual role revealed by the formation of Ni-rich agglomerates on top of the Si substrate and the growth of crystalline (Fig. 6.4(e)) metal silicide into the Si substrate (the black pyramidal structures). Elemental mapping showed that the metal agglomerates consisted of Ni and Fe and that the metal silicide was NiSix. Further evidence for the growth of pyramidal NiSi_x nanostructures into the surface of the Si substrate was obtained from STEM/EELS analysis (Fig. 6.6). The formation of nickel silicide at the Ni/Si interface as a result of thermal annealing is consistent with previous findings [47]. The TEM analysis of this study also revealed the preferential growth of NiSix at the NiFe/Si interface. Highresolution TEM of the bright region R1 revealed the conformal formation of PG on top of the NiFe agglomerate (Fig. 6.1(c)), validating the nucleation of PG at the NiFe/a-C boundary. The foregoing was followed by graphene growth from the nucleation site parallel to the a-C film surface, resulting in PG formation in region R2 (Figs. 6.5(b) and 6.5(c)) similar to graphene growth on top of residual *a*-C. The TEM analysis also showed that the formation of OGC was due to a mismatch-induced growth mechanism. Indeed, graphitic layers were observed to grow away from the PG surface at defect locations or grain boundaries, forming closely packed rolled graphene layers (Fig. 6.5(d)-(f)), which is the energetically favorable configuration [48]. The high intensity of the D and D+D' peaks in the Raman spectrum of the annealed sample (Fig. 6.1(b)) confirmed the presence of defects and grain boundaries in the grown graphene that acted as mismatch sites for OGC nucleation. In addition to the mismatch-induced growth mechanism of OGC, metal contamination of the PG structure and metal particles at the PG surface produced by NiFe segregation may also contribute to the formation of OGC. The presence of Fe particles at the PG surface was confirmed by elemental mapping (e.g., region R1 in Figs. 6.5(b) and 6.5(c)). Detecting the effects of the carbon solubilities in Ni and Fe and the uncontrollable metal segregation on the orientation of graphene is challenging and requires further investigation.

In the light of the obtained results, the growth mechanisms of PG and OGC in thermally annealed *a*-C films can be schematically illustrated as shown in Fig. 6.7. Segregation of the NiFe underlayer during thermal annealing resulted in the formation of NiFe agglomerates, resulting in direct contact of residual *a*-C with the Si substrate. Subsequent nucleation of PG on top of the NiFe agglomerates and OGC from defect sites and grain boundaries in the PG yielded a hybrid PG-OGC microstructure, which can be potentially used to fabricate novel 3D micro-assemblies by stacking and folding. In addition, the incorporation of NiSi_x in graphene makes the resulting structure compatible with electronic nanodevices, hence showing a potential of the NiSi_x/graphene hybrid microstructure for widespread applications [49].

6.4 Conclusions

A one-step process for synthesizing hybrid PG-OGC nanostructures using NiFe-catalyzed transformation of *a*-C thin films was developed in this study. Raman and XPS results confirmed *a*-C transformation to graphene during thermal annealing. Cross-sectional TEM and elemental mapping revealed the formation of NiFe agglomerates at the surface of the Si substrate as a result of metal migration and Oswald ripening. The produced graphitic carbon was found to comprise PG and OGC on top of the PG. SEM and cross-sectional TEM showed that the formation of PG can be attributed to graphene nucleation from NiFe agglomerates and graphene growth along the surface of the *a*-C film. The segregation of NiFe resulted in uncontrollable growth of OGC that nucleated at mismatch-induced growth sites in the PG nanostructure. Elemental mapping and STEM/EELS analysis revealed the growth of pyramidal NiSi_x nanostructure with pyramidal NiSi_x nanocrystals extending into the Si substrate presents an interesting prospect for nanoelectronic applications.

6.5 References

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Figure 6.1 (a) Raman spectra of an *a*-C film obtained before and after thermal annealing at 650 °C in Ar atmosphere. (b) The D (~1350 cm⁻¹) and G (~1580 cm⁻¹) peaks in the spectrum of the *a*-C film obtained before annealing were fitted with Gaussian distributions, whereas the D (~1350 cm⁻¹), G (~1580 cm⁻¹), 2D (~2680 cm⁻¹), and D+D' (~2950 cm⁻¹) peaks in the spectrum of the *a*-C film obtained after annealing were fitted with Lorentzian distributions. (c) & (d) Cross-sectional TEM images of thermally annealed Si/NiFe/*a*-C/Cr sample stacks revealing the formation of planar graphene (PG) and orbicular graphitic carbon (OGC) nanostructures. The magnified boxed insets show the measured spacing of the graphitic layers in the PG and OGC nanostructures. The white arrow in the TEM images points to the direction of the Si substrate. The scale bars are equal to 5 nm.



Figure 6.2 (a) Cross-sectional TEM image of a thermally annealed Si/NiFe/a-C/Cr sample stack revealing the formation of orbicular graphitic carbon (OGC) on top of planar graphene (PG) in the bulk of the a-C film capped by irregular shape graphitic carbon (GC) and (b) high-magnification TEM images showing OGC formation on top of PG in the bulk of the a-C film.



Figure 6.3 Deconvolution of the XPS C1s spectrum of an *a*-C film that was thermally annealed at 650 °C in Ar atmosphere with four Gaussian distributions assigned to sp^2 C, sp^3 C, C–O, and O–C=O.



Figure 6.4 SEM images of the surface morphology of an *a*-C film obtained (a) before thermal annealing (the small particles are contaminants from sample handling) and (b) after thermal annealing at 650 °C for 2.5 min in Ar atmosphere. (c) High-magnification images of two distinctly different regions A and B of the boxed region shown in (b). (d)-(f) Cross-sectional TEM images of Si/NiFe/*a*-C/Cr sample stacks obtained after thermal annealing at 650 °C for 2.5 min in Ar atmosphere showing (d) PG and OGC formation at the surface of the *a*-C film and (e) at the top of a NiFe agglomerate, and (f) a NiFe agglomerate in contact with the Si substrate produced by metal segregation.



Figure 6.5 Cross-sectional TEM images and elemental maps of Si/NiFe/*a*-C/Cr sample stacks obtained after thermal annealing at 650 °C for 2.5 min in Ar atmosphere revealing (a) NiFe agglomeration at the surface of the Si substrate and (b) graphene formation on top of a NiFe agglomerate and at the surface of the *a*-C film. (c) High-magnification TEM images of two regions marked as R1 and R2 in (b) illustrating the formation of graphene on top of a NiFe agglomerate (R1 region) and at the surface of the *a*-C film (R2 region). (d)-(f) Formation of OGC from defects or grain boundary (GB) of PG nanostructures. The two yellow arrows in (f) point toward the GB of the PG1 and PG2 nanostructures. All scale bars in (d)-(f) are equal to 5 nm.



Figure 6.6 (a) Cross-sectional STEM image of a Si/NiFe/*a*-C/Cr sample stack thermally annealed at 650 °C in Ar atmosphere (the red line indicates the scan path) and (b) EELS intensity of Ni and Fe along the scan path. The high Ni intensity and the negligible Fe intensity suggest that the composition of the pyramidal nanostructure grown into the Si substrate is nickel silicide (NiSi_x).



Figure 6.7 Schematic illustration of the mechanisms controlling the growth of planar graphene (PG) and orbicular graphitic carbon (OGC) by thermal annealing at 650 °C in Ar atmosphere: (a) NiFe agglomeration, PG nucleation on NiFe agglomerates, and PG growth on top of NiFe agglomerates and *a*-C film, and OGC growth from mismatch-induced growth sites, i.e., defects and grain boundaries (GB), in the PG yielding a hybrid PG-OGC microstructure and (b) mismatch-induced OGC growth from a PG defect and the GB of two PG nanostructures.

Chapter 7. Summary and outlook

This dissertation focused on two major topics in the development of HAMR – energy transport in the electromechanical-optical system and fundamental understanding of ultrathin amorphous carbon (a-C) protective overcoats. In the study of energy transport, FEM simulations involving multi-physics processes were carried out to investigate the near-field heat transfer in a HAMR head and the energy transmission in a HAMR stack. Ultrathin a-C films were studied with experimental methods, including PVD, TEM/EELS, Raman spectroscopy, etc., and MD simulations to elucidate the morphology, structure, stability, and tribomechanical properties of ultrathin a-C films. The main findings of the work can be summarized as following:

(1) An FEM model was developed to investigate the near-field heat transfer in a HAMR head. The model used a protrusion-dependent heat transfer coefficient to account for the near-field radiation and phonon conduction in HAMR head-disk interface. The simulation results revealed a significant effect of near-field heat transfer to the thermal deformation of the HAMR head.

(2) FEM simulations were performed for a HAMR stack including a waveguide/antenna-NFT system. The requirements for suitable optical properties of the NFT, magnetic medium, underlayer and heat-sink sublayer to achieve good energy transmission efficiency and thermal performance were discussed. The capabilities of the developed analytical framework demonstrated by the simulations illustrate its high potential for investigating the thermal performance of various thermo-plasmonic devices.

(3) The thermal stability and diffusion behaviors of *a*-C/Si and *a*-C/SiN_x/Si stacks exposed to a high temperature were experimentally investigated. TEM images and EELS depth profiling of the films confirmed their thermal stability. The *a*-C/SiN_x/Si exhibited more significant carbon diffusion into the SiN_x underlayer, while the SiN_x preserved the composition and structure of the Si substrate. The results suggested that SiN_x can be a good candidate for a diffusion barrier at high temperatures.

(4) MD simulations of ultrathin *a*-C film deposition and thermal annealing revealed a subplantation deposition process involving direct implantation and recoil implantation and an optimal carbon deposition energy for films with the highest sp^3 content. A high compressive stress in the *a*-C film due to the bombardment of energetic particles was shown to be a prerequisite for high sp^3 hybridization. The thermal annealing simulations demonstrated a temperature threshold between 200-250 °C for significant sp^3 -to- sp^2 rehybridization and internal stress relief, which mainly occurred in bulk layer of the *a*-C film. The rehybridization and stress relief at high temperature were found to be very rapid processes.

(5) MD simulations of ultrathin a-C film oxidation by energetic oxygen molecules showed a critical oxygen kinetic energy for continuous carbon oxidation and steady-state oxygen adsorption independent of oxygen kinetic energy. The most important finding was that film oxidation was a surface-dominated process characterized by the removal of

the surface layer and the gradual sp^3 -to- sp^2 rehybridization in the bulk layer adjacent to the interface with the surface layer.

(6) MD results of normal contact between identical *a*-C films in vacuum and oxygen atmosphere revealed similar adhesion forces due to the partial surface passivation. Simulation results of sliding contact between identical *a*-C films showed shear-induced sp^3 -to- sp^2 rehybridization in the bulk layer of the films. Film oxidation was found to be enhanced by the sliding process. The performed MD analysis provided a framework for investigating oxidation/tribo-oxidation of thin-film materials.

(7) A hybrid structure consisting of planar graphene (PG) and orbicular graphitic carbon (OGC) was created by thermal annealing of *a*-C films using NiFe as catalyst. The hybrid structure was characterized by SEM, HRTEM/EELS, Raman spectroscopy, and XPS. Transformation from amorphous carbon to crystalline graphitic structure, NiFe agglomeration and segregation, and crystalline NiSi_x at the film/substrate interface were observed. Based on SEM and cross-sectional TEM results, a metal-catalyzed nucleation mechanism and a mismatch-induced growth mechanism were proposed for the formation of the PG-OGC hybrid structure. The incorporation of NiSi_x in the hybrid PG-OGC structure indicates the potential of this single-step graphene synthesis process for widespread micro/nanoelectronic device applications.

The work in this dissertation provides basic knowledge of thermomechanical and plasmonic performance of HAMR devices and improves the fundamental understanding of ultrathin *a*-C protective overcoats, which should be of value to contemporary magnetic recording like the HAMR technology. With the continuous evolution of data storage technology, the demand is for hard-disk drives with even larger storage capacity and better performance. However, there are still important technical and scientific obstacles that must be overcome to further enhance the device longevity and functionality and achieving broad commercialization of HAMR products. There are several new research challenges, including novel design methods, sub-1nm-thick *a*-C film synthesis, and alternative protective overcoat materials, which must be faced to maintain a competitive edge for magnetic recording in the competition with rapidly growing solid-state storage.