Intrinsic stress and high temperature properties of metal-containing hydrogenated amorphous carbon coatings

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INTRINSIC STRESS AND HIGH TEMPERATURE PROPERTIES OF METAL-CONTAINING HYDROGENATED AMORPHOUS CARBON COATINGS

A Dissertation

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

in

The Department of Mechanical Engineering

by

Bo Shi
B.Eng., University of Science and Technology – Beijing, 1998
M.Eng., University of Science and Technology – Beijing, 2001
August 2005
To my wife, Wenjie.
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Abstract

A detailed examination of the intrinsic stress development and mechanical properties of titanium-containing hydrogenated amorphous carbon (Ti-C:H) and W-C:H coatings, deposited in an inductively coupled plasma (ICP) assisted hybrid chemical/physical vapor deposition (CVD/PVD) environment was carried out. Intrinsic stresses within those coatings were found to be compressive and dependent on compositions. The intrinsic compression within Ti-C:H was further shown to be significantly influenced by the energy of ionic species bombarding the substrate during growth. The results suggested that ion bombardment played a significant role in intrinsic stress generation within Ti-C:H, and was likely to influence stress development in other low temperature deposited amorphous hydrocarbon (a-C:H) based ceramic nanocomposite coatings.

A higher deposition temperature, ~600°C, promoted TiC precipitation and resulted in little Ti dissolution within the a-C:H matrix. High-temperature deposited Ti-C:H specimens were found to possess lower modulus and hardness values as compared to those deposited at low temperature, ~250°C, especially at low Ti compositions. This is rationalized by electron microscopy evidence of increased short and medium range graphitic order within the a-C:H matrix of high-temperature deposited Ti-C:H, and supported by additional Raman spectroscopic observations. Annealing treatment at 600°C combined with Raman scattering measurements showed that the a-C:H matrix in high temperature deposited Ti-C:H specimens appears to be less structurally sensitive to additional high temperature annealing.

The effective coefficients of thermal expansion (CTE) of Ti-C:H coatings were measured through temperature induced changes in the curvature of film/substrate assemblies.
Measured effective CTE values for Ti-C:H are consistent with previous measurements on a-C:H thin films, and show little dependence on the Ti composition.

Highly hydrogenated carbon coatings with hydrogen content approaching 60 atomic percent were deposited with a modified ICP-assisted CVD technique. The hydrogen release temperature was found to be above 500°C, which was 150°C higher than findings in previous experiments. Plasma diagnostics suggested that a decreased ratio of ionic species flux to activated neutral species flux at the substrate during deposition was responsible for the increased hydrogen incorporation into the film.
Chapter 1  Literature Review

1.1 Introduction to Me-C:H Coatings

Thin films and coatings are widely used in microelectronics and micro-electromechanical systems (MEMS). The physical properties and in service performance of these films and coatings make many of those applications possible. Amorphous carbon (a-C) and amorphous hydrocarbon (a-C:H) films have attracted much interest because of their moderately high hardness, chemical stability, optical transparency in the infrared region, low wear, and low friction\(^1,2\). However, typical deposition conditions for these films usually result in high residual stress. Furthermore, they have a significant disadvantage of low thermal stability at higher working temperatures\(^3\). Metals have been incorporated into a-C:H coatings to form metal-containing hydrocarbon (Me-C:H) coatings since the late 1980’s to modify their mechanical, electrical, and optical properties\(^4\). Metal incorporation is also suggested to alleviate the problems of high residual stresses and low thermal stability. However, studies on these issues are still in their infancy. This chapter presents a summary of related works in the literature.

1.1.1 a-C and a-C:H

The synthesis of diamond-like carbon (DLC) coatings began in the late 1960’s with ion beam deposition of a-C thin films\(^2\). The a-C coatings have moderately high hardness and high chemical stability similar to that of diamond, though their structures are distinct from crystalline diamond. DLC coatings are predominantly amorphous composed of different \(sp^2\)
and $sp^3$ bonded network structures. Micro- or nano-scale crystalline diamond clusters can also be present. Their diamond-like properties are attributed to the significant extent of $sp^3$ bonding $^5$.

The deposition rate of a-C coatings was soon found to be very limited (20-40 Angstroms/min) because of the low sputter yield of carbon $^6$. Hydrocarbon gases such as methane (CH$_4$) or acetylene (C$_2$H$_2$) were introduced into plasma assisted deposition systems to provide carbon species for deposition through plasma assisted gas phase decomposition. Through these means, the deposition rate was increased by up to 30 times $^7$. Composition analysis revealed that hydrogen content within the coating could be as much as 50 atomic percent $^8$. The a-C:H coatings are also nearly completely amorphous and exhibit extensive $sp^3$ bonding. It is found that hydrogen stabilizes $sp^3$ bonding in a-C:H $^9$. Many properties of a-C:H coatings are similar to that of a-C. Generally, mechanical softening is observed as the hydrogen content increases within a-C:H. Hydrogen evolution at high temperatures, e.g. above 450°C, makes a-C:H structurally unstable at that temperature or higher. A substitute coating needs to be found for high temperature use, and so far the high temperature stability for a-C:H coatings has not been completely resolved.

1.1.2 Me-C:H Coatings

Incorporation of appropriate amount of metals, e.g. Ti or Ta, into a-C:H coatings is reported to improve coating toughness while keeping the hardness and Young’s modulus unchanged $^{10}$. Composite dielectric/conductive films made by incorporation of Pd into a-C:H were reported to have higher thermal stability than composite basing on plasmapolymers $^{11}$. Special magnetic behaviors were observed in Co-C:H $^{12}$. These improvements of physical properties make Me-C:H coatings attractive for research and development.
Depending on the nature of the mixture, the mechanism of structural modification by introducing metal into a-C:H may include doping, second phase formation, and change of the carbon matrix. The structure and properties of the final composite vary. Some carbide-forming metals have been incorporated into a-C:H, including W and Ti\textsuperscript{13,14}. Meng et al has studied the structure and mechanical properties of the Ti-C:H coating system intensively\textsuperscript{14,15,16}. Ti-C:H coating was made by plasma assisted physical vapor deposition using C\textsubscript{2}H\textsubscript{2} gas as a precursor. The structure of Ti-C:H was found to be one with nano-crystalline TiC clusters embedded in an a-C:H matrix. The dissolution limit of Ti atoms within the a-C:H matrix is between 0.9\% and 2.5\% from studies combining transmission electron microscopy (TEM) and x-ray absorption near edge structure (XANES) spectroscopy. Instrumented nano-indentation showed that Ti-C:H have a hardness around 20GPa. Coatings with Ti compositions below 25 at\% show low friction and low wear, but exhibit high friction coefficient and high wear rate when Ti composition goes beyond 25 at\%. These results suggest that properties of Me-C:H coatings may depend strongly on composition.

While Ti-C:H coatings have mechanical properties which are controllable by tuning the coating composition, the residue stresses within them need to be studied, including their magnitude and variation with film thickness and deposition condition. Moreover, the issue of high temperature stability remains to be elucidated.

1.2 Residual Stress in as-deposited Thin Films

1.2.1 Origins of Residual Stresses

Residual stresses in thin films have attracted much attention. Residual stresses developed in thin films and coatings can be tensile or compressive. Tensile stresses can lead
to film cracking and peeling whilst compressive stresses cause delamination and buckling, both effects affecting mechanical performance such as film integrity and adhesion to the substrate.

The types of stresses observed in thin films include thermal stresses and intrinsic stresses. When the substrate and the film have different thermal expansion coefficients, thermal stresses may be produced due to a temperature change. Intrinsic stresses are generated during film growth and are dependent on film chemistry as well as the synthesis method. Coherency stresses may exist due to lattice mismatch between film and substrate. It is generally observed in metal films that the evolution of residual stress typically occurs in alternating stages of compression, tension, followed by compression\textsuperscript{17}. The compressive stress observed during island growth prior to coalescence has been attributed to the surface stress on isolated clusters\textsuperscript{18}. The tensile stress which develops at the point of crystallite coalescence is explained by the interfacial energy reduction\textsuperscript{19}. When the film grows into a fully continuous film, a finally stable compressive stress occurs and has been explained by a model based on atoms incorporated into grain boundaries\textsuperscript{17}.

1.2.1.1 Compressive Stress during Island Growth

The surface and interior atoms in a solid are different in their bonding environment. The interatomic spacing of the surface atoms is different from that of the interior atoms. This difference leads to a force acting on the surface of a solid; this force per unit length is called the surface stress.

Two effects have been considered when understanding the compressive stress during island growth\textsuperscript{20,21}. First, because of the surface stress, the equilibrium lattice spacing of the
island is different from the bulk. Second, when an island grows to a critical size, it can firmly attach to the substrate. During further growth of the island, the deviation of island lattice parameter from that of the bulk, caused by surface stress, is frozen in by the substrate. If further growth of an attached island occurs at a smaller lattice spacing than that of the bulk, a compressive stress will be generated in the island.

1.2.1.2 Crystallite Coalescence and Zipping-Induced Tensile Stress

The earliest stage of film growth occurs through nucleation and growth of individual crystallites at certain sites on the substrate, in the so called island growth mode. These islands grow bigger and finally coalescence to form a continuous polycrystalline film. The driving force for the coalescence is the reduction in interfacial energy when the surfaces of the crystallites come together to form grain boundaries.\(^{22}\)

The development of tensile stresses in the early stages of thin film depositions has been investigated by Koch and Abermann\(^ {23, 24}\), their experiments have shown that the tensile stresses in polycrystalline film has something to do with the coalescence point. Nix and Clemens\(^ {19}\) presented a mechanism for intrinsic tensile stress development in thin polycrystalline films. In their models free energies of the crystallite surfaces and grain boundaries play a direct role in calculating the stresses in the film. In the crystallite coalescence model, a regular array of hexagonal crystals growing on a substrate was considered, and the free energies per unit film area before and after crystallite coalescence are compared. The crystallites are free to slide and stretch along the surface of the substrate. Their calculation shows that for very small grains, crystallite coalescence can lead to very large tensile stresses in the film. They also presented a two-dimensional model, “zipping”, for the
tensile stress as a result of coalescence. In this model, an array of two-dimensional elliptical crystallites coalesces to form a surface with a cycloid shape (Figure 1-1). The coalescence is driven by the decrease in boundary energy and limited by the increase in strain energy within the crystallites.

Before coalescence

After coalescence

Figure 1-1 Crystallite coalescence (zipping) process

1.2.1.3 Compressive Stress in the Growth of a Continuous Film

After island coalescence, the tensile stress is observed to decrease. It can change sign from tensile to compressive and eventually reaches a steady state value which depends on the growth conditions. Cammarata et al believe that the contribution from surface stress effects can lead to a compressive stress at large film thicknesses.

Chason et al presented another model for this compressive stress. During deposition in which there are continuous fluxes of atoms and ions to the surface, the chemical potential on the surface may be higher. In this case the deposition does not occur at equilibrium. The
deviation from equilibrium may result in a supersaturation of adatoms on the surface. The possibilities of these adatoms moving into the grain boundaries within the film are determined by the difference in chemical potential between the surface and the grain boundary. By varying the growth conditions the chemical potential difference can reach a value establishing grain boundary incorporation. It is the incorporation of excess atoms into grain boundaries that caused the compressive stress. Since the compressive stress leads to an increase in the chemical potential of atoms that have moved into the grain boundaries, the incorporation process would slow down and eventually reach a steady state.

1.2.2 Measurement of Residual Stress

X-ray diffraction, substrate curvature measurement, and Raman spectroscopy are three common methods to determine residual stresses in thin films. The Raman method uses the shift in Raman line to evaluate the residual stress, and has been applied extensively in diamond films. It can also give valuable information about the film properties including film phase purity. This method of stress quantification can encounter difficulties due to peak splitting because of optical phonon degeneracy and the presence of inhomogeneous stresses. Consequently, a large number of spectra may have to be recorded and averaged to obtain a representative spectrum. This would not be practical for real-time measurements. Raman measurements are also largely restricted to materials with structures which allow first order active Raman modes.

X-ray diffraction has been used for in-situ film stress measurement. For systems consisting of more than one phase the traditional \( \sin^2 \psi \) method becomes more complex. For films containing amorphous phases or nano-crystallites, the absence of crystalline diffraction
signatures or diffraction line broadenings are problematic. Me-C:H coatings are composed of nano-crystallites of metals or metal carbides embedded in an amorphous matrix and are not suitable for stress measurements by X-ray methods. Therefore, the substrate curvature method is the one most suitable for stress evaluation in Me-C:H coatings.

1.2.2.1 Stress Determination by Substrate Curvature Measurements

Consider a film/substrate assembly (Figure 1-2), the thickness of the film is very small as compared to that of the substrate. It is assumed that lateral dimensions of the film and substrate are much greater than their thicknesses. If there is a stress in the film, it can cause the substrate to deform elastically in biaxial bending. The change in the curvature of the substrate with and without the film, $\Delta K$, is given by the Stoney equation 30

$$\Delta K = \frac{K_{ts}Y_{ts}t_f^2}{6}$$

Equation 1-1

where $Y_s$ is the biaxial modulus of the substrate, $t_s$ is the substrate thickness, $t_f$ is the film thickness and $\sigma_f$ the stress in the film. A negative $\Delta K$ denotes increasing substrate convexity on the film side in response to a compressive stress in the film. For cubic single crystal substrates, the biaxial elastic moduli are isotropic in (001) and (111) planes.
Stoney equation makes it possible to determine stresses in thin films by measuring the substrate curvature change \(^3\). Figure 1-3 shows a measurement scheme using a laser reflection method. The substrate curvature change, \(\Delta K\), is related to the change in relative spacing between reflected spots, \(\Delta D/D_0\), by

\[
\Delta K = -\frac{\cos \theta}{2L} \left( \frac{\Delta D}{D_0} \right)
\]

Equation 1-2

where \(\theta\), \(L\), and \(D_0\) are the incidence angle, the path length, and the initial spacing between spots reflected from a flat surface, respectively. \(L\) is usually calibrated using mirrors with known radius of curvature.

1.2.2.2 Thermal Corrections in the Curvature Measurement

It was found that the total curvature change, which is measured by the laser reflection scheme, usually includes a thermal stress contribution, \(\Delta K_{\text{thermal}}\). This thermal component,
referred as thermal strain, may be as large as 50% of \( \Delta K \). The thermal strain in the film, \( \varepsilon_f \), is given by

\[ \varepsilon_f = -(\alpha_f - \alpha_s)\Delta T = -\Delta \alpha \Delta T \]  

Equation 1-3

where \( \alpha_f \) and \( \alpha_s \) are the linear thermal expansion coefficients of the film and the substrate, respectively, \( \Delta T \) is the temperature change in the substrate/film assembly. The thermal stress in the film is \( \sigma_f \varepsilon_f \), where \( \sigma_f \) is the biaxial modulus of the film. A simple analysis using Stoney equation gives

\[ \Delta K_{\text{thermal}} = -\frac{6}{Y_s t_s^2} Y_f t_f \Delta \alpha \Delta T \]  

Equation 1-4

When there is a temperature gradient across the substrate thickness, the substrate bending caused by this gradient should also be considered. Usually the substrate thickness is very small, e.g. 150~300 μm, so that a linear temperature gradient across the thickness can be assumed. Consider the two surfaces have temperatures \( T_1 \) and \( T_2 \), respectively, the radius of curvature, \( R \), caused by this temperature gradient is related to the substrate thickness by

\[ \frac{t_s}{R} = \alpha_s (T_2 - T_1) \]  

Equation 1-5

1.3 Thermal Stability of a-C and a-C:H Coatings

Annealing has been applied to remove residual stresses in films. The samples have to be heated to a suitable temperature and held at that temperature for a sufficiently long time. The compressive stress in amorphous tetrahedral carbon (a-tC) coatings can be completely
removed by annealing at 600°C in vacuum. Annealing treatments at high temperatures are useful if no structural or property changes are induced. High temperature stability of a-C and a-C:H coatings is discussed in this section.

1.3.1 Effects of Deposition Temperature

Hard amorphous carbon (a-C) coatings consist of $sp^3$ and $sp^2$ bonded carbon atoms, with $sp^3$ bonded a-C known as amorphous tetrahedral carbon (a-tC). It was found that hard carbon coatings deposited at elevated temperatures are more graphitic, whereas cooling of the substrate during deposition leads to a higher $sp^3$ content. The deleterious effects of elevated deposition temperature have been investigated for different deposition methods.

Figure 1-4 Variations of $sp^3$ fraction, density and residual compressive stress as functions of deposition temperature under different ion energies. (S. Sattel, J. Robertson, H. Ehrhardt, J. Appl. Phys. 82, 4566 (1997))
Sattel et al. studied hydrogenated carbon films deposited at different temperatures using plasma-enhanced chemical vapor deposition (PECVD). They found two transition temperatures $T_1$ and $T_2$, which are around 250°C and 450°C, respectively. The $sp^3$ content (Figure 1-4) and the hydrogen concentration (Figure 1-5) measurements make it clearer to understand the structure transitions. At $T_1$, C-C network graphitize without loss of hydrogen. $T_2$ indicates a loss of H and C-C network begins to reconstruct. The hardness, Young’s modulus, adhesion and residual stress decrease abruptly around $T_1$ while the friction coefficient and surface roughness increase around the same temperature.
1.3.2 Thermal Stability after Deposition

a-tC coatings deposited by pulsed laser ablation show excellent thermal stability in vacuum up to 800°C. Above this temperature the coating converts to nano-crystalline graphite\(^{37}\). Raman spectra of these coatings show a peak at \(\sim 1560\text{cm}^{-1}\) and a weak shoulder at \(\sim 1350\text{cm}^{-1}\), forming the G and D bands of graphitic carbon\(^{38}\). In single crystal graphite, the only first-order Raman active mode is observed at 1580cm\(^{-1}\)\(^{39}\). In polycrystalline graphite, the G peak reflects the vibrations of \(sp^2\) bonded atoms whereas the D peak arises from the disorder-activated zone boundary mode and indicates the presence of nm scale graphitic domains\(^{40}\). The ratio of the peak intensities, I(D)/I(G), have been correlated to film \(sp^3\) content.

Annealing experiments conducted on a-C coatings with different \(sp^3\) content shows that the thermal stability of these DLC coatings decreases with decreasing \(sp^3\) fraction (Figure 1-6). Pure carbon coatings of up to 85% \(sp^3\) content has been studied by Anders\(^{41}\) with near edge x-ray absorption fine structure (NEXAFS) spectroscopy. The NEXAFS spectra show no change up to 700°C instead of 800°C from Raman spectra. They believe the difference in the NEXAFS and the Raman results is attributed to sensitivity factors.

Figure 1-6 The G peak position and the ratio of the peak intensities as a function of annealing temperature for the DLC coatings with different \(sp^3\) content. (R. Kalish, Y. Lifshitz, K. Nugent, S. Prawer, Appl. Phys. Lett. 74 (20), 2936 (1999).)
Because of hydrogen evolution, the a-C:H coatings show relatively poor thermal stability. A I(D)/I(G) ratio transition similar to that in a-C coatings (Figure 1-6) was found, with a lower graphitic conversion temperature of 300–400°C. Akkermann et al believe that as deposited a-C:H coatings consist of polymeric, highly hydrogenated C(sp³) structural regions and mixed C(sp²)-C(sp³) structures which are much less hydrogenated. In a-C:H coatings, hydrogen are mostly bonded to C(sp³) atoms. A schematic picture of the transformation in the bonding structure occurring during annealing is shown in Figure 1-7.

Instead of doing annealing in high vacuum, Zhang et al carried out annealing experiments for a-C:H coatings in oxygen gas flow. The results show that O₂ can lower the graphitic transformation temperature by greatly promoting hydrogen evolution. This makes it more challenging to use a-C:H coatings in air at high temperatures.

Some elements such as W, Ti and Si have been doped into a-C:H coating to improve the thermal stability as well as influencing the residual stresses. Si incorporated a-C:H coatings show lower intrinsic stresses and higher thermal stability compared to the unmodified coatings, a promising sign for finding out novel DLCs with better thermal stability.

1.4 Dissertation Scope of Work

In this dissertation, the effects of deposition conditions on the structures, stress development, and mechanical properties of Ti-C:H coating are studied. The possible origins of intrinsic stress and optimized deposition conditions are presented. The results are expected to have some general applications to other carbon-based, two-phase, nano-composite coating systems.
Figure 1-7 Bond reconstruction processes in the C-C network during annealing. The dashed lines correspond to newly formed bonds. (a) transformation of C\((sp^3)\)–H bonds into C\((sp^2)\)–H bonds; (b) formation of H\(_2\); (c) formation of methane; (d) formation of methane and a double bond; (e) formation of double bonds without methane formation. (Z.L. Akkermann, H. Efstathiadis, F.W. Smith, J. Appl. Phys. 80(5), 3068 (1996).)
The high temperature stability of Ti-C:H coatings are also examined. High temperature performance of both high temperature and low temperature deposited coatings has been studied. A new method is presented to make a-C:H coatings with high hydrogen contents and moderately high thermal stability.

1.5 References


Chapter 2  A Percolation-Type Structure Transition Related Intrinsic Stress Evolution within Nanocomposite Ceramic Coatings *

2.1  Introduction

Surface engineering of macro-scale ¹ and micro-scale ² mechanical systems using nano-structured ceramic coatings is being pursued intensely. Refractory ceramic coatings deposited far from equilibrium typically possess a significant level of intrinsic stress, which furnishes driving forces for cracking of the coating and delamination from the substrate ³. Ceramic coatings are typically made by plasma-assisted vapor deposition techniques, in which low-energy ion bombardment plays an important role in the film formation process ⁴. Both the energy and flux of the ions can have a significant influence on the development of intrinsic stresses ⁵.

Ti-containing hydrocarbon (Ti-C:H) coatings form prototypical pseudo-binary ceramic nanocomposites. Consisting of a nm-scale mixture of crystalline titanium carbide (TiC) and amorphous hydrocarbon (a-C:H) ⁶, these coatings possess mechanical properties and tribological characteristics that depend systematically on coating composition ⁷, demonstrating the potential to engineer coatings tailored for specific applications. The dependence of the tribological characteristics of Ti-C:H coatings on the Ti composition has been related to a percolation-type transition in the coating microstructure ⁸. In addition to the influence of various plasma parameters, the coating composition may therefore also exert a significant influence on intrinsic stress development.

This chapter examines the dependence of intrinsic stresses within Ti-C:H coatings on the Ti composition. Ti-C:H deposition was accomplished using a high-density plasma-assisted hybrid chemical/physical vapor deposition (CVD/PVD) process. Under nominally identical plasma conditions, a series of Ti-C:H coatings, ranging from nearly pure a-C:H to nearly pure TiC, was deposited onto Si(100) substrates. The development of intrinsic stresses was monitored by in-situ measurements of changes in substrate curvature. Our results show that the intrinsic stress within Ti-C:H depends systematically on the Ti composition. Furthermore, a significant increase in stress was observed as the Ti composition rose beyond 25 at.% , correlating well with a previously suggested percolation transition.

2.2 Experimental

Coating deposition was carried out in a hybrid CVD/PVD tool, which combines an inductively coupled plasma (ICP) with balanced magnetron sputtering, and enables independent control of the ion energy and flux. Each Ti-C:H deposition run consisted sequentially of a 500 s substrate etch in a pure Ar(99.999%) ICP, a 200 s plasma-off period, a 600 s deposition of a Ti interlayer in pure Ar, and finally a 2500 s Ti-C:H deposition in an Ar/C\textsubscript{2}H\textsubscript{2}(99.99%) mixture. The ICP input power was held at 1000W during etching and Ti-C:H deposition, and at zero during plasma-off and Ti-interlayer deposition. The substrate bias was –100 V during etching and –50 V during deposition. The Ar input flow rate was 50 sccm throughout the run and the C\textsubscript{2}H\textsubscript{2} input flow rate was 5 sccm during Ti-C:H deposition. Total pressure was 1.6 - 1.7 mTorr throughout the deposition. The Ti cathode current was kept constant at 1.0 A during Ti-interlayer deposition and was varied in the range of 0.3 - 1.8A during Ti-C:H deposition in order to vary the Ti composition.
A series of W-C:H coatings were also made following the same procedure stated above, switching Ti cathodes to W cathodes. The W cathode current was kept at 0.5 A during interlayer deposition and was varied in the range of 0.1-0.5 A during W-C:H deposition.

Two-side-polished Si(100) wafers, 300 µm in thickness, were cut along <100> directions into 4 mm x 30 mm beams. These beams were mounted on a sample holder, with one end fixed and the other free. Two additional Si wafer shields were placed along both sides of each beam, with ~ 1 mm gaps (Figure 2-1), to ensure that deposition occurred only on the beam front surface. A multi beam optical sensing (MBOS) technique\textsuperscript{10}, consisting of a linear array of parallel beams incident upon the Si(100) beam substrate generated from a single 658 nm AlGaInP diode laser passing through a multi-pass optical etalon and a 2-D CCD array for reflected spot detection, was used to monitor the change in curvature of stationary Si(100) beams during deposition (Figure 2-2). The incidence angle of the laser beams on the substrate was ~ 1.5°. The substrate curvature change, ΔK, is related to the change in relative spacing
between reflected spots, $\Delta D/D_0$, by Equation 1-2. L was 104.4 cm in the present setup; hence a $\Delta K$ of $\sim 1/21$ m$^{-1}$ corresponds to a $\Delta D/D_0$ of $\sim 10\%$.

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![Diagram](image_url)

Figure 2-2 Top view of the deposition chamber. Specimen is placed at the center of the chamber. (A) Laser monitoring port; (D) Plasma probe assembly; (B) and (E) are ICP generators; (C) and (F) are balanced magnetron sputtering sources.

No intentional substrate heating or cooling was applied. Temperatures were measured separately on sacrificial substrates of the same dimension by K-type thermocouples attached to the front and back beam surfaces as well as the Si deposition shields.

Rutherford Backscattering Spectrometry (RBS) and hydrogen elastic recoil detection (ERD) measurements were performed on Ti-C:H specimens to obtain the average Ti, C, and hydrogen compositions. RBS measurements were carried out using a 1.6 MeV He$^+$ ion beam and a detector angle of 137° off the beam direction. Specimen tilt varied depending on the Ti-C:H film thickness. Hydrogen content measurements by ERD were carried out using a 1.5
MeV He\(^+\) ion beam, at a scattering geometry of 15\(^\circ\) incidence angle and 15\(^\circ\) detector takeoff angle. Hydrogen compositions determined by ERD were benchmarked against a previously characterized Ti-C:H specimen with known hydrogen content. These specimens were in turn used as secondary standards for X-ray Photoelectron Spectroscopy (XPS) measurements on a Kratos AXIS165 system, using a monochromatic Al K\(\alpha\) excitation source. Prior to XPS spectrum acquisition, the Ti-C:H specimen surface was etched with a 5kV 10mA Ar\(^+\) ion beam for 10min. Survey scans in the binding energy range of 0 – 1000eV in 1eV steps and high resolution scans of the C1s and Ti2p regions in 0.1eV steps were acquired immediately after ion etching. Raw XPS spectral data were converted into Ti to C atomic ratios (\(R_{\text{Ti/C}}\)) using Kratos supplied sensitivity factors and compared to \(R_{\text{Ti/C}}\) obtained from RBS, which demonstrated a good correlation between the two techniques. For the specimens on which RBS measurements were not carried out, only the atomic ratio determined by XPS was taken as the composition.

Electrical sheet resistance of the entire Ti-C:H/Ti/Si(100) specimen structure was measured with a Veeco FPP-100 four-point probe setup. Resistance measurements on 4mm × 30mm Ti-C:H/Ti/Si specimens were carried out at a probe spacing of 1.6mm. Raw sheet resistance was measured by continuously scanning the outer probe current, until the inner probe voltage reaches a constant value of 10mV, with no geometric correction factor applied\(^\text{11}\).

Coating thickness was measured post deposition by cross-sectional scanning electron microscopy, and ranged between 1 to 2 \(\mu\)m. Cross sectional transmission electron microscopy (TEM) examinations were performed on the Ti-C:H/Ti/Si(100) specimens using a JEOL JEM2010 instrument operated at 200kV.
Instrumented nanoindentation was carried out on a Hysitron Triboscope interfaced to a Digital Instrument Dimension3100 atomic force microscope (AFM) using a Berkovich diamond indenter tip. Instrument load frame compliance and indenter tip area function calibration was carried out using a Hysitron supplied fused silica specimen assuming a contact-depth ($h_c$) independent elastic modulus. The calibration load range was 100 - 13000µN, corresponding to an indenter contact depth range of 8 - 220nm. Indentations on Ti-C:H/Ti/Si specimens were carried out at multiple loads, ranging from 3000 – 11000µN. The Oliver/Pharr data analysis procedure was followed to extract values of the indentation modulus, $E_{\text{ind}} = E/(1-\nu^2)$, where $E$ and $\nu$ are respectively the Young’s modulus and Poisson’s ratio, and the hardness, $H$, from experimental load vs. displacement curves. Results taken at contact depths less than 10% of the total coating thickness were averaged to obtain the modulus and hardness values. Coating surface profiles were examined in the contact AFM mode with the Berkovich indenter tip, and the average roughness of the as-deposited coatings was determined to be ~ 40 nm.

2.3 Results and Discussion

A series of Ti-C:H/Ti/Si(100) specimens was deposited. Figure 2-3(a) shows a high-resolution (HR) TEM micrograph of a typical Ti/Si(100) interface. Figure 2-3 (a) shows a disordered interface, which likely results from the Ar$^+$ ion bombardment during etching and discourages epitaxial alignment between Ti and the Si(100) substrate. Figure 2-3(b) shows a cross-sectional bright-field (BF) TEM micrograph of a Ti-C:H specimen, showing a ~ 80nm thick Ti interlayer on Si followed by a Ti-C:H top layer. The Ti interlayer exhibits a columnar structure with ~ 20nm column width, typical of low temperature deposited metal films. Additional TEM investigations showed that Ti-C:H growth occurred on a consistent columnar Ti template, as exemplified in Figure 2-3.
Figure 2-3 Nature of the Ti interlayer template for Ti-C:H growth: (a) a HRTEM micrograph of the Ti/Si(100) interface. The inset SADP is taken from an area including both the Si(100) substrate and the Ti interlayer; (b) a cross-sectional BF micrograph of a Ti-C:H/Ti/Si(100) specimen. The Ti interlayer was deposited at a bias voltage of $-50\text{V}$. The inset selected area electron diffraction pattern (SADP) is taken from an area including both the Si(100) substrate and the Ti interlayer.
Figure 2-4 Composition of the Ti-C:H coatings as a function of the Ti cathode current during deposition.

Figure 2-4 shows the average composition of the Ti-C:H layers as a function of the Ti cathode current obtained by combining the RBS and ERD measurements. The Ti and hydrogen compositions respectively increase and decrease in a monotonic fashion with increasing Ti cathode current. The observed trend is consistent with our previous results and demonstrates that the coatings are pseudo-binary TiC/a-C:H nanocomposites, in which hydrogen inclusion occurs only through incorporation into the a-C:H phase\textsuperscript{13}. Figure 2-5 shows the $R_{\text{Ti/C}}$ obtained from XPS plotted against that obtained from RBS. The data show good consistency between those two methods. Figure 2-6 shows the W/C atomic ratio as a function of W cathode current obtained from XPS measurements. The W/C ratio appears to increase linearly as the W cathode current increases.
Figure 2-5 Comparison of $R_{\text{TUC}}$ between RBS data and XPS data

Figure 2-6 W/C atomic ratio of the W-C:H coatings as a function of the W cathode current during deposition.
The dissolution limit of Ti atoms within an a-C:H matrix was shown to be <2.5at.% Ti, beyond which precipitation of nano-crystalline B1-TiC occurs\(^\text{14}\). Figure 2-7 shows a typical XPS survey spectrum of a Ti-C:H coating with a R\(_{Ti/C}\) of 0.3. In agreement with RBS measurements, the Ar and O contents as determined by XPS are less than a few atomic percent. Figure 2-8 shows a typical XPS survey spectrum of a W-C:H coating with a R\(_{W/C}\) of 0.35. Compared to that of the Ti-C:H coating, the O content is even lower. Figure 2-9 shows C1s core level spectra of several Ti-C:H coatings as a function of the Ti composition. At low Ti compositions, the C1s spectra are dominated by a component with a binding energy of \(\sim 284.5\text{eV}\). As the Ti composition increases, a second component with a binding energy of \(\sim 281.8\text{eV}\) grows relative to the first component, and dominates the spectra at high Ti compositions. These two components are attributed to a-C:H and B1-TiC, respectively. These observed binding energies show excellent agreement with previous in-situ XPS measurements on Ti-C:H\(^\text{15}\). The overall XPS results agree with previous findings, and show that the volume fraction of nanocrystalline B1-TiC increases with increasing Ti composition. Figure 2-10 shows C1s core level spectra of several W-C:H coatings as a function of the W/C atomic ratio (R\(_{W/C}\)). At low R\(_{W/C}\), the C1s spectra are dominated by a component with a binding energy of \(\sim 284.5\text{eV}\). As the R\(_{W/C}\) increases, a second component with a binding energy of \(\sim 283.2\text{eV}\) grows relative to the first component, and dominates the spectra at high R\(_{W/C}\). These two components are attributed to a-C:H and WC, respectively. The overall XPS results agree with previous findings, and show that the volume fraction of nanocrystalline WC increases with increasing W composition\(^\text{16}\).

Figure 2-11 shows typical substrate temperature vs. time histories during three complete Ti-C:H deposition runs. The Ti cathode current was 0.3 A, 1.0 A and 1.6 A,
Figure 2-7 a XPS survey spectrum of a Ti-C:H coating with a RTi/C of 0.3.

Figure 2-8 a XPS survey spectrum of a W-C:H coating with a RW/C of 0.35
Figure 2-9 High-resolution XPS C1s spectra as a function of the Ti composition.

Figure 2-10 High resolution XPS C1s spectra as a function of the W/C atomic ratio.
Figure 2-11 Substrate temperature vs. time histories during entire Ti-C:H deposition runs at different Ti cathode currents: 0 – 500 sec, substrate etching; 500 – 700 sec, plasma-off; 700 – 1300 sec, Ti interlayer deposition; 1300 – 2500 sec, Ti-C:H deposition.
respectively. Temperature measurements at different Ti cathode currents produced similarly small deviations. Take Ti cathode current 1.0 A as an example, during the etch and plasma-off stages, the substrate temperature rose from ~ 30 °C to ~ 210 °C and fell to ~ 140 °C. It stayed at ~ 140 °C during Ti deposition, and rose to ~ 225 °C during Ti-C:H deposition. During the entire deposition run, the temperature difference between the front and back beam surfaces was ≤ 5 °C for all the three different cathode currents. A temperature difference of 5 °C across a 300 µm thick Si wafer would induce a ΔK of ~ 1/21 m⁻¹, or a ΔD/D₀ of ~ 10 % (Equation 1-5). Figure 2-11 shows that, during Ti-interlayer and Ti-C:H deposition, the ΔD/D₀ induced by the temperature gradient across the Si substrate is substantially smaller than 10 %.

Any temperature change, ΔT, induces a substrate curvature change, ΔK_{thermal}, due to the difference in thermal expansion, Δα, between the Si substrate and the Ti-C:H coating, as given in Equation 1-4. Δα was taken to be ~ −4×10⁻⁶ K⁻¹, according to measurements on W-C:H ¹⁷ and Ti-C:H coatings in chapter 5. A conservative estimate yields ΔD/D₀ ~ +5% for ΔT = +100°C ¹⁸. It is thus concluded that any thermal contribution to the present measurements can be neglected, and that in all cases the measured ΔD/D₀ reflects the intrinsic stress development. Thus from the beginning of Ti-C:H deposition onward, the change in Si substrate curvature predominantly reflects the development of intrinsic stresses within the Ti-C:H layer. Additional measurements showed that temperature differences between the beam and the adjacent shields were also ≤ 5°C.

Typical change in Si substrate curvature during an entire Ti-C:H/Ti/Si(100) deposition run is illustrated in Figure 2-12. After an initial 200sec for measuring D₀, the 500sec plasma etch produced a ΔD/D₀ ~ 5%. The next 200sec plasma off period followed by 600sec of Ti interlayer deposition produced a ΔD/D₀ < 10%.
Figure 2-12 Typical Si substrate curvature changes during the entire Ti-C:H/Ti/Si(100) specimen deposition sequence: measurement of $D_0$ (0 – 200 sec), plasma etch, plasma off, Ti interlayer deposition, and Ti-C:H deposition. The particular Ti-C:H deposition was run at a bias voltage of $-50 \text{V}$ and a Ti cathode current of 1.0 A.

During each deposition, the change in curvature of the Si(100) beam substrate was monitored by MBOS. Figure 2-13 shows $\Delta D/D_0$ measured as a function of time during Ti-C:H deposition. The time origin coincides with the onset of Ti-C:H deposition. Only the curvature change due to Ti-C:H deposition is taken into account, as $\Delta D/D_0$ was set to zero at time zero. In all cases, the data indicate that the intrinsic stress within Ti-C:H is compressive ($\Delta D/D_0$ positive) and suggest the existence of two growth stages. In the early stage of growth, $\leq 400 \text{ s}$, $\Delta D/D_0$ increases to $\sim 30\%$, independent of the Ti composition. Later, from $\sim 400$ to 2500 s, $\Delta D/D_0$ continues to increase approximately linearly with time, but with a distinctly different and clearly composition dependent slope. The linear dependence of $\Delta D/D_0$ on time during late stage growth therefore indicates a constant intrinsic stress as the Ti-C:H layer thickens. Similar trends were observed in W-C:H coatings (Figure 2-14), with the late stage appearing up around 1000 s.
Figure 2-13 Changes in reflected spot relative spacing from Si(100) beam substrates during Ti-C:H deposition for several Ti-C:H coatings with various Ti compositions.

Figure 2-14 Changes in reflected spot relative spacing from Si(100) beam substrates during W-C:H deposition for several W-C:H coatings with various W/C ratio.
Figure 2-15 Average intrinsic stress, $\sigma$, during late stage Ti-C:H growth as a function of the Ti composition. For all cases, $\sigma$ was measured within the duration of 400 – 2500 sec.

Figure 2-15 shows the average intrinsic stress, $\sigma$, during the late stage of Ti-C:H growth (400 to 2500s), defined as the integrated stress divided by the film thickness increment, as a function of the Ti composition. The intrinsic stress in the Ti-C:H layers is compressive at all Ti compositions; the magnitude of $\sigma$ ranges from 0.3 to 2.0 GPa. $\sigma$ decreases from $\sim -1.7$ GPa at low Ti compositions, to $\sim -0.5$ GPa between 20 and 30 at.% Ti, then increases substantially for Ti compositions $> 25$ at. %. The observed stress minimum coincides with a previously observed transition in unlubricated sliding friction coefficient and coating wear rate in the Ti-C:H system$^{19}$. We suggest that the intrinsic stress minimum and the friction/wear transition are both manifestations of a percolation-type transition in the structure of the Ti-C:H coating. As the Ti composition increases, the Ti-C:H structure evolves from one with isolated TiC nanocrystals embedded in an a-C:H matrix at below the percolation threshold to one with TiC nanocrystalline cluster aggregates percolating through
the a-C:H matrix at above the percolation threshold. Because a-C:H is highly resistive while B1-TiC is metallic, electrical resistivity measurements were used to probe this percolation type transition in the structure. Figure 2-16 shows the total sheet resistance of the Ti-C:H/Ti/Si(100) specimen series as a function of the Ti composition. A relatively constant and low sheet resistance is observed at Ti compositions > 25at.%. At Ti compositions < 25at.%, the sheet resistance rises monotonically with decreasing Ti composition. Although the value of the total sheet resistance is influenced by the presence of the Ti interlayer, the trend observed in Figure 2-16 is consistent with percolating nanocrystalline TiC clusters developing within Ti-C:H at Ti compositions > 25at.%.

Figure 2-16 Total sheet resistance of the Ti-C:H/Ti/Si(100) specimens as a function of the Ti composition.
W-C:H was also found to have a nano-composite structure which is similar to that of Ti-C:H\textsuperscript{16}. Figure 2-17 shows the average intrinsic stress during the late stage of growth as a function of W/C ratio in W-C:H coatings. Only compressive stresses were observed. Again, the stress decreases then increases as W/C ratio increases. A broad stress minimum shows around W/C~0.3. Figure 2-18 shows the total sheet resistance of the W-C:H/W/Si(100) specimen series as a function of the W/C ratio. The resistance decreases as the W/C ratio goes up. Compared to Ti-C:H, the resistance variation of W-C:H is smoother.

![Figure 2-17 Average intrinsic stress, $\sigma$, during late stage W-C:H growth as a function of W/C ratio. For all cases, $\sigma$ was measured within the duration of 1000 – 2500.](image)

Figure 2-19(a) and (b) show respectively the hardness and indentation modulus of Ti-C:H coatings as a function of the Ti composition. In contrast to the relatively abrupt variations in intrinsic stress, a smooth variation of modulus and hardness is observed as the Ti
composition increases through the percolation threshold, from below to above 25at.%. Same trends are observed in W-C:H (Figure 2-20). The Ti-C:H hardness increases from ~ 15GPa at low Ti compositions to ~ 30GPa at close to 50at.% Ti. This higher hardness is in agreement with previously measured hardness of bulk TiC \(^{20}\). Consistent with previous results, the Ti-C:H hardness stays below the linear rule-of-mixtures values over the entire Ti composition range\(^{16}\). In contrast to models of rigidity percolation where the network stiffness is expected to exhibit discontinuous changes near the percolation threshold \(^{21}\), our present results indicate that the average modulus/hardness of TiC/a-C:H nanocomposites behaves according to bounds for two-phase composite materials, without abrupt changes at the percolation threshold \(^{22}\).

Figure 2-18 Total sheet resistance of the W-C:H/W/Si(100) specimens as a function of the W/C ratio.
Figure 2-19 Mechanical properties of Ti-C:H coatings: (a) hardness as a function of the Ti composition, (b) indentation modulus as a function of the Ti composition.

Figure 2-20 Mechanical properties of W-C:H coatings: (a) hardness as a function of the W/C ratio, (b) indentation modulus as a function of the W/C ratio.

Coating design involves an optimization of mechanical properties, such as stiffness and hardness, tribological characteristics, such as friction coefficient and coating wear resistance, and residual stress. Whilst the hardness/modulus shows no abrupt changes at percolation threshold, the tribological properties and intrinsic stresses are apparently correlated to a percolation type transition in coating structure. The mechanisms controlling
such complex transitions are still not clear. The universal stress behavior observed during the early stage of Ti-C:H growth may be related to the process of nucleation, detailed understanding of which awaits further study.

2.4 Conclusion

A detailed experimental study of the dependence of intrinsic stress within Ti-C:H and W-C:H coatings on the Ti and W composition was performed by measuring, in situ, the substrate curvature change. The intrinsic stresses were found to vary significantly in magnitude, and to depend systematically on the metal composition. The observed dependence of the stress on the coating composition is suggested to arise from a percolation-type transition in the coating structure.

2.5 References


18. For the present Si(100) beam substrates, $Y_s=180$ GPa and $t_s=300$ µm. $t_f$ is taken to be 1µm, the entire thickness of the Ti-C:H layer. The maximum biaxial modulus for Ti-C:H coatings is ~ 180 GPa (ref. 8), thus $Y_f$ is taken to be 180 GPa.


Chapter 3  Ion Peening as a Possible Mechanism Controlling the Intrinsic Stress Evolution within Titanium-Containing Hydrogenated Carbon Coatings *

3.1 Introduction

Wear-resistant ceramic coatings have been utilized in industrial metal cutting applications for two decades 1. More recently, nanostructured ceramic coatings are being researched intensely for wide ranging surface engineering applications. Nanostructured metals offer additional deformation mechanisms not present in their microstructured counterparts 2. Ceramic nanocomposites have been shown to possess increased toughness 3. Two-phase ceramic nanocomposite coatings synthesized by vapor phase deposition have been shown to possess mechanical and tribological properties varying systematically with the coating composition, offering possibilities of coating design4.

Ceramic thin films made by plasma-assisted vapor deposition techniques at temperatures low relative to the relevant melting temperatures typically possess structures out of equilibrium, and consequently retain a significant level of intrinsic stress. These stresses furnish driving force for cracking of coating and delamination of coating from the substrate5. Low-energy ions bombarding the substrate surface during growth play an important role in the film formation process6. Early studies on thin films deposited by glow discharge sputtering showed that residual stresses can be varied by varying the deposition pressure, due to the variation of particle energies as pressure changes 7. Such “ion peening” effects were

also observed in ceramic thin films\textsuperscript{8, 9}. Further studies showed that both the energy and the flux of ionic species bombarding the substrate during growth have a significant influence on intrinsic stress development in single-phase ceramic thin films\textsuperscript{10}. In contrast, there are few analogous studies on two-phase ceramic nanocomposite thin films at the present time.

The Ti-containing hydrocarbon (Ti-C:H) coating system forms a prototype of pseudo-binary thin film ceramic nanocomposites. Deposited by glow discharge reactive sputtering\textsuperscript{11} and high-density plasma assisted hybrid chemical/physical vapor deposition (CVD/PVD)\textsuperscript{12}, Ti-C:H coatings consist of a nm-scale mixture of B1-TiC and amorphous hydrocarbon (a-C:H)\textsuperscript{13}. Increasing the average Ti composition of the coating increases the volume fraction of nanocrystalline TiC clusters. We have recently shown, through in-situ substrate curvature measurements, that intrinsic stress within Ti-C:H coatings shows a systematic dependence on the Ti composition and exhibit a relatively sharp kink at \(\approx 25\text{at.\% Ti}\)\textsuperscript{14}. In this chapter, the study on the Ti-C:H system is expanded. By combining substrate curvature measurements with plasma probe measurements, we examined the dependence of intrinsic stress within Ti-C:H on energy of ionic species bombarding the substrate during growth. The present results are discussed in terms of possible mechanisms contributing to intrinsic stress generation.

3.2 Experimental

Coating deposition was carried out in a hybrid CVD/PVD tool, which combines an inductively coupled plasma (ICP) with balanced magnetron sputtering, and enables independent control of the ion energy and flux\textsuperscript{15, 16}. Each Ti–C:H deposition on Si(100) substrates consisted sequentially of a 500sec substrate etch in a pure Ar(99.999\%) ICP, a 200sec plasma-off period, a 600sec sputter deposition of an elemental Ti interlayer in pure Ar,
followed by a 2500sec Ti–C:H deposition in an Ar/C₂H₂ (99.99%) mixture. The entire deposition sequence resulted in a Ti-C:H/Ti/Si(100) specimen structure. The total ICP input power was held at 1000W during etching and Ti–C:H deposition, and at zero during Ti interlayer deposition. The substrate bias was -100V during etching. The Ar input flow rate was 50sccm throughout the run and the C₂H₂ input flow rate was 5sccm during Ti–C:H deposition. Total pressure was 1.6–1.7mTorr throughout the entire deposition process. The Ti cathode current was kept constant at 1.0A during Ti-interlayer deposition. The energy of ionic species bombarding the substrate was varied by varying the substrate bias at a fixed ICP input power. A series of Ti-C:H specimens were deposited at different substrate bias voltages, holding the Ti cathode current fixed at 0.8A and all other deposition variables constant. The substrate bias ranged from –20 to –100V. No intentional substrate heating or cooling was applied during any deposition.

Two-side polished, 300µm thick Si(100) wafers were cut along <100> directions into 4mm × 30mm beams. Specimen mounting and stress monitoring were described in chapter 2 and reported previously. The optical path length L was calibrated to be ~ 1m, accomplished by placing an optical mirror with a radius of curvature of 4.0m at the specimen position within the deposition chamber. The accuracy of the substrate curvature measurements is limited by the error in the curvature standard to ~ 2.5%. The curvature measurement precision is such that a ΔD/D₀ ~ 1% can be resolved easily, i.e., curvature changes can be resolved to at least 1/200m.

Ti-C:H coating thicknesses were measured post-deposition by cross-sectional scanning electron microscopy (SEM), and ranged between 1 - 2µm. Compositions were measured by X-ray Photoelectron Spectroscopy (XPS) measurements on a Kratos AXIS165
system, using a monochromatic Al Kα excitation source. Prior to XPS spectrum acquisition, the Ti-C:H specimen surface was etched with a 5kV 10mA Ar⁺ ion beam for 10min. Survey scans in the binding energy range of 0 – 1000eV in 1eV steps and high resolution scans of the C1s and Ti2p regions in 0.1eV steps were acquired immediately after ion etching. Raw XPS spectral data were converted into Ti to C atomic ratios (R_{Ti/C}). Cross sectional transmission electron microscopy (TEM) examinations were performed on the Ti-C:H/Ti/Si(100) specimens using a JEOL JEM2010 instrument operated at 200kV.

Instrumented nanoindentation was carried out on a Hysitron Triboscope interfaced to a Digital Instrument Dimension3100 atomic force microscope (AFM) using a Berkovich diamond indenter tip. Instrument load frame compliance and indenter tip area function calibration was carried out using a Hysitron supplied fused silica specimen assuming a contact-depth (h_c) independent elastic modulus. The calibration load range was 100 - 13000μN, corresponding to an indenter contact depth range of 8 - 220nm. Indentations on Ti-C:H/Ti/Si specimens were carried out at multiple loads, ranging from 3000 – 11000μN. The Oliver/Pharr data analysis procedure was followed to extract values of the indentation modulus, $E_{ind} = E/(1-\nu^2)$, where $E$ and $\nu$ are respectively the Young’s modulus and Poisson’s ratio, and the hardness, $H$, from experimental load vs. displacement curves. Results taken at contact depths less than 10% of the total coating thickness were averaged to obtain the modulus and hardness values. Coating surface profiles were examined in the contact AFM mode with the Berkovich indenter tip, and the average roughness of the as-deposited coatings was determined to be ~ 40 nm.

Plasma potential and ion current density within the ICP assisted CVD/PVD environment were measured by an electron emissive wire probe and a conventional planar
Langmuir disk probe. Figure 2-2 shows where the probe assembly is mounted and Figure 3-1 shows the circuit of the probes. In the emissive wire probe technique, thermionic emission from a 75µm diameter W probe wire was turned on by passing current through the W wire in a separate floating bias loop. The wire probe current – bias voltage (I-V) curves, with and without electron emission, were collected consecutively. The probe bias at which I-V curves separate was taken as the plasma potential \(^{19}\). Ion current density was measured using a 3mm diameter two-sided W disk probe at a constant probe bias of \(-80\) V.

![Figure 3-1 Circuit for planar disk probe and electron emissive wire probe.](image)

3.3 Results and Discussion

Figure 3-2 shows two typical emissive wire probe I-V curves collected during a Ti-C:H deposition run. The two I-V curves were acquired with and without electron emission from the wire filament by subjecting the floating bias loop to a voltage of 10.5V and 0V, respectively. The I-V curves coincide well at higher probe bias, and clearly separate at below
Figure 3-2 Electron emissive wire probe I-V characteristics obtained within an Ar/C\textsubscript{2}H\textsubscript{2} ICP during Ti-C:H deposition with and without electron emission from the wire probe. The difference spectrum shown in the inset shows I-V curve separation below the substrate bias V\textsubscript{b} of 19V.

a certain bias voltage. The difference spectrum, shown in the inset, allows a determination of the probe bias at which the I-V curves separate, ~ +19V in the present case. This potential was taken as the plasma potential φ\textsubscript{p}. Figure 3-3 shows φ\textsubscript{p} measured at plasma conditions used to deposit the Ti-C:H/Ti/Si(100) specimen series as a function of the substrate bias V\textsubscript{b}, and indicates that φ\textsubscript{p} is independent of V\textsubscript{b}. Additional Langmuir disk probe measurements showed that the total ion current density was ~ 10.5 mA/cm\textsuperscript{2}, also independent of V\textsubscript{b}. At the total deposition pressure of ~ 1.7 mTorr, the plasma was taken to be collisionless. The emissive wire probe and disk probe measurements thus showed that the total ion flux stayed
approximately constant during Ti-C:H deposition, while the energy of ionic species, given by \( \phi_p - V_b \), varied as \( V_b \) varied. Assuming that \( e\phi_p = 5k_B T_e \), where \( e \), \( k_B \), and \( T_e \) are respectively the electron charge, Boltzmann’s constant, and the electron temperature, the plasma density at the present Ti-C:H deposition condition is estimated to be \( \sim 4 \times 10^{11}/\text{cm}^3 \). During the deposition of the Ti-C:H/Ti/Si(100) specimens, the substrate bias was varied between –20 and –100V while the Ti cathode current was fixed at 0.8A. Figure 3-4 shows \( R_{\text{Ti/C}} \) of the second series of Ti-C:H/Ti/Si(100) specimens, as determined by XPS, as a function of \( V_b \). Figure 3-4 shows that the composition of the second series of Ti-C:H/Ti/Si(100) specimens remained approximately constant while the energy of ionic species bombarding the substrate changed from \( \sim 39 \) to \( \sim 119 \) eV.

![Figure 3-3 Plasma potential \( \phi_p \) as a function of substrate bias \( V_b \)](image_url)
Figure 3-4 $R_{Ti/C}$ of the second series of Ti-C:H/Ti/Si(100) specimens as a function of substrate bias $V_b$.

Figure 3-5 shows the Si substrate curvature change, measured during a Ti-C:H growth period and the substrate cooling period immediately following, after the growth had been stopped. The presence of significant intrinsic stresses is reflected in a total $\Delta D/D_0$ of $\sim 130\%$. The measured curvature change suggests the presence of two growth stages, with the integrated stress increasing approximately linearly with time or film thickness in the late stage, 400 sec and after. In addition, Figure 3-5 shows a $\Delta D/D_0$ change of less than 10% during the entire growth stop/substrate cool period, verifying in the present case that there is a negligible amount of stress relaxation within the film and that the substrate temperature variation does not cause significant curvature change. Figure 3-6(a) shows integrated stress within Ti-C:H layers as a function of the layer thickness for several specimens of the Ti-C:H/Ti/Si(100) with varying Ti composition presented in chapter 2. In all cases, the data indicate that the intrinsic stress within Ti-C:H is compressive and suggest the existence of two growth stages. In the
Figure 3-5 Si substrate curvature as measured by $\Delta D/D_0$ as a function of time during Ti-C:H deposition. A growth stop and cool down period of 1500 sec immediately followed the deposition.

In the early growth stage, $\sigma_f$ increases to $\sim$-500N/m at $\sim$200nm in thickness, relatively independent of the Ti composition. In the late growth stage, $\sigma_f$ exhibits an approximately linear increase with thickness, but with a clearly composition dependent slope. Since the average intrinsic stress is given by the increment in integrated stress divided by the increment in film thickness, Figure 3-6(a) shows that the average intrinsic stress during late stage growth depends significantly on the Ti composition.

Figure 3-6(a) shows the development of significant intrinsic compression during the early growth stage, $\sim$ -500N/m/200nm or -2.5GPa. It also suggests that this early stage intrinsic compression is not dominated by percolation, since the dependence of $\sigma_f$
Figure 3-6 Integrated stress within Ti-C:H as a function of thickness for (a) specimens deposited under the same ion energy (69eV) with varying compositions; (b) specimens with same composition (R_{Ti/C}=0.35) deposited under ion energies ranging from 39 to 89eV.
on composition is weak. The observation of early stage compression seems to rule out cluster coalescence as the sole mechanism for stress generation, since this would lead to an overall tensile stress \(^\text{21}\). Reversible atom incorporation into boundaries within the growing film has been suggested as a possible mechanism for generating intrinsic compressive stresses. In the present case, we observed no significant stress relaxation after a growth interruption, which rules out this mechanism as contributing significantly to the observed intrinsic compression, since atom out-migration from boundaries would be expected once the growth flux is interrupted \(^\text{22}\). The model for reversible atom incorporation into boundaries, developed for growth of high mobility polycrystalline metal films, is not expected to apply to the present case, where the deposition temperature of \(\leq 250^\circ\text{C}\) is low compared to the melting temperature of TiC and the system is expected to have low surface mobility. Surface stresses can also induce significant intrinsic stresses within thin films. As the film thickness increases to large values, a limiting intrinsic stress \(\sigma_{ss}\) is reached,

\[
\sigma_{ss} = -\left(f + g\right)/t_o
\]

where \(f\) and \(g\) are respectively surface stresses associated with the Ti-C:H top surface and the Ti-C:H/Ti interface, and \(t_o\) is the thickness at which the Ti-C:H layer is firmly anchored to the growth template \(^\text{23}\). Given the usual magnitude of surface stresses and \(t_o\), \(\sim +1\text{N/m}\) and \(1\text{nm}\), respectively, GPa level intrinsic compression can be generated.

Figure 3-6(b) shows integrated stress within Ti-C:H layers as a function of the layer thickness, for several specimens of the Ti-C:H/Ti/Si(100) specimen series as a function of the ion energy. In all cases, the data indicate that the intrinsic stress within Ti-C:H is compressive
and again suggest the existence of two growth stages. In the late growth stage, the slope of $\sigma_{tf}$ vs. thickness is clearly dependent on the ion energy. Figure 3-7 shows this dependence for the Ti-C:H/Ti/Si(100) specimen series. The late stage average compressive stress increases in magnitude as the ion energy increases from 20 to 80eV, and appears to saturate at ~ -2.5GPa at ion energies above 80eV.

![Graph showing the relationship between substrate bias (V) and average stress (GPa).](image)

Figure 3-7 Late stage average intrinsic stress within Ti-C:H as a function of the ion energy.

While Figure 3-6(a) shows that the early stage $\sigma_{tf}$ vs. thickness curves are similar when the energy of ionic species bombarding the substrate was fixed, Figure 3-6(b) clearly shows that ion energy exerts a significant influence on the early stage intrinsic stress development. Considering that the composition of the Ti-C:H/Ti/Si(100) specimen series deposited under varying ion energies is approximately a constant, data shown in Figure 3-6(b) seem to rule out surface stress as the sole mechanism for stress generation in the early stage,
since this would lead to a relative independence of stress on ion energy. In contrast to the mechanism of reversible atom incorporation into boundaries, “ion peening” leads to the incorporation of extra atoms into the film in an irreversible fashion, generating intrinsic compression which does not relax when the growth flux is interrupted. The increased compression with increasing ion energy, as shown in Figure 3-6(b), is suggestive of ion peening contributing to the overall stress development. Further, ion bombardment is known to influence nuclei size and nucleation rate \(^{24}\). Figure 3-8 (a) and (b) show cross-sectional HRTEM micrographs of two Ti-C:H specimens of the second Ti-C:H/Ti/Si(100) specimen series, deposited at ion energies of 39 and 109eV, respectively. In both cases, B1-TiC nanocrystals embedded within an a-C:H matrix are visible. Based on statistics on larger regions than that are shown in Figure 3-8, the average sizes of the TiC nanocrystals are 2.3 and 3.7nm, respectively. Figure 3-8 thus supplies indirect evidence that ion energy influences the nucleation process of Ti-C:H, although the details of which are complicated by the presence of two phases, TiC and a-C:H. Differences in nucleation rate and nuclei size may contribute to intrinsic stress development when nucleated individual clusters coalesce. Thus the detailed mechanisms governing the development of early stage intrinsic stress within the Ti-C:H layer are likely complex, reflecting a combination of possible factors including surface stress, ion peening, and cluster coalescence.

Figure 3-9(a) and Figure 3-9(b) show respectively the hardness and indentation modulus of Ti-C:H coatings, as a function of the ion energy during deposition. The variations of hardness and modulus parallel each other, and the hardness to modulus ratio is approximately a constant. The variation of hardness with ion energy appears to track the variation of intrinsic compression, increasing from \(~7\) to \(~16\)GPa as the ion energy increases
Figure 3-8 Influence of ion energy on the structure of Ti-C:H coatings: cross-sectional HRTEM micrograph of a Ti-C:H layer deposited at ion energies of (a) 39eV; (b) 109eV, respectively.

from 40 to 80eV and saturates at ~ 16GPa, suggesting some form of coating structure alteration as the ion energy increases. One common contributor to decreased hardness of nanostructured ceramics is the presence of porosity. In the present case, the HRTEM evidence as shown in Figure 3-8(a) showed no indication of nanoscale porosity, thus requiring a more subtle mechanism for the observed increase in hardness with increasing ion energy. Whether
the higher energy ion bombardment alters the nature of the B1-TiC phase, the a-C:H phase, or
the TiC/a-C:H interfaces remains to be clarified.

Metal-containing hydrocarbon coatings, of which Ti-C:H forms a prototype, are of
interest in a variety of surface engineering applications. For example, the W-C:H coating
system has been shown to prolong surface related contact fatigue life in gear systems\textsuperscript{25}. W
and Ti, as well as other transition metals employed in metal-containing hydrocarbon coatings
such as Cr and Nb, are strong carbide formers\textsuperscript{26}. Analogous to the Ti-C:H system, W-C:H
coatings possess a nanocomposite structure, consisting of nanocrystalline WC embedded
within an a-C:H matrix. The thermodynamic and kinetic aspects of coating growth in these
systems share similarities. It is expected that the general trends regarding intrinsic stress
development within Ti-C:H would manifest themselves during growth of other amorphous
hydrocarbon based ceramic nanocomposite coatings deposited at low temperatures.

Figure 3-9 Mechanical properties of Ti-C:H coatings at a fixed composition: (a) hardness as a
function of the ion energy during deposition, (b) indentation modulus as a function of the ion
energy during deposition.
3.4 Conclusion

A detailed experimental study of the dependence of intrinsic stress within Ti-C:H coatings on the energy of ionic species was performed by measuring the substrate curvature change in situ. The intrinsic compression within Ti-C:H has been shown to depend significantly on the energy of ionic species bombarding the substrate during growth. Although there are likely multiple mechanisms influences intrinsic stresses within Ti-C:H coatings, the present results combining with the previous study of intrinsic stress dependence on coating composition suggest that the ion peening mechanism significantly influences the development of intrinsic stresses in this case, and is likely to play a significant role in stress development in other amorphous hydrocarbon based ceramic nanocomposite coating systems deposited at low temperatures.

3.5 References

4.1 Introduction

Application of single phase ceramic coatings, such as TiN and TiC, on metal cutting tools has been practiced in industry for decades. More recently, coatings have been applied to macroscale mechanical components, such as gears \(^1\) and bearings, \(^2\) and to microfabrication tools, such as microscale mold inserts, \(^3\) to engineer the chemical, mechanical, and tribological properties of the relevant near-surface regions. For these applications, ceramic nanocomposite coatings consisting of mixtures of two or more phases with characteristic structural length scales on the order of a few nanometers have attracted attention. Mechanical and tribological properties of ceramic nanocomposite coatings are observed to vary systematically with the average composition, \(^4\) and offer the potential of tailoring coating properties to suit the intended application.

Various macro and micro manufacturing processes demand coatings that perform well chemically and tribologically at high temperatures, including dry machining of metals \(^5\) and compression micromolding of metals. \(^6\) In dry machining applications where cutting temperatures can reach 400-800\(^\circ\)C, cutting improvements have been observed when cast iron was machined with tools coated with single-phase metal nitride coatings, such as TiN, CrN, and TiAlN. \(^7\) In contrast, tools coated with carbon-based coatings have been found to cause less material build-up on cutting edges in Al dry machining tests as compared to nitride coated tools. \(^8\) Recent experiments showed that microscale features can be successfully formed

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in Al by micromolding at \(-450^\circ\text{C}\) with electrodeposited Ni mold inserts conformally coated with a carbon based coating. In contrast, severe adhesion-induced damage occurs when Al micromolding was carried out with uncoated Ni inserts.\(^9\) These observations show that chemistry and tribology of high temperature coating-metal contacts significantly influence manufacturing performance, and suggest that carbon based coatings may be favorable for high temperature contacts with Al alloys. Because efficient and environmentally benign manufacturing of Al-alloy based macro and micro components is of broad interest, a need exists for carbon-based coatings that are functional and durable at high temperatures.

Hard amorphous carbon (a-C) and hydrogenated amorphous carbon (a-C:H) coatings deposited from energetic beams have been a subject of long-standing interest.\(^{10, 11}\) Metal-containing amorphous carbon (Me-aC) and metal-containing hydrogenated amorphous carbon (Me-C:H) coatings have been investigated so as to tailor their tribological characteristics by varying the metal composition.\(^{12}\) Plasma assisted vapor phase techniques have been used to deposit nanostructured Ti-aC\(^{13}\) and Ti-C:H\(^{14}\) coatings at temperatures of 250\(^\circ\text{C}\) or below. Ti-C:H coatings deposited at such low-temperatures have been shown to consist of nanocrystalline B1-TiC clusters embedded within an a-C:H matrix, which contains a significant fraction of hydrogen.\(^{15}\)

Thermal stability of low temperature deposited, hard carbon coatings has been investigated previously. The atomic bonding configurations of low temperature deposited a-C and a-C:H thin films are known to change as a function of annealing. Through Raman spectroscopic evidence, increasing amounts of three-fold coordinated, graphite-like regions were suggested to form within a-C and a-C:H films when they are subjected to increasing annealing temperatures.\(^{16}\) The stability temperatures for a-C:H films and F-C:H films
deposited at low temperatures were reported to range from ~400°C to ~550°C. Similarly, Si-C:H films deposited at low temperatures were reported to lose hydrogen and graphitize in the temperature range of 550-700°C. Furthermore, a correlation between the thermal stability of Si-C:H films in air and the Si-C:H film wear rates under unlubricated sliding conditions was suggested. The structure and mechanical properties of Me-C:H coatings deposited at high temperatures, to our knowledge, have not been studied in detail. In this chapter, we report results of characterization of Ti-C:H coatings deposited at ~600°C. Detailed structural characterization and mechanical properties measurements were carried out and compared to results obtained on Ti-C:H coatings similarly deposited at low temperatures.

4.2 Experimental

Ti-C:H coating deposition was carried out in a hybrid chemical/physical vapor deposition (CVD/PVD) tool, which combines an inductively coupled plasma (ICP) with balanced magnetron sputtering from multiple sources. Si(100) substrates were radiatively heated by a planar, boron nitride covered graphite resistance heater placed behind the substrate at a distance of ~5mm. The bias voltage on the heater was kept constant during each deposition. With an ultimate base pressure of ~5×10⁻⁹Torr for the CVD/PVD tool, the run time base pressure after the substrate reached steady state temperature was ~5×10⁻⁸Torr.

Each Ti–C:H deposition on Si(100) substrates began with heating the substrate to 550°C, as measured by an infrared pyrometer using a factory supplied emisivity of 0.68. After the substrate temperature reached steady state, the Si(100) wafer was placed in the deposition zone and etched for 10min in a pure Ar(99.999%) ICP. The total ICP input power during etching was 1000W, and the bias voltage on the substrate during etching was -100V.
Following substrate etching, a 40min Ti–C:H deposition commenced immediately in an Ar/C2H2(99.99%) mixture by combining the ICP generated Ar/C2H2 plasma with dc magnetron sputtering of two pure Ti(99.99%) cathodes in the current-controlled mode. The Ar and C2H2 input flow rates were 50sccm and 5sccm, respectively. During Ti-C:H deposition, the substrate bias was –50V, and the total ICP input power was held constant at 1000W. Previous planar and electron emissive probe measurements conducted within Ar/C2H2 plasmas used to deposit Ti-C:H coatings showed that the plasma potential is ~19V, and the plasma density is ~4×10^{11}/cm^3.21 Total pressure was 1.6–1.7 mTorr throughout the entire deposition process. A series of Ti–C:H coatings were deposited following the same procedure, varying only the Ti cathode current to vary the Ti composition in the coating. Separate measurements with K-type thermocouples attached to sacrificial Si substrates showed an additional temperature rise of ~50°C during deposition due to plasma heating. Therefore the deposition temperatures for this series of Ti-C:H coatings were estimated to be ~600°C.

For comparison, a second series of Ti-C:H coatings were deposited following the procedure as outlined above. A pure Ti interlayer, ~80nm in thickness, was sputter deposited onto plasma etched Si(100) prior to Ti-C:H deposition. For this series of specimens, no intentional heating was applied to the Si(100) substrates. Previous substrate temperature measurements indicated that the substrate temperature during Ti-C:H deposition was ~250°C.22

Chemical compositions of Ti-C:H coatings were measured with X-ray photoelectron spectroscopy (XPS) on a Kratos AXIS165 system, using a monochromatic Al Kα excitation
source. Prior to XPS spectrum acquisition, the Ti–C:H specimen surface was etched with a 5kV 10mA Ar\(^+\) ion beam for 5min. Survey scans in the binding energy range of 0–1000eV in 1eV steps and high resolution scans of the C1s region in 0.1eV steps were acquired immediately after ion etching. Coating chemical compositions in the form of Ti to C atomic ratios (R\(_{\text{Ti/C}}\)) were obtained from raw XPS spectral data using Kratos supplied sensitivity factors.

Ti–C:H coating thicknesses were measured post-deposition by cross-sectional scanning electron microscopy (SEM), and ranged between 1-2\(\mu\)m. Cross-sectional transmission electron microscopy (TEM) studies on Ti-C:H coatings were carried out on a JEOL JEM2010 microscope operated at 200kV. Cross-sectional TEM specimens were prepared following standard procedures, with mechanical polishing followed by ion beam milling with a Gatan 691 Precision Ion Polishing System at an ion-energy of 4kV and an incidence angle of ~5\(^\circ\).

Electrical sheet resistances of high temperature deposited Ti-C:H/Si(100) specimen structures were measured with a Veeco FPP-100 four-point probe setup. Resistance measurements on 20mm \(\times\) 20mm Ti-C:H/Si specimens were carried out at a probe spacing of 1.6mm. Raw sheet resistance was measured by continuously scanning the outer probe current, until the inner probe voltage reaches a constant value of 10mV, with no geometric correction factor applied.\(^{23}\)

Instrumented nanoindentation was carried out on a Hysitron Triboscope interfaced to a Digital Instrument Dimension 3100 atomic force microscope (AFM) using a Berkovich diamond indenter tip. Instrument load frame compliance and indenter tip area function
calibration was carried out using a Hysitron supplied fused silica specimen assuming a contact-depth ($h_c$) independent elastic modulus. Indentations on Ti–C:H/Si(100) specimens were carried out at multiple loads, ranging from 500 to 3000μN. The Oliver/Pharr data analysis procedure\textsuperscript{24} was followed to extract values of the indentation modulus, $E_{\text{ind}}=E/(1-\nu^2)$ where $E$ and $\nu$ are respectively the Young’s modulus and Poisson’s ratio, and the hardness, $H$, from experimental load versus displacement curves. Results taken at $h_c$ less than 10% of the total coating thickness were averaged to obtain the coating modulus and hardness values. Coating surface profiles were examined with contact mode AFM with the Berkovich indenter tip, and the average roughness of the as-deposited coatings was determined to be ~40nm.

X-ray absorption near-edge structure (XANES) spectroscopy was performed on the double crystal monochromator (DCM) beamline of the synchrotron facility at the Louisiana State University Center for Advanced Microstructures and Devices (LSU CAMD). Ti K-edge spectra of the Ti-C:H specimens were recorded in the fluorescence mode. Photon energy selection was provided by a Ge(220) DCM. The incident photon intensity was monitored with a He-filled ionization chamber. A 12-channel Ge detector with individual energy discrimination was used to collect twelve fluorescence spectra simultaneously for each specimen. A typical Ti K-edge scan consisted of approximately 1.0, 0.3 and 0.8eV steps with integration times of 2.0, 4.0, and 4.0sec in the spectral regions of 4900-4950, 4950-5010, and 5010-5400eV, respectively. For each run, the twelve fluorescence channel spectra were averaged. The averaged XANES spectra were normalized to unit edge height by fitting the pre-edge and post-edge regions respectively with a first-degree and a third-degree polynomial using the WinXAS97 analysis package.\textsuperscript{25}
Annealing of Ti-C:H specimens deposited at ~600°C and at ~250°C was carried out in a custom-built, high-vacuum tube furnace. Pumped by a turbomolecular pumping system, the system base-pressure is \( \sim 2 \times 10^{-8} \text{Torr} \). High and low temperature deposited Ti-C:H specimens were annealed at 600°C for one hour at pressures \( < 3 \times 10^{-7} \text{Torr} \).

Raman scattering measurements were performed on as-deposited and annealed Ti-C:H specimens. Scattering signals were collected at room temperature from a Jobin-Yvon Horiba LabRam Micro-Raman instrument with a 20mW 632.8nm HeNe laser. Filters were used to attenuate the incident beam such that spectra were obtained with 2mW of incident laser power with the laser beam focused to a spot several \( \mu \text{m} \) in size. To avoid effects of laser heating, spectra were acquired repeatedly until a steady state condition was observed. All spectra reported were acquired under steady state conditions with exactly the same acquisition settings, to facilitate the comparison of peak intensities on a relative basis as a measure of scattering signal strength. Raw Raman spectra in the energy range of 800-2000 cm\(^{-1}\) were fitted with a linear background and two separate peaks. For the Ti-C:H specimens deposited at \( \sim 600°C \) and \( \sim 250 \, ^°\text{C} \), Lorentzian and Gaussian peak profiles were used respectively in the fitting.

4.3 Results and Discussion

Figure 4-1(a) shows a XPS survey spectrum of one Ti-C:H coatings deposited at \( \sim 600°C \). At an \( R_{\text{Ti/C}} \) of 0.36, the coating contains, besides Ti and C, \( \sim 1.5 \text{at.}% \) Ar and less than 3at.% O. The impurity levels are typical of the entire series of Ti-C:H coatings deposited at \( \sim 600°C \). Hydrogen composition within the coatings was not probed by XPS. Figure 4-1(b) shows the average \( R_{\text{Ti/C}} \) for the series of Ti-C:H specimens deposited at \( \sim 600°C \) as a function
Figure 4-1 XPS examination of Ti-C:H specimens: (a) a XPS survey spectrum of a Ti-C:H specimen deposited at ~600°C with $R_{Ti/C} = 0.36$; (b) Ti to C atomic ratios as a function of the Ti cathode current during deposition for two series of Ti-C:H specimens deposited respectively at ~250°C and ~600°C.
of the Ti cathode current. Values of $R_{Ti/C}$ for the second series of Ti-C:H specimens deposited at $\sim 250^\circ C$ are also shown in Figure 4-1(b). This comparison indicates that, at fixed $Ar/C_2H_2$ plasma density and plasma potential, substrate bias voltage, and incoming Ti atom flux to the substrate, increasing the substrate temperature from $\sim 250^\circ C$ to $\sim 600^\circ C$ leads to a preferential increase in C incorporation into the film, and consequently a decrease in the $R_{Ti/C}$ of the resulting film.

Figure 4-2 shows two C1s core level XPS spectra from two Ti-C:H specimens deposited under the same plasma conditions and the same Ti cathode current of 1.8A. The deposition temperatures for these two specimens were $\sim 250^\circ C$ and $\sim 600^\circ C$, respectively. The C1s spectra show two prominent components, which were fitted with two Gaussians. The result of the fitting shows that binding energies of the first component are 281.9eV and 282.0eV for the specimens deposited at $\sim 250^\circ C$ and $\sim 600^\circ C$, respectively. The full width at half maximum (FWHM) of this component is $\sim 0.6eV$, showing no significant dependence on the deposition temperature. The binding energies of the second component are 285.1eV and 284.7eV for the specimens deposited at $\sim 250^\circ C$ and $\sim 600^\circ C$, respectively. The binding energy of the second component appears to shift somewhat with the deposition temperature. The FWHM of the second component is $\sim 1.6eV$, again showing no significant dependence on the deposition temperature. The presently observed binding energies are in good agreement with those previously observed in XPS spectra of Ti-C:H coatings. The first and second components are attributed to a crystalline B1-TiC phase and an amorphous carbonaceous phase, respectively. At fixed flux of incoming Ti atoms and flux of hydrocarbon ionic species to the substrate, increasing the deposition temperature from $\sim 250^\circ C$ to $\sim 600^\circ C$ increases the
fraction of the amorphous carbonaceous phase within Ti-C:H, according to data shown in Figure 4-2. This is in qualitative agreement with information shown in Figure 4-1(b).

![Figure 4-2](image)

Figure 4-2 High-resolution C1s XPS spectra of two Ti-C:H specimens deposited at the same Ti cathode current of 1.8A at ~250°C and ~600°C, respectively.

The nature of the Ti bonding environment in high temperature deposited Ti-C:H coatings is further elucidated by Ti K-edge XANES spectra taken from the series of Ti-C:H specimens deposited at ~600°C. As shown in Figure 4-3, identical spectral features, consisting of a pre-edge bump at ~4972eV, a double peak structure at ~4985eV and ~4998eV, and four additional peaks around ~5035eV, ~5060eV, ~5082eV, and ~5136eV are observed on all Ti-C:H specimens. The signal-to-noise ratio of the spectra increases with increasing Ti composition. The positions of the spectral features and the amplitudes of the post-edge oscillations show little change as the average Ti composition increases. The presently
Figure 4-3  Normalized Ti K-edge XANES spectra of a series of Ti-C:H specimens deposited at ~600°C.

measured Ti K-edge XANES spectra agree well with previously observed XANES from bulk crystalline B1-TiC,\cite{27} and indicate that Ti atoms incorporates into high temperature deposited Ti-C:H coatings as B1-TiC, even at the lowest $R_{\text{Ti/C}}$ of 0.01. The Ti K-edge XANES spectra corroborate the B1-TiC component observed in the XPS C1s spectra shown in Figure 4-2, and indicate that the short-range Ti bonding environment is overwhelmingly that of B1-TiC. Judging from the XANES spectrum of the coating with a $R_{\text{Ti/C}}$ of 0.01, precipitation of B1-TiC has already occurred within this specimen. Therefore the amount of Ti dissolved within the amorphous carbonaceous phase should be less than $R_{\text{Ti/C}}=0.01$ at the deposition temperature of ~600°C. The substantial similarity of the post-edge XANES oscillations observed from Ti-C:H specimens deposited at ~600°C as compared to those observed from bulk B1-TiC suggests that the TiC crystals forming within the Ti-C:H are bulk-like in terms
of bonding distances and coordination, similar to previous observations made on Ti-C:H coatings deposited at ~250°C.27

Figures 4-4(a) and 4-4(b) show respectively average $E_{ind}$ and $H$ of the series of Ti-C:H specimens deposited at ~600°C. Values of $E_{ind}$ and $H$ for the second series of Ti-C:H specimens deposited at ~250°C are also shown for comparison. Both $E_{ind}$ and $H$ increase with increasing Ti composition. The most pronounced difference between the high temperature and low temperature deposited specimens is observed at low values of $R_{Ti/C}$, where $E_{ind}$ and $H$ of the high temperature deposited specimens are about a factor of 10 lower than the low temperature deposited specimens at similar Ti compositions. Given the structural similarity of the crystalline TiC phase within the Ti-C:H specimens to bulk B1-TiC, the difference in the modulus and hardness of high temperature deposited Ti-C:H specimens is suggested to arise from a substantial change in the structure of the carbonaceous phase due to the increased deposition temperature.

Figure 4-5 shows a cross-sectional high-resolution TEM micrograph of the Ti-C:H specimen deposited at ~600°C with $R_{Ti/C}$=0.01. The inset in Figure 4-5 shows the corresponding selected area electron diffraction pattern (SADP), from an area which included both the Ti-C:H film as well as the Si(100) substrate. In addition to the Si<110> zone axis pattern, several polycrystalline diffraction rings are evident in the SADP. The diffraction rings can be indexed to that of a cubic system, with a lattice parameter of ~0.422nm. This lattice parameter is close to that of bulk B1-TiC, 0.433nm.28 Corresponding to the polycrystalline diffraction rings, nanocrystalline clusters, ~2.0-2.4nm in size and decorated with lattice fringes, are clearly evident in Figure 4-5. These observations corroborate the XANES data
Figure 4-4  Mechanical characterization of two series of Ti-C:H specimens deposited respectively at ~250°C and ~600°C by instrumented nanoindentation: (a) indentation modulus versus Ti composition; (b) hardness versus Ti composition.
shown in Figure 4-3, and indicate the formation of nanocrystalline B1-TiC clusters within Ti-C:H at this low Ti composition. In contrast to low temperature deposited Ti-C:H coatings where about 1at.% of Ti can be dissolved within the a-C:H matrix, increasing the deposition temperature to ~600°C leads to the formation of B1-TiC at all Ti compositions studied. The uniformity of the polycrystalline diffraction rings indicates that the B1-TiC nanoclusters nucleated with random orientation. An additional diffraction feature is observed in the SADP in between the Si{111} spots, corresponding to a real space distance of ~0.35nm. This distance is close to the 0.34nm spacing observed in partially graphitized carbon, and suggests the possible presence of graphitic order. Correspondingly, the high-resolution micrograph shows approximately parallel fringes in the a-C:H regions. These quasi-parallel fringes extend over longer distances than what is typically observed in truly amorphous
carbon and hydrogenated carbon materials. Such microscopic evidence suggests that the amorphous carbonaceous phase in Ti-C:H specimens deposited at ~600°C contains increased graphitic short and medium range order as compared to low temperature deposited a-C and a-C:H structures, while still lacking the long-range translational order of well graphitized structures. It is suggested that this increased graphitic order within the amorphous carbonaceous matrix is responsible for the observed low modulus and low hardness of high temperature deposited Ti-C:H coatings with low Ti compositions.

Figure 4-6(a) shows a cross-sectional high-resolution TEM micrograph of a Ti-C:H specimen deposited at ~600°C, with a $R_{Ti/C}$ of 0.37. The inset in Figure 4-6(a) shows the corresponding SADP from an area which included both the Ti-C:H film and the Si(100) substrate. A multitude of polycrystalline diffraction rings are evident in the SADP, which can all be indexed to that of a cubic system, with a lattice parameter of ~0.436nm which closely matches that of bulk B1-TiC. An increase in the size of individual B1-TiC nanoclusters is evident in the high-resolution micrograph with the increase in the Ti composition, where cluster sizes of 4.5nm or larger are observed. Regions of the amorphous carbonaceous phase have similar appearance as in Figure 4-5. Each B1-TiC nanocluster appears to be free of internal dislocations. Figure 4-6(b) shows that, at this increased Ti composition, separate TiC nanoclusters touch and coalesce. Dislocations are observed at these TiC nanocrystalline boundaries. One such example is shown in Figure 4-6(b), where a few isolated dislocations delineate a low-angle boundary where two TiC nanocrystals meet. Indirect evidence for the coalescence of individual TiC nanoclusters with increasing Ti composition is obtained from electrical sheet resistance measurements. The electrical resistivity of the series of Ti-C:H specimens deposited at ~600°C is shown in Figure 4-7 as a function of the average $R_{Ti/C}$.
Figure 4-6  TEM examination of a Ti-C:H specimen deposited at ~600°C with $R_{TiC} = 0.37$:
(a) a high-resolution micrograph with the corresponding SADP shown in the inset. The circle highlights a single crystal TiC grain greater than 3nm in size and the arrow points to quasi-parallel fringes within the a-C:H region; (b) a high-resolution micrograph showing the coalescence of two TiC nanocrystals. The coalescence boundary is highlighted with two arrows.
A pronounced drop in resistivity as the Ti composition increases is consistent with coalescence of the metallic TiC nanoclusters, leading to conducting paths of increasing spatial extents. An estimate of the resistivity of the amorphous carbonaceous matrix can be obtained from measured resistivity at low $R_{Ti/C}$. The estimated resistivity is $\sim 2 \times 10^4 \mu\Omega \cdot \text{cm}$, and suggests that the high temperature deposited amorphous carbonaceous matrix, while possessing an increased degree of short and medium range graphitic order, is still by no means well graphitized. The electrical resistivity observations are consistent with the TEM evidence, showing the absence of micro- or nano-scale single crystal graphite in the a-C:H matrix within high temperature deposited Ti-C:H.

![Graph showing electrical resistivity as a function of Ti/C atomic ratio](image)

**Figure 4-7** Electrical sheet resistivity of a series of Ti-C:H specimens deposited at ~600°C as a function of Ti composition.
The nature of the amorphous carbonaceous matrices in Ti-C:H specimens deposited at low and high temperatures was further probed by Raman scattering, which has been used extensively for characterizing the bonding configurations of a-C:H.\textsuperscript{16} Figures 4-8(a) and 4-8(b) show two series of Raman spectra obtained from as-prepared Ti-C:H specimens with different Ti contents, deposited at \$250^\circ\text{C}\$ and \$600^\circ\text{C}\$, respectively. For all Ti-C:H specimens examined, D band (associated with the disorder-allowed zone-edge modes of graphite) and G band (associated with the optically allowed $E_{2g}$ zone center mode of crystalline graphite)\textsuperscript{16} above a smoothly varying background are observed in the spectral range of 800-2000cm$^{-1}$.

Visual inspection of the spectra suggests that the two bands from Ti-C:H specimens deposited at \$600^\circ\text{C}\$ are sharper than those from Ti-C:H specimens deposited at \$250^\circ\text{C}\$. Following Ferrari and Robertson,\textsuperscript{30} Raman spectra from low temperature deposited Ti-C:H specimens were fitted with a linear background together with two Gaussians, whereas spectra from high temperature deposited specimens were fitted with a linear background together with two Lorentzians.

As the Ti content within Ti-C:H increases, one similar trend in the Raman spectra can be observed in both low and high temperature deposited specimens, namely, that the overall intensity of the Raman signal shows a significant decrease. This is reflected in the fitted Raman band parameters shown in Table 4-1. For the low temperature deposited Ti-C:H specimens, fitted Raman band positions and FWHMs do not change significantly as the Ti content increases from $R_{\text{Ti/C}} = 0.02$ to $R_{\text{Ti/C}} = 0.21$, while the band heights exhibit a significant decrease. A decrease in the Raman band heights of similar magnitude is also observed for the high temperature deposited Ti-C:H specimens as the Ti content increases from $R_{\text{Ti/C}} = 0.02$ to $R_{\text{Ti/C}} = 0.37$. The observed decrease in the overall Raman intensity as the Ti content increases is consistent with the Ti-C:H specimens being B1-TiC/a-C:H two-phase
Figure 4-8  Raman scattering examination of as-deposited Ti-C:H specimens: (a) scattering intensity versus wavenumber for four Ti-C:H specimens deposited at ~250°C. The dashed lines indicate the two Gaussian components of the fit; (b) scattering intensity versus wavenumber for four Ti-C:H specimens deposited at ~600°C. The dashed lines indicate the two Lorentzian components of the fit.
Table 4-1 Summary of fitting parameters for Raman spectra obtained from as-deposited Ti-C:H specimens. The deposition temperatures of ~250°C and ~600°C are denoted as LT and HT, respectively. Raman spectra of Ti-C:H specimens deposited at LT are fitted with a linear background and two Gaussians, while those of Ti-C:H deposited at HT are fitted with a polynomial background and two Lorentzians.

<table>
<thead>
<tr>
<th>Deposition temperature</th>
<th>Ti to C atomic ratio</th>
<th>D peak</th>
<th>G peak</th>
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<tr>
<td></td>
<td></td>
<td>Position (cm⁻¹)</td>
<td>FWHM (cm⁻¹)</td>
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</tr>
<tr>
<td></td>
<td>0.62</td>
<td>1385</td>
<td>280</td>
</tr>
<tr>
<td>HT</td>
<td>0.02</td>
<td>1329</td>
<td>141</td>
</tr>
<tr>
<td></td>
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<tr>
<td></td>
<td>0.37</td>
<td>1341</td>
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</tbody>
</table>

mixtures, regardless of the deposition temperature. As the Ti content within Ti-C:H increases, the fraction of the a-C:H phase which gives rise to the Raman signal decreases while the fraction of the first-order Raman-inactive B1-TiC phase increases, leading to the overall decrease in Raman intensity. A spectral similarity is observed from Ti-C:H specimens deposited at ~250°C with different Ti contents, in terms of the Raman band positions and FWHMs. This spectral similarity suggests that the bonding configurations of the a-C:H matrices within low temperature deposited Ti-C:H do not change significantly as the Ti composition changes. For high temperature deposited Ti-C:H specimens, very similar Raman spectral shapes are also observed at R_{Ti/C} values of 0.02 and 0.05, suggesting similar bonding configurations of the a-C:H matrices. As the higher Ti contents of R_{Ti/C} = 0.22 and R_{Ti/C} = 0.37, the FWHMs of the two Raman bands show an increase, together with some shift in the Raman band positions. These changes in the Raman spectra suggest that, at the deposition
temperature of \(\sim 600{^\circ}C\), the structure of the a-C:H matrix may be influenced by the presence of a significant volume fraction of the TiC phase.

At Ti contents less than \(R_{Ti/C}=0.10\), a marked difference exists between Raman spectra obtained from Ti-C:H specimens deposited at \(\sim 250{^\circ}C\) and \(\sim 600{^\circ}C\). Raman spectra from low temperature deposited Ti-C:H specimens, shown in Figure 4-8(a), appear typical of hydrogenated amorphous carbon and consist of two broad bands. The center of one band is located at \(\sim 1373\text{cm}^{-1}\), with a FWHM of \(\sim 300\text{cm}^{-1}\). The center of the other band is located at \(\sim 1554\text{cm}^{-1}\), with a FWHM of \(\sim 120\text{cm}^{-1}\). These two bands are respectively the D and G bands commonly observed in a-C:H films, with similar band center positions and FWHMs as compared to previous observations.\(^{31}\) In contrast, Raman spectra from high temperature deposited Ti-C:H specimens, shown in Figure 4-8(b), show sharper D and G bands. For the high temperature deposited Ti-C:H specimens, the center of the D band is located at \(\sim 1330\text{cm}^{-1}\), with a FWHM of \(\sim 155\text{cm}^{-1}\). The center of the G band is located at \(\sim 1594\text{cm}^{-1}\), with a FWHM of \(\sim 80\text{cm}^{-1}\). The position of the G band shifts to higher energy and its FWHM decreases as compared to the low temperature deposited Ti-C:H specimen of similar Ti composition. The position of the D band shifts to lower energy as compared to the corresponding low temperature deposited Ti-C:H specimen, and its FWHM is also significantly reduced. These differences in the Raman spectra from high and low temperature deposited Ti-C:H specimens are consistent with those previously observed during ordering transformations from mechanically hard and structurally disordered amorphous carbon to nanocrystalline graphite,\(^{30}\) and suggest increased graphitic order in the a-C:H matrices of high temperature deposited Ti-C:H specimens. The presence of the strong D band in high temperature deposited Ti-C:H is related to the presence of \(sp^2\) bonded carbon atoms in the
configuration of aromatic rings and the breathing-mode carbon motions with $A_{1g}$ symmetry.

Taken together, the Raman data shown in Figure 4-8 suggest that increasing the deposition temperature of Ti-C:H from $\sim 250^\circ$C to $\sim 600^\circ$C while fixing other plasma parameters leads to increased short and medium range graphitic order in the a-C:H matrix, and are consistent with the electron microscopy evidence presented in Figure 4-5.

The sensitivity of the a-C:H phase within Ti-C:H to high temperature annealing is further probed by examining the Raman spectra of Ti-C:H specimens before and after annealing at $600^\circ$C in vacuum for one hour. The Ti-C:H specimens examined had identical Ti contents of $R_{Ti/C} = 0.02$. Raman spectral changes due to the annealing treatment are shown in Figure 4-9, and summarized in Table 4-2. Figure 4-9(a) shows Raman spectra of two low temperature deposited Ti-C:H specimens before and after annealing. As a result of the annealing, the position of the G band shifts to higher energy, from 1551cm$^{-1}$ to 1586cm$^{-1}$, and the D band position shifts to lower energy, from 1371cm$^{-1}$ to 1355cm$^{-1}$. The FWHM of the G band also decreases, from 130cm$^{-1}$ to 91cm$^{-1}$. These spectral changes are consistent with those observed previously during high temperature annealing of mechanically hard and structurally

Table 4-2 Summary of fitting parameters for Raman spectra obtained from Ti-C:H specimens in the as-deposited and the annealed state. The deposition temperatures of $\sim 250^\circ$C and $\sim 600^\circ$C are denoted as LT and HT, respectively. Annealing was carried out at $600^\circ$C for one hour in vacuum.

<table>
<thead>
<tr>
<th>Deposition temperature</th>
<th>Ti to C atomic ratio</th>
<th>Heat treatment</th>
<th>D peak</th>
<th>G peak</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Position (cm$^{-1}$)</td>
<td>FWHM (cm$^{-1}$)</td>
</tr>
<tr>
<td>LT</td>
<td>0.02</td>
<td>Not annealed</td>
<td>1371</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>Annealed</td>
<td>1355</td>
<td>292</td>
</tr>
<tr>
<td>HT</td>
<td>0.02</td>
<td>Not annealed</td>
<td>1329</td>
<td>141</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>Annealed</td>
<td>1330</td>
<td>138</td>
</tr>
</tbody>
</table>
Figure 4-9  Raman scattering examination of Ti-C:H specimens before and after vacuum annealing at 600°C: (a) scattering intensity versus wave number for two Ti-C:H specimens deposited at ~250°C. The dashed lines indicate the two Gaussian components of the fit; (b) scattering intensity versus wave number for two Ti-C:H specimens deposited at ~600°C. The dashed lines indicate the two Lorentzian components of the fit.
disordered amorphous carbon films, and suggest that the disordered a-C:H matrix in the low temperature deposited Ti-C:H transformed to a more graphitically ordered matrix due to annealing.

Although the a-C:H matrix in the high temperature deposited Ti-C:H specimen exhibits more graphitic order in the as-deposited state as compared to low temperature deposited specimens, Figure 4-9(b) shows that the same annealing treatment induces little change in their Raman spectral shape. Positions of the D and G bands remain respectively at ~1330 cm\(^{-1}\) and ~1596 cm\(^{-1}\), while their FWHMs remain respectively at ~140 cm\(^{-1}\) and ~73 cm\(^{-1}\), showing no dependence on annealing (see Table 4-2). The Raman data therefore indicate that the a-C:H matrix in high temperature deposited Ti-C:H is relatively stable against annealing at 600\(^{0}\)C, and further graphitization may require annealing to much higher temperatures. According to the model of Ferrari and Robertson, the Raman spectrum for well-crystallized graphite changes as defects are introduced into crystalline graphite, leading eventually to predominantly sp\(^{3}\) bonded amorphous carbon (ta-C) or hydrogenated amorphous carbon (ta-C:H). They proposed a three stage model to describe expected changes in the Raman spectrum resulting from the following structural transformations: graphite to nanocrystalline graphite, nanocrystalline graphite to a-C (or a-C:H), and a-C (or a-C:H) to ta-C (or ta-C:H). For transformations in the reverse direction, where a-C (or a-C:H) with a significant fraction of Csp\(^{3}\)-Csp\(^{3}\) bonding undergoes structural changes to structures with increasing degree of graphitic order, Csp\(^{3}\)-Csp\(^{3}\) bonds convert to Csp\(^{2}\)-Csp\(^{2}\) bonds, Csp\(^{2}\)-Csp\(^{2}\) bonded clusters increase in size, and ordered aromatic rings form. While these structural changes within the a-C or a-C:H matrix may involve changes in bond distances or bond angles in the short to medium range, further graphitization by forming well-defined crystalline graphite domains
may involve longer range atomic reordering. Our high temperature Ti-C:H deposition at
~600°C has apparently allowed the a-C:H matrix to form a structure with more graphitic order
as compared to the low temperature deposition at ~250°C, without forming well-defined
crystalline graphite domains (see Figure 4-5). The present observations regarding responses to
annealing suggest that this last step of developing well-defined crystalline graphite domains
may involve higher activation energies as compared to the processes needed to form local
aromatic ring structures. This would be consistent with the observation that while the a-C:H
matrix within low temperature deposited Ti-C:H was rendered more graphitic by annealing to
600°C, the a-C:H matrix within high temperature deposited Ti-C:H appears to be stable under
the same annealing treatment.

4.4 Conclusion

We have completed a detailed structural and mechanical characterization of Ti-C:H
specimens deposited at ~600°C, and compared their structural and mechanical characteristics
to Ti-C:H specimens deposited at ~250°C. The present structural characterization, combining
XPS, electron diffraction, high-resolution TEM, and Ti K-edge XANES, indicates that Ti
atoms incorporate into Ti-C:H predominantly as B1-TiC, and that Ti-C:H specimens are
TiC/a-C:H nanocomposites. Deposition at ~600°C promotes TiC precipitation, resulting in
even less Ti dissolution within the a-C:H matrix as compared to low temperature deposited
specimens. High temperature deposited Ti-C:H specimens were found to possess lower
modulus and hardness values as compared to low temperature deposited specimens, especially
at low Ti compositions. This is rationalized by TEM evidence of increased graphitic order
within the a-C:H matrix of high temperature deposited Ti-C:H, and supported by additional
Raman spectroscopic observations. Annealing treatment at 600°C combined with Raman
scattering measurements showed that the a-C:H matrix in high temperature deposited Ti-C:H specimens appears to be less structurally sensitive to additional high temperature annealing.

4.5 References


Chapter 5 Thermal Expansion of Ti-Containing Hydrogenated Amorphous Carbon Nanocomposite Thin Films *

5.1 Introduction

Modern macro- and micro-scale manufacturing processes often involve high temperature contact between the part and the tool. Examples include dry machining of metals at the macroscale \(^1\) and compression molding of metals at the microscale.\(^2\) Engineering the tool surface by thin film deposition can improve a manufacturing process or even enable an otherwise impossible process. For example, dry machining of cast iron, at upwards of 400-800°C, was improved with tools coated with single-phase metal-nitrides.\(^3\) Further, replication of high-aspect-ratio microscale features on Ni inserts onto aluminum was achieved by conformally coating the Ni insert with a Ti-containing hydrogenated amorphous carbon (Ti-C:H) thin film and using compression micromolding at ~450°C.\(^4\) During these manufacturing processes, coated tools undergo large and repeated temperature excursions. Thermal stresses due to differences between the coefficient of thermal expansion (CTE) of the film and the substrate furnish a driving force for the film to crack or delaminate from the substrate.\(^5\) Knowledge regarding CTE of thin films is a critical factor for determining stability of film/substrate assemblies.

CTE of hydrogenated amorphous carbon (a-C:H) thin films has been studied previously\(^6,7\). However, little is known about the CTE of a-C:H films containing more than a few atomic percent of carbide forming metals (Me-C:H). In contrast to a-C:H films, which are

homogeneous on length scales larger than a few nm, Me-C:H films are nanocomposites with nm-sized crystalline metal-carbide clusters embedded within an a-C:H matrix.\textsuperscript{8} Although Me-C:H thin films have been applied to macroscale gears\textsuperscript{9} and microscale bearings,\textsuperscript{10} their CTE dependence on the metal composition has not been measured. Ti-C:H thin films were shown to consist of B1-TiC nanoclusters embedded within an a-C:H matrix.\textsuperscript{11} Due to the orientational isotropy of a-C:H and the cubic symmetry of B1-TiC, the CTEs of both phases are represented by scalar quantities.\textsuperscript{12} In this chapter, effective CTEs of Ti-C:H thin films are measured as a function of the Ti composition.

5.2 Experimental

Ti-C:H thin films were synthesized with an inductively coupled plasma (ICP) assisted hybrid chemical/physical vapor deposition (CVD/PVD) technique.\textsuperscript{13} A series of Ti-C:H thin films with different Ti compositions were deposited onto the front sides of two-side polished, 300\(\mu\)m thick Si(100) substrates, cut along \(<100>\) directions into 4\(\times\)30mm beams. The curvature change of the Si(100) beam substrates due to Ti-C:H deposition were measured in-situ with a multi beam optical sensing (MBOS) technique, and the results were reported elsewhere.\textsuperscript{14} Each Ti-C:H specimen was deposited following the same procedure (in the configuration of Ti-C:H/Ti/Si(100) with a ~80nm thick Ti interlayer), fixing all deposition parameters except the incoming Ti atom flux, which was changed to vary the Ti composition of Ti-C:H. Substrate temperatures during Ti-C:H deposition were ~250\(^\circ\)C. Compositions of Ti-C:H films were characterized previously by Rutherford Backscattering Spectrometry (RBS) and hydrogen elastic recoil detection (ERD) measurements,\textsuperscript{14} from which the Ti to C atomic ratio (\(R_{\text{Ti/C}}\)) within Ti-C:H was obtained. The total film thickness was measured post-deposition by cross-sectional scanning electron microscopy (SEM), and ranged between 1 to 2\(\mu\)m.
Plan-view transmission electron microscopy (TEM) specimens of Ti-C:H were fabricated by mechanical polishing from the Si substrate side followed by ion milling until perforation. Electron energy loss spectroscopy (EELS) measurements at the C K-edge were performed on a JEOL JEM3010 microscope operated at 300kV. EELS spectra were collected with a Gatan Imaging Filter (GIF200) calibrated to yield the following energies for the edge maxima: Ni-L\textsubscript{3} (NiO) = 855.00±0.03eV; Ca-L\textsubscript{3} (CaCO\textsubscript{3}) = 349.27±0.04eV. The following conditions were used during collection of EELS spectra: an illumination angle 2\alpha=4-10 mrad, a collection angle 2\beta=11.2±0.3 mrad, a 2mm entrance aperture, and an energy dispersion of 0.1eV/channel. Spectra were collected in diffraction mode and were corrected for dark current and channel-to-channel gain variation of the charge coupled device (CCD) detector. Low-loss spectra were acquired with an integration time of 0.128s (15 spectra were summed). Core-loss spectra were acquired with an integration time of 2s (100 spectra were summed). For the core-loss spectra, an inverse power-law was used for background subtraction and plural scattering was removed using Fourier deconvolution methods. Twenty five regions (~200nm in diameter) along thin edge of the perforated hole were analyzed for each thin film and the resulting spectra were summed. Raman scattering spectra were collected at room temperature in reflection from as-deposited Ti-C:H/Ti/Si(100) specimens with a Jobin-Yvon Horiba LabRam Micro-Raman instrument. Further details on the Raman measurement were reported elsewhere.\textsuperscript{15}

The effective CTEs of Ti-C:H films were probed by measuring the curvature change of Ti-C:H/Ti/Si(100) beam assemblies with the MBOS technique during heating induced temperature excursions. Because of the large thickness disparity between the Ti-C:H film and the Ti interlayer, 1\mu m vs. 80nm, the thermal expansion of the Ti interlayer can be neglected.
As shown in Figure 5-1, the beam assembly was clamped on one end onto a specimen holder with the other end free, and placed in the center of a 6-inch uniform heating zone of a high vacuum tube furnace. The tube furnace was sealed at one end with an optical quality glass allowing laser beam access, and evacuated by a turbomolecular pumping system to a base pressure of \( \sim 2 \times 10^{-8} \) Torr. The specimen temperature was monitored by a K-type thermocouple placed 3mm away from the beam assembly. During each CTE measurement cycle, the specimen temperature was increased slowly over \( \sim 120 \) min from room temperature to \( < 230^\circ \) C, followed by a slow decrease over a similar time span to room temperature. A linear array of parallel beams generated from a single 658nm AlGaInP diode laser passing through a multi-pass optical etalon were incident on the film side of the specimen assembly, and the reflected spots were detected by a CCD array. The curvature of the beam assembly, \( K \), is related to the relative change in spacing between reflected spots, \( (D - D_0)/D_0 \), by

\[
K = - \left( \frac{D - D_0}{D_0} \right) \frac{\cos \theta}{2L} \tag{Equation 5-1}
\]

where \( D \) is the reflected spot spacing from a specimen with curvature \( K \), and \( \theta, L, \) and \( D_0 \) are respectively the incidence angle, the optical path length from the specimen to the CCD, and the spacing between reflected spots from a flat surface. In the present setup, \( L \) was 163cm and \( \theta \) was \( \sim 1.5^\circ \). A negative change in \( K \) denotes increasing substrate convexity on the film side.

5.3 Results and Discussion

When the film/substrate assembly is subjected to a temperature change, \( \Delta T \), the thermal stress generated within the film, \( \sigma_f \), due to the mismatch between the CTE of the Si(100) substrate, \( \alpha_s \), and the effective CTE of the Ti-C:H film, \( \alpha_f \), is given by
Figure 5-1  Schematic of the thermally induced bending measurement setup: reflected laser spots from the film/substrate beam assembly were captured by the CCD array and recorded in a computerized data acquisition system.

\[ \sigma_f = -\frac{E_f}{1-\nu_f} (\alpha_f - \alpha_s) \Delta T \]  \hspace{1cm} \text{Equation 5-2}

This thermal stress induces a change in curvature, \( \Delta K \), of the film/substrate assembly according to the Stoney’s equation,

\[ \sigma_f t_f = \frac{1}{6} t_s^2 \left( \frac{E_s}{1-\nu_s} \right) \Delta K \]  \hspace{1cm} \text{Equation 5-3}

where \( t_f \) and \( t_s \) are the thickness of film and substrate, respectively. In Equations 5-2 and 5-3, \( E_f/(1-\nu_f) \) and \( E_s/(1-\nu_s) \) are respectively the biaxial moduli of the film and substrate.

The CTE mismatch, \( \Delta \alpha_{f-s} \equiv \alpha_f - \alpha_s \), is obtained by equating Equations 5-2 and 5-3, and is a function of \( \Delta K/\Delta T \) as well as the biaxial moduli and thicknesses of both the film and substrate. For the present measurements, parameters related to the Si(100) substrate are known: \( E_s/(1-\nu_s) = 1.805 \times 10^{11} \text{Pa} \) \(^{16} \) and \( t_s = 300 \mu\text{m} \). The Ti-C:H film thickness, \( t_f \), was
directly measured by cross-sectional SEM. Although the biaxial moduli of the Ti-C:H films were not measured, their indentation moduli, \( E_{ind} = E_f/(1-\nu_f^2) \) where \( E_f \) and \( \nu_f \) are respectively the Young’s modulus and Poisson’s ratio of the film, were determined previously from instrumented nanoindentation measurements.\(^{17} \) The knowledge of \( E_{ind} \) allows one to determine \((1+\nu_f)\Delta \alpha_{f-s}\),

\[
(1+\nu_f)\Delta \alpha_{f-s} = -\frac{1}{6} \frac{t_f^2}{t_s} \left( \frac{E_s}{1-\nu_s} \right) \frac{1}{E_{ind}} \frac{\Delta K}{\Delta T}
\]

Equation 5-4

If \( \Delta \alpha_{f-s} \) is independent of temperature in the temperature excursion range, it then follows from Equation 5-4 that \( \Delta K \) is linearly proportional to \( \Delta T \).

Because of the presence of compressive intrinsic stresses within Ti-C:H, ranging from 0.5-2GPa in magnitude,\(^{14} \) and the absence of stress relaxation,\(^{17} \) as-deposited Ti-C:H/Ti/Si(100) film/substrate assemblies possessed significant curvatures. Because of this initial curvature, one caveat exists regarding the \( \Delta K \) measurements. Applying Equation 5-1, one obtains

\[
\Delta K = K_2 - K_1 = -\left( \frac{\cos \theta}{2L} \right) \frac{D_2 - D_1}{D_0} = -\left( \frac{\cos \theta}{2L} \right) \left( \frac{D_2 - D_1}{D_1} \right) \left( 1 + \frac{D_1 - D_0}{D_0} \right)
\]

Equation 5-5

where \( D_1 \) is the reflected spot spacing at the beginning of the temperature excursion, corresponding to the curvature \( K_1 \) of the as-deposited film/substrate assembly. The last term in Equation 5-5 is usually insignificant for bare substrates. Because of the significant curvatures of the as-deposited Ti-C:H/Ti/Si(100) beam assemblies, the last term in Equation 5-5 is substantially different from unity. However, it is known from previous substrate curvature measurements during specimen deposition,\(^{14} \) and was applied to obtained \( \Delta K(T) \).
Structural stability of the Ti-C:H films during the temperature excursion is of concern, since the CTE measurements assumes that thermally induced strains are elastic in origin, and excludes any structural changes within Ti-C:H. Figure 5-2 shows measured $\Delta K$ as a function of temperature for a Ti-C:H/Ti/Si(100) beam assembly, in which the Ti-C:H film has $R_{Ti/C} \approx 0.43$. As the temperature increases, $\Delta K$ becomes more negative, indicating that $\alpha_f$ is greater than $\alpha_s$. Results of three separate $\Delta K$ measurements are shown, two of which were executed during one continuous temperature increase and decrease over $\sim 300$min, and the third was conducted 24 hours later. Figure 5-2 shows that, within experimental error, the thermally induced $\Delta K$ is reproducible over repeated temperature excursions up to $\sim 230^\circ C$ and
linearly proportional to $\Delta T$. The former suggests that no structural modification occurred within the film during the measurement, and this inference is not unexpected, since $\Delta K$ was measured at temperatures below the film deposition temperature of $\sim 250^\circ$C.

![Figure 5-3](image)

Figure 5-3  Measured CTE mismatch between Ti-C:H and Si as a function of the Ti composition. The use of the film indentation modulus instead of the biaxial modulus results in an additional factor of $(1+\nu_f)$.

Measured values of $(1+\nu_f)\Delta \alpha_{f-s}$ for Ti-C:H as a function of the Ti composition are shown in Figure 5-3. The reported error bars are derived from measurement errors in $\Delta K$, $t_f$, and $E_{ind}$, and are dominated by scatter in the $E_{ind}$ measurement.$^{17}$ Separate data points at the same $R_{Ti/C}$ denote results of repeat measurements on the same specimen. Data shown in Figure 5-3 indicate that $(1+\nu_f)\Delta \alpha_{f-s}$ approaches $\sim 3.5 \times 10^{-6} K^{-1}$ and $\sim 3.0 \times 10^{-6} K^{-1}$ as $R_{Ti/C}$ approaches respectively 0 or 1, and demonstrate only marginal variation outside of measurement error as a function of the Ti composition.
The bonding configuration of the a-C:H phase in Ti-C:H was further probed by EELS\textsuperscript{18} and Raman scattering.\textsuperscript{19} Figure 5-4(a) shows a C K-edge EELS spectrum collected from a Ti-C:H film with $R_{Ti/C} \approx 0.10$. For carbon allotropes, the peak near 285eV is attributed to the 1s-$\pi^*$ transition of planar sp$^2$ hybridized C bonds. The intensity of the 1s-$\pi^*$ (often abbreviated $\pi^*$) peak relative to the C K-edge as a whole is proportional to the fraction of sp$^2$ bonded C atoms, $f_{sp^2}$. \textsuperscript{18} Quantitative evaluation of $f_{sp^2}$ in this case is complicated by the presence of the TiC phase within Ti-C:H. Although TiC contains no sp$^2$ bonded C, it displays a strong EELS peak near 285eV relative to the C K-edge.\textsuperscript{20} Adding the C K-edge signal from TiC to that of a-C:H can result in a spectral distortion, and the composite spectra is no longer reflective of the true sp$^2$ bonded C component.

Figure 5-4(b) shows a number of Raman spectra obtained from Ti-C:H specimens with different Ti contents. Raw Raman spectra in the energy range of 800-2000cm$^{-1}$ were fitted with a linear background and two Gaussians.\textsuperscript{19} At all Ti compositions, Raman spectra contained the D and G bands commonly observed in a-C:H films. Through fitting, the D band center is located at 1368 to 1375cm$^{-1}$, with its full width at half maximum (FWHM) ranging from 296 to 303cm$^{-1}$. The G band center is located at 1551 to 1557cm$^{-1}$, with its FWHM ranging from 108 to 130cm$^{-1}$. As $R_{Ti/C}$ increases from 0.02 to 0.17, the D and G band positions and their FWHMs do not change significantly, however, the band heights decrease by approximately a factor of five. The similarity in Raman spectral shapes observed from Ti-C:H specimens with different $R_{Ti/C}$ suggests that the structure of the a-C:H phase within Ti-C:H does not change significantly as the Ti composition changes. Moreover, the amount of Ti atoms dissolved within the a-C:H matrix is less than 2.5at.%.\textsuperscript{11} Noting that bulk B1-TiC is centrosymmetric and first-order Raman-inactive, an increase in the fraction of the TiC phase
Figure 5-4 Probing the bonding configuration of the a-C:H phase within Ti-C:H: (a) C K-edge EELS spectra of a Ti-C:H thin film with $R_{Ti/C}=0.10$, an evaporated amorphous carbon (a-C) film, and TiC.\textsuperscript{20} Note that the $\pi^*$ peak for Ti-C:H is stronger relative to that for a-C; (b) Raman scattering spectra of Ti-C:H specimens as a function of the Ti composition. A linear background was removed from the raw Raman data, and the dashed lines indicate the two Gaussian components for the spectral fit.
relative to the a-C:H phase as $R_{Ti/C}$ increases would result in an overall decrease in Raman intensity for Ti-C:H, as observed. Previous X-ray absorption spectroscopy measurements on Ti-C:H thin films showed that the bonding environment surrounding Ti atoms is similar to that in bulk TiC, even though the TiC clusters are a few nm in size. These observations suggest that the structure of the TiC phase within Ti-C:H is likewise not significantly modified as $R_{Ti/C}$ increases.

Since the structures of the a-C:H and TiC phases within Ti-C:H show no strong evidence of being modified from their corresponding pure forms, $\Delta \alpha_{fs}$ can be approximated, to first order, from Equation 5-4 using the Poisson’s ratio of bulk TiC ($\nu=0.17$) and pure a-C:H ($\nu\sim0.3$, independent of $f_{sp^2}$). Using those values for $\nu_f$ yields $\Delta \alpha_{fs} = 2.7 \times 10^{-6} K^{-1}$ and $2.6 \times 10^{-6} K^{-1}$ for Ti-C:H at compositions approaching pure a-C:H and pure TiC, respectively. As temperature increases from 300 to 500K, $\alpha_s$ increases from $2.6 \times 10^{-6} K^{-1}$ to $3.6 \times 10^{-6} K^{-1}$ for the Si substrate. Taking the average value of $\alpha_s$ in this temperature range of $3.1 \times 10^{-6} K^{-1}$, the data shown in Figure 5-3 yields effective CTE values for Ti-C:H, in the temperature interval of 300-500K, of $5.8 \times 10^{-6} K^{-1}$ (nearly pure a-C:H) and $5.7 \times 10^{-6} K^{-1}$ (nearly pure TiC). According to Marques et al., a CTE value of $5.8 \times 10^{-6} K^{-1}$ for a-C:H corresponds to $f_{sp^2} \approx 0.8$. Given the low Ti content ($R_{Ti/C}\sim0.10$) of the Ti-C:H film examined by EELS, qualitative comparison between the EELS data shown in Figure 5-4(a) and previous EELS data on amorphous carbon films with varying $sp^2$ content suggests a high $f_{sp^2}$ value in the a-C:H phase. Moreover, Weiler et al. reported a relationship between intrinsic stress within a-C:H films and $f_{sp^2}$. They demonstrated that a compressive intrinsic stress of $\sim2$GPa (as measured for Ti-C:H films at compositions approaching pure a-C:H) corresponds to a $f_{sp^2}$ of $\sim0.8$. 

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The presently determined effective CTE for the TiC phase within Ti-C:H is, however, lower than the value of $7.0 \times 10^{-6} \text{K}^{-1}$ for bulk TiC.\textsuperscript{25} Likewise, the measured $E_{ind}$ value of $\sim 250 \text{GPa}$ for Ti-C:H films with composition approaching pure TiC is significantly below the corresponding value for bulk TiC.\textsuperscript{21} This suggests that the CTE and $E_{ind}$ of single-phase TiC can be significantly altered by forming a TiC/a-C:H nanocomposite with only a minor fraction of a-C:H. Detailed structure/defect configurations responsible for the discrepancies between presently measured CTE and $E_{ind}$ values and the corresponding bulk values for TiC have not been determined.

To obtain CTE for Ti-C:H, one need to consider the variation of the Poisson’s ratio $\nu$ of Ti-C:H as the Ti composition varies. Variations of $\nu$ in two-phase composites have been analyzed from a continuum mechanics view point. Simple analysis for long-fiber composites indicates a linear rule-of-mixtures variation.\textsuperscript{26} Effective medium theory analysis of random two-phase composites, in which the two phases have identical Poisson’s ratios, has shown that the composite $\nu$ exhibits no pronounced variation with composition when $\nu$ values of the component phases range from 0.1 to 0.4.\textsuperscript{27} Within the average relative error of $\sim 18\%$ for the data shown in Figure 5-3, the present measurements indicate essentially no composition dependence to the effective CTE of Ti-C:H, regardless of whether $\nu$ is taken to be 0.3, 0.17, or the linear rule-of-mixtures values. The presently measured effective CTEs are consistent with thermal expansion measurements by Wang et al.\textsuperscript{28} on W-C:H thin films, although they did not explore the dependence on W composition in detail.

Mechanical properties of ceramic nanocomposite thin films do not always exhibit a monotonic variation with composition. In the Ti-C:H case, the average modulus and hardness increases smoothly and monotonically with increasing Ti composition.\textsuperscript{17} In contrast, the
intrinsic stress within Ti-C:H varies with the Ti composition in a markedly non-monotonic fashion, with a stress minimum observed at the composition close to the percolation threshold of TiC nanoclusters.\textsuperscript{14} According to continuum mechanics, thermal expansion of the composite shows no compositional dependence when the CTEs of the component phases are equal.\textsuperscript{29} The lack of composition dependence of the presently measured effective CTE for Ti-C:H is therefore expected from continuum mechanics analysis, based on the near equality of CTEs for nearly pure a-C:H and TiC. Since an abundant amount of TiC/a-C:H interfaces exists within Ti-C:H, our measurements suggest that these internal interfaces do not exert any anomalous influence over the average thermal expansion behavior of this nanocomposite.

5.4 Conclusion

In summary, we have performed a detailed measurement on the compositional dependence of thermal expansion for Ti-C:H thin films. The effective CTE of Ti-C:H was found to be essentially independent of the Ti composition, and is $\sim 5.7 \times 10^{-6} \text{K}^{-1}$.

5.5 References

Chapter 6  Deposition of Highly Hydrogenated Carbon Films by a Modified Plasma Assisted Chemical Vapor Deposition Technique

6.1 Introduction

Hydrogen-free, amorphous carbon (a-C) thin films are typically made by laser ablation\(^1\), cathodic arc deposition\(^2\) or mass-selected ion beam deposition\(^3\) and often possess large intrinsic stresses. The line-of-sight nature of these deposition techniques also leads to difficulties when conformal film coverage of high-aspect-ratio microscale structures is desired\(^4\). Chemical vapor deposition (CVD) techniques, including those with plasma assist, have been employed for synthesis of diamond or nanocrystalline diamond coatings, which are reported to be hydrogen-free and almost completely \(sp^3\) bonded\(^5,6\).

By incorporating hydrogen into carbon films, amorphous hydrogenated carbon (a-C:H) films have been synthesized, usually through plasma decomposition of CH\(_4\)\(^7\) or C\(_2\)H\(_2\)\(^8,9\). Plasma assisted a-C:H deposition can achieve reasonably high deposition rates and smooth film surfaces\(^10\). Various plasmas have been utilized in plasma assisted CVD of a-C:H films, including radio-frequency (rf) capacitively coupled plasmas\(^9\) and inductively coupled plasmas (ICP)\(^11\). Hydrogen content and the fraction of C-C \(sp^3\) bonding play key roles in determining the physical properties of a-C:H films.

Studies of a-C:H films generally report hydrogen evolution from the film at temperatures exceeding 300-350\(^\circ\)C. During high temperature annealing, hydrogen removal from the film is accompanied by changes in bonding. The annealed films are generally more graphite-like\(^8,12\). Certain applications, however, may require the use of a-C:H films at elevated temperatures. For example, in Al dry-machining applications, cutting tools coated...
with an a-C:H film showed less Al accumulation on cutting edges as compared to tools coated with metal-nitride based coatings. First-principle simulations based on density functional theory showed that adhesion between diamond and Al can be strongly affected by hydrogen at the interface. The lower work of adhesion between pure and composite a-C:H and metals as compared to that for metal-metal contacts makes these films effective barriers to adhesive wear in tribological contacts of mechanical components. a-C:H films with higher hydrogen content and increased thermal stability, e.g., higher hydrogen evolution temperature, are thus of interest.

Amorphous carbon films with fraction of $sp^3$ bonding as high as 80% have been made by filtered cathodic arc deposition, in which energetic (~100eV), singly-charged, carbon ions were believed to be responsible for film deposition and the formation of such a high $sp^3$ fraction. Typically, a-C:H films prepared by plasma assisted CVD exhibit lower fractions of $sp^3$ bonding, possibly due to the lower fraction of ionized species within the deposition flux. Weiler et al. used a plasma beam source (PBS) to increase the ionization fraction and create a relatively mono-energetic plasma beam. Carbon coatings deposed with this PBS technique were reported to possess a hardness of ~60GPa and a high $sp^3$ bonding fraction of ~0.75. This PBS methodology suggests that physical properties of carbon-based thin films can be altered by modifying conventional plasma assisted CVD. This chapter reports results of structural and mechanical characterization on a-C:H thin films deposited by a modified ICP assisted CVD technique.

6.2 Experimental

Deposition of hydrogenated carbon thin films was accomplished by ICP assisted CVD. The deposition chamber was an electrically-grounded, stainless-steel, Conflat®, eight-inch,
six-way cross. As shown schematically in Figure 6-1, plasma generation within the deposition chamber was accomplished by coupling with an external, four-turn, flat induction coil through a glass plate mounted on one of the six cross flanges. The coil was powered by a 13.56MHz rf generator through a standard matching network. Film deposition occurred in either conventional or modified ICP assisted CVD mode. In the conventional mode, the ICP is in contact with the grounded stainless-steel cross tube before it comes into contact with the substrate placed at the center of the Conflat® cross. In the modified mode, a glass tube with its outer diameter fitting the cross tube was placed in contact with the glass plate at one end. The other end of the glass tube was covered with an electrically grounded, stainless-steel, wire-mesh screen. The square-grid wire-mesh screen had 16 wires per inch, and a wire diameter of 230µm. In this modified mode, the plasma is initially confined within the glass tube, and comes into contact with the grounded screen before reaching the substrate. The substrate was

Figure 6-1  Schematic of the experimental setup used to deposit hydrogenated carbon films by conventional and modified ICP assisted CVD.
held in a holder electrically isolated from the ground, parallel to the wire-mesh screen and facing the ICP. In the modified mode, the substrate-glass plate and substrate-screen distances were ~6.5inches and ~1.5inches, respectively. Film depositions occurred on 2-inch Si(100) substrates. Each deposition consisted of a 10min substrate etch in an Ar(99.999%) ICP, followed by deposition in an Ar/CH₄(99.99%) ICP. The rf power input into the induction coil was held constant at 500W and the substrate bias was -100V during both etching and deposition. Unless otherwise noted, the Ar input flow rate was 100sccm throughout the run and the CH₄ input flow rate was 5sccm during film deposition, i.e., a CH₄/Ar input flow ratio of 1/20. Total pressure during substrate etching and film deposition was ~5mTorr. No intentional substrate heating or cooling was applied during etching or deposition.

Annealing of as-deposited hydrogenated carbon films was carried out post-deposition in a custom-built, high-vacuum tube furnace. Pumped by a turbomolecular pumping system, the system base pressure was ~2×10⁻⁸ Torr. All specimens were annealed at specified temperatures for one hour at pressures <5×10⁻⁷ Torr.

Film thicknesses were measured post-deposition by cross-sectional scanning electron microscopy (SEM) and ranged between 250-500nm, depending on the deposition conditions. Hydrogen content within the as-deposited films was measured by hydrogen elastic recoil detection (ERD), which was performed with 4 MeV He⁺ beam and an Al foil “He⁺ particle filter” in front of the detector. Raw ERD data were normalized using mica as the calibration standard, which had a known hydrogen content of 11at.%. X-ray Photoelectron Spectroscopy (XPS) measurements were carried out on a Kratos AXIS165 system, using a monochromatic Al Kα excitation source. No Ar⁺ ion-etch or other...
surface cleaning procedures were taken prior to XPS spectra acquisition. All spectra were taken with the electron energy analyzer normal to the specimen surface. For each specimen, one survey scan in the binding energy range of 0–1000eV was acquired in 0.5eV steps and three high resolution scans of the C1s region were collected in 0.1eV steps and averaged. During all spectra acquisition, a charge neutralization filament is turned on to minimize possible effects of electrical charging of highly resistive specimens.

Raman scattering measurements were performed on as-deposited and annealed films. Signals were collected at room temperature from a Jobin-Yvon Horiba LabRam Micro-Raman instrument with a 20mW, 632.8nm, HeNe laser as the excitation source. Filters were used to attenuate the incident beam such that spectra were obtained with 2mW of incident laser power with the laser beam focused to a spot several µm in size. To avoid laser heating effects, Raman spectra were acquired repeatedly until a steady state condition was observed. All spectra reported were acquired under steady state conditions with exactly the same acquisition settings, to facilitate the comparison of peak intensities on a relative basis as a measure of scattering signal strength.

Langmuir wire probes were utilized to characterize the deposition environment. Current-voltage (I-V) curves were acquired from 75µm diameter W wire probes placed at the substrate position with the actual substrate removed. Additional plasma potential measurements were accomplished with an electron emissive W wire probe. In the emissive probe technique, thermionic emission from a 75µm diameter W probe wire was induced by passing electrical current through the wire in a separate floating bias loop. I-V curves, with and without electron emission, were collected consecutively. The probe bias at which I-V curves separate was taken as the plasma potential. For both conventional and electron emissive probes, the total length of wire exposed to the plasma was ~1.9cm.
Instrumented nanoindentation was carried out on a Hysitron Triboscope® interfaced to a Digital Instrument Dimension3100® atomic force microscope (AFM). A Berkovich diamond indenter tip was used. Instrument load frame compliance and indenter tip area function calibration was carried out using a Hysitron supplied fused silica specimen with loads ranging from 200 to 13000µN, assuming a contact-depth (hc) independent elastic modulus. The calibrated tip area function was effective in the range of 20nm<hc<220nm. Indentations on a–C:H/Si(100) specimens were carried out at multiple loads, ranging from 50 to 600µN. The Oliver/Pharr data analysis procedure19 was followed to extract values of the indentation modulus, \(E_{\text{ind}}=E/(1-\nu^2)\) where \(E\) and \(\nu\) are respectively the Young’s modulus and Poisson’s ratio, and the hardness, \(H\), from experimental load versus displacement curves. Results taken at \(h_c\) less than 10% of the total film thickness were averaged to obtain the coating modulus and hardness values.

6.3 Results and Discussion

Figure 6-2 shows a XPS survey spectrum of a hydrogenated carbon film deposited in the conventional mode and annealed at 500°C for an hour. Cross-sectional SEM examination showed that the thickness of this film is ~300nm. This survey spectrum shows that this film contains no perceptible impurities other than oxygen. The oxygen content is <2at.% according to factory supplied sensitivity factors. This low oxygen content includes possible oxygen incorporation during annealing, and is not expected to cause substantial structural change within the film. A series of high-resolution C1s scans are shown in the inset of Figure 6-2. These high-resolution C1s scans were obtained from the same hydrogenated carbon film in the as-deposited state and after annealing to temperatures of 300°C, 400°C, and 500°C. All
Figure 6-2  XPS survey spectrum of a hydrogenated carbon film deposited in the conventional mode and annealed at 500°C. The inset shows high-resolution C1s scans from this film in the as-deposited state and after annealing to different temperatures.

Figure 6-3  XPS survey spectrum of a hydrogenated carbon film deposited in the modified mode and annealed at 700°C. The inset shows high-resolution C1s scans from this film in the as-deposited state and after annealing to different temperatures.
C1s spectra show a single peak at a binding energy of ~284.5eV, in good agreement with observed C1s binding energy corresponding to graphitic carbon. The C1s binding energies obtained from as-deposited and annealed films show no apparent shift due to C-O bonding.

Figure 6-3 shows a XPS survey spectrum of a hydrogenated carbon film annealed at 700°C for an hour. This film was deposited in the modified mode. The film thickness was ~450nm. The survey spectrum again shows no perceptible impurities other than oxygen, with an oxygen content <2at.%. High-resolution C1s scans obtained from the as-deposited film and films annealed to temperatures of 300°C, 400°C, 500°C, and 700°C are shown in the inset of Figure 6-3. The C1s peak obtained from the as-deposited film shows an apparent down-shift in binding energy, from ~284.5eV to ~282.2eV. As the annealing temperature increases from 300°C to 400°C, the C1s peak location shifts back to ~284.5eV, and remains constant in location at higher annealing temperatures. This apparent binding energy down-shift is believed to be likely an artifact due to specimen charging, since C1s spectra collected from similarly deposited films of smaller thickness showed peak locations at ~284.5eV, without the apparent down-shift. In addition, separate XPS spectra collected from SiO2 under the same spectrometer settings also showed an apparent down-shift in binding energy of ~2eV. Because charging effects, accentuated at low film conductivity, were present from the C1s spectrum collected from the film in the as-deposited state, diminish after annealing to 300°C and 400°C, and disappears after annealing to 500°C and above, the C1s spectra shown in Figure 6-3 suggest that the electrical conductivity of the hydrogenated carbon film increased with annealing to higher temperatures.

Figure 6-4 shows hydrogen compositions of hydrogenated carbon films measured by ERD as a function of annealing temperature. The hydrogen content measured for the film
Figure 6-4  Hydrogen composition as a function of annealing temperature for a 450nm thick hydrogenated carbon film deposited in the modified mode and a 300nm thick hydrogenated carbon film deposited in the conventional mode. Hydrogen contents of several other films in the as-deposited state, deposited in the modified and conventional modes, are also shown. Identical symbols at the same temperature denote results of repeat measurements.

Figure 6-5  A SEM image showing buckling of a hydrogenated carbon film deposited in the conventional mode from the Si substrate. The film was annealed for one hour at 500°C.
deposited in the modified mode in the as-deposited state is ~60 at.%, which approaches the upper limit of hydrogen incorporation within a-C:H films, as stated by Angus and Jansen. The ERD data show a slight decrease in hydrogen content from ~60 at.% to ~50 at.% after annealing, and show no significant hydrogen content variation after annealing to temperatures of 300°C, 400°C and 500°C. After annealing to 700°C for one hour, a significant decrease in the hydrogen content was observed. As compared to previous observation of hydrogen release around 350°C in hydrogenated carbon films, the current data indicate that hydrogen release from the hydrogenated carbon film deposited by this modified ICP-CVD begins at above 500°C. In contrast, the hydrogen content for the film deposited in the conventional mode was much lower, ~17 at.%. ERD measurements performed on this film also showed no significant decrease in hydrogen content occurring after annealing to 400°C. However, as shown in Figure 6-5, film buckling from the Si substrate occurred after annealing of this film to 500°C for one hour. Consequently, the hydrogen content of this film after annealing to temperatures of 500°C and higher was not measured. Another hydrogenated carbon film was deposited in the conventional mode at a much higher CH₄/Ar input flow ratio of 3/5 and a lower total pressure of 1.6 mTorr. The hydrogen content of that film in the as-deposited state as measured by ERD is also shown in Figure 6-4. Even with this much increased CH₄/Ar input flow ratio, the measured hydrogen content of ~40 at.% is still lower than that in the film deposited in the modified mode. Hydrogen content of several other films in the as-deposited state, deposited in the conventional and modified modes, were also measured by ERD and shown in Figure 6-4.

Raman scattering was used to further characterize the hydrogenated carbon films. Figure 6-6 shows a series of Raman spectra collected from a film deposited in the modified mode, in the as-deposited state and after annealing to different temperatures. As mentioned
above, the measured hydrogen content of this film in the as-deposited state approached 60at.%. The Raman spectra consist of two broad bands centered at ~1350cm\(^{-1}\) and ~1580cm\(^{-1}\), consistent with the commonly observed D and G bands of amorphous carbon films. The D band grows in relative proportion to the G band with increasing annealing temperature. According to Ferrari and Robertson,\(^{21}\) such evolution in Raman spectra is consistent with transformations from a disordered amorphous carbon network structure to a more graphitic structure. It is also apparent from Figure 6-6 that the as-deposited film exhibits a large photoluminescence (PL) background. This PL background, ~4000 in the as-deposited state, decreases somewhat after annealing to 300\(^\circ\)C and reaches to below 1000 after annealing to 500\(^\circ\)C. After annealing to 700\(^\circ\)C, the PL background disappears. Adamopoulos et al\(^{22}\) reported that hydrogen content within a-C:H thin films can be correlated to the PL slope observed in Raman scattering spectra. A larger PL slope can be related to a higher hydrogen content within the film. Although the laser excitation wavelength used in the current experiments and those carried out by Adamopoulos et al. are different and therefore the spectra obtained cannot be directly compared, it is evident from data shown in Figure 6-6 that the PL background slope decreases with increasing annealing temperature. In addition, the absolute PL background also decreases significantly.

The Raman scattering spectra for a film deposited in the conventional mode are shown in Figure 6-7, collected from the film in the as-deposited state and after annealing to 300\(^\circ\)C and 400\(^\circ\)C. All spectra shown in Figure 6-7 show D and G bands centered at ~1350cm\(^{-1}\) and ~1580cm\(^{-1}\), with relatively little difference due to annealing. As compared to data shown in Figure 6-6, the absolute PL backgrounds and the PL slopes of these Raman spectra are much lower. The present Raman data thus show that, at the excitation wavelength of 632.8nm,
Figure 6-6  Raman scattering spectra collected from a hydrogenated carbon film deposited in the modified mode in the as-deposited state and after annealing to 300°C, 500°C, and 700°C. Note the change in scale on the intensity axis.

Figure 6-7  Raman scattering spectra collected from a hydrogenated carbon film deposited in the conventional mode in the as-deposited state and after annealing to 300°C and 400°C. The scattering signature between 900 and 1000 cm\(^{-1}\) is due to the Si substrate.
higher PL background and PL slope is observed from the film with higher hydrogen content, and are qualitatively consistent with the previous data of Adamopoulos et al.\textsuperscript{22} Changes in the PL slope and D and G band intensity ratio, shown in Figure 6-6, suggest that annealing the high hydrogen content film deposited in the modified mode induces a process of hydrogen evolution and graphitic ordering within the film, and that increased graphitization occurs after annealing to 500$^\circ$C before significant hydrogen release happens. In contrast, Raman spectra collected from the lower hydrogen content film deposited in the conventional mode show a clear D band in the as-deposited state, and show no significant difference after annealing to 300$^\circ$C and 400$^\circ$C. This suggests that this film is more graphitic in the as-deposited state, and that no significant structural change occurs in this film after annealing to 400$^\circ$C.

![Figure 6-8](image)

**Figure 6-8** Nanoindentation of hydrogenated carbon films: indentation modulus(a) and hardness(b) of films deposited in the conventional and modified modes. Indentation measurements were carried out on films in the as-deposited state and after annealing to various temperatures.

Structural differences between hydrogenated carbon films deposited in the conventional and modified modes, and their structural stability with respect to annealing, are further illustrated by the instrumented nanoindentation results shown in Figures 6-8(a) and
6-8(b), which show respectively measured film indentation modulus and hardness as a function of annealing temperature. Indentation moduli for films deposited by conventional ICP assisted CVD are ~100GPa in the as-deposited state, and show a slight decrease to ~90GPa after annealing to 300°C and 400°C. Similarly, hardnesses of these films are ~12GPa in the as-deposited state, and remain largely unchanged after annealing to 300°C and 400°C. In contrast, indentation moduli and hardnesses for films deposited by modified ICP assisted CVD are measured to be respectively ~20GPa and ~2GPa, and show no significant variation after annealing to temperatures of up to 500°C. Also to be noted, increases in both the film indentation modulus and hardness to respectively ~40GPa and ~4GPa are observed after annealing to 700°C for one hour. The presently measured values of indentation modulus and hardness of hydrogenated carbon films deposited in the conventional mode are in line with those commonly observed for a-C:H films. In contrast, the indentation modulus and hardness of films deposited in the modified mode are much lower. As pointed out by Angus et al,23 univalent hydrogen atoms act as bond terminators in an amorphous random network of hydrogen and carbon atoms. High hydrogen content tends to make the network floppy, and therefore mechanically soft. The present observations are consistent with such a picture, with the film of higher hydrogen content (~60at.%) being softer and elastically more compliant.

Langmuir probe measurements were performed to better understand the difference between deposition environments in the conventional and modified modes. Figure 6-9(a) shows two I-V curves obtained from CH₄/Ar plasmas with and without the glass tube-grounded wire-mesh screen assembly in place. The probe location was not changed while taking these curves. The same conventional wire probe was placed at the same position. In both cases, positive ion and negative electron currents are obtained when the probe is
Figure 6-9  Conventional Langmuir wire probe characterization of the deposition environment: (a) I-V characteristics with and without the glass tube-grounded wire-mesh screen assembly in place. The inset shows a magnification of the I-V curves at negative probe bias voltages; (b) I-V characteristics of Ar and CH$_4$/Ar ICP, obtained with the glass tube-grounded wire-mesh screen assembly in place. The two Ar I-V curves are collected before and after CH$_4$ introduction. The inset shows a magnification of the I-V curves at negative probe bias voltages.
respectively biased negatively and positively, indicating the presence of plasma at the substrate position in either deposition modes. It is also apparent from Figure 6-9(a) that the presence of the glass tube-grounded wire-mesh screen assembly acts to significantly reduce the plasma density at the substrate position. The plasma density without the assembly in place was estimated from the I-V curve to be $\sim 1 \times 10^{10}/\text{cm}^3$. The inset in Figure 6-9(a) shows that, at the same input power of 500W into the induction coil, inserting the assembly reduces the ion current at large negative probe bias by almost five times. Difference in density of Ar and CH$_4$/Ar plasmas is also observed, as shown in Figure 6-9(b). Introduction of CH$_4$ gas into an Ar plasma acts to reduce the collected ion current at large negative probe bias by more than a factor of two.

Figure 6-10 Electron emissive Langmuir wire probe characterization of the deposition environment: (a) I-V curves obtained without the glass tube-grounded wire-mesh screen assembly in place. The two curves are measured with and without electron emission from the probe wire; (b) I-V curves obtained with the glass tube-grounded wire-mesh screen assembly in place. The two curves are measured with and without electron emission from the probe wire.

Additional plasma potential measurements were carried out with electron emissive wire probes. Figure 6-10(a) shows two I-V curves, collected with and without electron
emission from the wire probe, as a function of probe bias voltage. These I-V curves were collected without the glass tube-grounded wire-mesh screen assembly in place, and show a separation occurring at \( \sim +20 \text{V} \). A plasma potential of \( \sim +20 \text{V} \) is consistent with previous measurements carried out in \( \text{C}_2\text{H}_2/\text{Ar} \) ICP. Similarly collected I-V curves with the glass tube-grounded wire-mesh screen assembly in place are shown in Figure 6-10(b), and show a curve separation at \( \sim +25 \text{V} \). Thus the presence of the assembly appears to lead to a slight increase in the plasma potential.

Film deposition rates were estimated by dividing the total film thickness obtained from cross-sectional SEM by the total deposition time, and were respectively \( \sim 7 \text{nm/min} \) and \( \sim 15 \text{nm/min} \), in the modified and conventional deposition modes. Although introduction of the glass tube-grounded wire-mesh screen assembly does lead to a decrease in the deposition rate, the difference is however not in proportion to the corresponding difference in measured probe currents, or plasma densities. The grounded wire-mesh screen interacts with charged particles within the plasma through its sheath. Although transport of the neutral gas-phase species from one side of the screen to the other is also influenced by the presence of the screen due to collisions with the wire-mesh, because of the relatively large openings on the wire-mesh screen, this influence may not be as significant as compared to that exerted on the charged gas-phase species. Although the density of activated neutral gas-phase species at the substrate position is difficult to estimate, we make the qualitative suggestion that activated neutral species present in the gas-phase near the substrate contribute significantly to the deposition of hydrogenated carbon films in the current environment. The difference in hydrogen content in films deposited in the modified and conventional modes is a reflection of the difference in the ratio of ionic species flux and neutral species flux to the substrate surface during deposition.
In the modified mode, the lower ionic species flux to the substrate surface results in increased hydrogen incorporation within the film. Although the highly hydrogenated carbon films (~60at.%) do not show significant hydrogen release and hardness decrease upon annealing to 500°C, these compliant and soft films are not likely to be wear resistant. The abundance of hydrogen within the film may lead to a low fraction of dangling bonds and consequently high electrical resistivities. Potential electrical applications of such highly hydrogenated carbon films remain to be explored.

6.4 Conclusion

Highly hydrogenated carbon films were deposited with a modified ICP assisted CVD technique. By inserting a glass tube-grounded wire-mesh screen assembly between the ICP and the substrate, flux of ionic gas-phase species to the substrate surface is significantly reduced. We suggest that a decreased ratio of ionic species flux to activated neutral species flux to the substrate surface during deposition is responsible for the increased hydrogen incorporation into the film.

6.5 References

Chapter 7  Summary

Metal-containing hydrogenated carbon (Me-C:H) coatings have been studied for a few decades and have proven to have extensive applications. As members of the Me-C:H family, Ti-containing hydrogenated carbon (Ti-C:H) and W-C:H coatings have been developed typically for mechanical purposes. However, their applications are constrained by the presence of large residual stresses within the coating and degradation at high temperature. Both issues were addressed in this dissertation.

A detailed examination of the intrinsic stress development within and mechanical properties of Ti-C:H and W-C:H coatings deposited in an inductively coupled plasma (ICP) assisted hybrid chemical vapor deposition (CVD)/physical vapor deposition (PVD) environment was carried out, combining in-situ substrate curvature measurements with plasma probe measurements, ex-situ electrical resistivity measurements, and instrumented nanoindentation measurements. Intrinsic stresses within Ti-C:H and W-C:H were found to be compressive over wide-ranging compositions and plasma parameters. The intrinsic compression within Ti-C:H was found to depend significantly on the Ti composition, and was related to a percolation type transition in the nanoscale structure. The intrinsic compression within Ti-C:H was further shown to be significantly influenced by the energy of ionic species bombarding the substrate during growth. Measured stress – thickness history was discussed in terms of possible mechanisms contributing to intrinsic stress generation. Although there are likely multiple mechanisms influencing intrinsic stress development, the presented results suggested that ion bombardment played a significant role in intrinsic stress generation within
Ti-C:H, and was likely to influence stress development in other low temperature deposited amorphous hydrocarbon based ceramic nanocomposite coatings.

Structural and mechanical characterization was performed on Ti-C:H specimens deposited at ~600°C by combining the techniques of X-ray photoelectron spectroscopy, electron diffraction and transmission electron microscopy, instrumented nanoindentation, X-ray absorption spectroscopy, and Raman scattering spectroscopy. The structural and mechanical characteristics of these specimens were compared to those deposited at the lower temperature of ~250°C. The results indicated that Ti-C:H consisted of a nanocrystalline TiC phase and an hydrogenated amorphous carbon (a-C:H) phase, and that Ti atoms were incorporated into Ti-C:H predominantly as B1-TiC. Deposition at ~600°C promoted TiC precipitation, resulting in little Ti dissolution within the a-C:H matrix. High temperature deposited Ti-C:H specimens were found to possess lower modulus and hardness values as compared to low temperature deposited specimens, especially at low Ti compositions. This was rationalized by electron microscopy evidence of increased short and medium range graphitic order within the a-C:H matrix of high temperature deposited Ti-C:H, and supported by additional Raman spectroscopic observations. Annealing treatment at 600°C combined with Raman scattering measurements showed that the a-C:H matrix in high temperature deposited Ti-C:H specimens appears to be less structurally sensitive to additional high temperature annealing.

The effective coefficients of thermal expansion (CTE) of Ti-C:H coatings with compositions ranging from nearly pure a-C:H to nearly pure TiC were measured. Effective CTEs were determined from temperature induced changes in the curvature of film/substrate assemblies, measured with a multi beam optical sensing technique. Measured effective CTE
values for Ti-C:H are consistent with previous measurements on a-C:H thin films, and show little dependence on the Ti composition, and is \( \sim 5.7 \times 10^{-6} \text{K}^{-1} \).

Highly hydrogenated carbon films, with hydrogen content approaching 60 at.\%, were deposited with a modified ICP assisted CVD technique. Flux of gas-phase ionic species to the substrate surface was greatly reduced by inserting a glass tube-grounded wire-mesh screen assembly between a CH\(_4\)/Ar inductively coupled plasma and the Si substrate. Characterization of films deposited by conventional and modified ICP assisted CVD was accomplished by combining the techniques of hydrogen elastic recoil detection, Raman scattering spectroscopy, and instrumented nanoindentation. Film thermal stability was studied through high temperature annealing in vacuum. It was suggested that a decreased ratio of ionic species flux to activated neutral species flux at the substrate during deposition is responsible for the increased hydrogen incorporation into the film.
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