INFORMATION TO USERS

The most advanced technology has been used to photograph and reproduce this manuscript from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI
University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Road. Ann Arbor. MI 48106-1346 USA
313-761-4700  800-521-0600
Preparation, properties, and structure of hydrogenated amorphous carbon films

Chen, Hsiung, Ph.D.
Case Western Reserve University, 1990
PREPARATION, PROPERTIES, AND STRUCTURE OF HYDROGENATED AMORPHOUS CARBON FILMS

by

HSIUNG CHEN

Submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy

Thesis Advisor: R. W. Hoffman

Department of Physics
CASE WESTERN RESERVE UNIVERSITY
January 1990
We hereby approve the thesis of

HSIUNG CHEN

candidate for the Ph.D. degree.*

Signed:  

(Chairman)

Date Nov. 17, 1989

*We also certify that written approval has been obtained for any proprietary material contained therein.
I grant to Case Western Reserve University the right to use this work, irrespective of any copyright, for the University's own purposes without cost to the University or to its students, agents and employees. I further agree that the University may reproduce and provide single copies of the work, in any format other than in or from microforms, to the public for the cost of reproduction.

[Signature]

[Signature]
PREPARATION, PROPERTIES, AND STRUCTURE OF HYDROGENATED AMORPHOUS CARBON FILMS

Abstract
by
HSIUNG CHEN

Hydrogenated amorphous carbon films (a-C:H) have been deposited on glass, fused silica, Si, Mo, Al, and 304 stainless steel at room temperature by plasma enhanced chemical vapor deposition (PECVD). The rf glow discharge and plasma kinetics of the deposition process were investigated. Negative self-bias voltage $V_b$ and gas pressure $P$ were used as two major deposition parameters.

The hydrogen concentration, internal stress, mass density, hardness, and thickness of the deposited films were measured. In the low energy deposition region, $0 > V_b > -100 \, \text{V}$, soft polymerlike films with high hydrogen concentration and low density were found. Hard diamondlike films with high stress were deposited in the bias voltage range, $-100 \, \text{V} > V_b > -1000 \, \text{V}$. Dark graphitic films with low hydrogen concentration were grown at $V_b < -1000 \, \text{V}$.

The optical absorption of a series of a-C:H films have been measured. Optical energy gaps deduced from optical absorption data using the Tauc relation lie between 0.8 eV and 1.4 eV. Doping of a-C:H films by boron
and sulfur is accompanied by an increasing number of gap states, i.e., the absorption coefficient is increased and the optical gap is reduced. The thermal stability was studied by thermal desorption spectroscopy and heat treatment at atmospheric pressure.

A structural study of a–C:H films was performed using data taken on our films and from literature sources. The relation between cluster size and the intensity ratio of Raman peaks was studied. A comparison of the films as described by the graphitic cluster two–phase (GCT) model, the random covalent network (RCN) model and the all–sp$^2$ defect graphite (DG) model was made.

The properties and structure of a–C:H films are sensitively dependent on the preparation conditions. Correlations between the deposition conditions, structure, and properties are determined.
To my parents whom I love and respect.
ACKNOWLEDGEMENTS

I sincerely appreciate the support from and discussions with my dissertation advisor, Professor R. W. Hoffman. His continuous encouragements made this hard work enjoyable.

I am grateful to Professor J. C. Angus who led me into this interesting field and gave me so much enthusiastic support. I wish to thank Dr. P. H. Schmidt, and C. C. Hayman for their guidance, inspiration, and fruitful discussions.

Many thanks also go to Susan Heidger for her contributions in the DLC laboratory and proof reading. I thank Virginia Jefferis and Scott Black who performed the mass density measurements, and Larry Hinkley who was helpful with the electronic equipment.

I wish to thank Dane Clark, at North America Coating Labs., for his efforts on the optical measurements.

I am grateful to all members of the thin film and surface science group in the Physics Department at Case Western Reserve University for creating such a pleasurable learning atmosphere. Specifically, I wish to thank Kevin Chaffee who performed the RBS for impurity analysis and Yaxin Wang for his discussions on structural characterizations.

I have to express my appreciation to my entire family members, especially my father, who gave me tremendous support through the long period of graduate study.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>DEDICATION</td>
<td>iv</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>v</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>viii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>x</td>
</tr>
<tr>
<td>I \ INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II PREPARATION OF a–C:H FILMS</td>
<td>4</td>
</tr>
<tr>
<td>2.1 Overview</td>
<td></td>
</tr>
<tr>
<td>2.2 Apparatus and Procedure</td>
<td></td>
</tr>
<tr>
<td>2.3 Substrate Materials</td>
<td></td>
</tr>
<tr>
<td>2.4 Capacitively Coupled rf Glow Discharge</td>
<td></td>
</tr>
<tr>
<td>2.5 Plasma Kinetics of Methane</td>
<td></td>
</tr>
<tr>
<td>III PHYSICAL PROPERTIES</td>
<td>18</td>
</tr>
<tr>
<td>3.1 Film Density</td>
<td></td>
</tr>
<tr>
<td>3.2 Hardness</td>
<td></td>
</tr>
<tr>
<td>3.3 Internal Stress</td>
<td></td>
</tr>
<tr>
<td>IV OPTICAL PROPERTIES</td>
<td>25</td>
</tr>
<tr>
<td>4.1 Optical Measurements</td>
<td></td>
</tr>
<tr>
<td>4.2 Optical Constants</td>
<td></td>
</tr>
<tr>
<td>4.3 Optical Gap</td>
<td></td>
</tr>
<tr>
<td>4.4 Experimental Data on Absorption Edge</td>
<td></td>
</tr>
<tr>
<td>V ATOMIC STRUCTURE AND MODELLING</td>
<td>40</td>
</tr>
<tr>
<td>5.1 Structural Determinations</td>
<td></td>
</tr>
<tr>
<td>5.2 Graphitic Cluster Two–Phase Model</td>
<td></td>
</tr>
<tr>
<td>5.3 Random Covalent Network Model</td>
<td></td>
</tr>
<tr>
<td>5.4 All–sp² Defect Graphite Model</td>
<td></td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure

2.2.1 Schematic diagram of rf self-bias deposition system.

2.2.2 RF matching network.

2.4.1 Development of a negative self-bias on the power electrode in contact with an rf glow discharge.

2.4.2 Illustrative plasma potentials and powered electrode voltages.

2.4.3 Spatial distribution of average potential in a flat parallel reactor.

2.5.1 An example of measured electron energy distribution with the same energy of 4.4 eV in comparison with the Maxwellian distribution and Druyvesteynian distribution. (From K. Tachibana et al., 1984).

3.1.1 The relation between ion impact energy and the mass density of as-deposited a-C:H films.

4.4.1 Optical absorption $\alpha$ vs photon energy for a-C:H films prepared from methane plasma decomposition with different bias voltage.

4.4.2 The Tauc relation, $\sqrt{\alpha h \nu}$ vs photon energy, for a-C:H films prepared from methane plasma decomposition with different bias voltage.

4.4.3 Extinction coefficient $k$ vs photon energy for a-C:H films prepared from methane plasma decomposition with different bias voltage.

4.4.4 Optical absorption coefficient $\alpha$ vs photon energy for annealed a-C:H films.

4.4.5 The Tauc relation, $\sqrt{\alpha h \nu}$ vs photon energy, for annealed a-C:H films.

4.4.6 Extinction coefficient vs photon energy for annealed a-C:H films.

4.4.7 Optical absorption coefficient $\alpha$ vs photon energy for boron and sulfur doped a-C:H films.

4.4.8 The Tauc relation, $\sqrt{\alpha h \nu}$ vs photon energy, for boron and sulfur doped a-C:H films.
4.4.9 Extinction coefficient $k$ vs photon energy for boron and sulfur doped a–C:H films.

6.1.1 The deposition rate vs (bias voltage x pressure) for 100% methane rf plasma deposition.

6.2.1 Hydrogen content vs (bias voltage / sqrt(pressure)).

6.2.2 Hydrogen content vs (bias voltage x pressure).

6.2.3 Hydrogen content vs mass density.

6.2.4 Hydrogen content vs bias voltage.

6.3.1 Thermal desorption spectrum of a–C:H film on a Mo substrate.

6.3.2 Companion sample of thermal desorption spectrum of a–C:H film on a Mo substrate.

6.3.3 Thermal desorption spectrum of a blank Mo substrate.
LIST OF TABLES

Table

2.2.1 The range of available deposition conditions.

3.1.1 Density measurements of matrix samples.

3.2.1 Scratch width for various materials using Vickers diamond indenter.

3.2.1 Stress measurements of matrix samples.

4.1.1 The list of a—C:H samples for optical measurements and the measured optical gaps.

6.1.1 The deposition rate as a function of the different source gas combinations.

6.2.1 Hydrogen concentration of matrix samples.
I. INTRODUCTION

Carbon is an especially fascinating element for scientists because it presents a great diversity of possible structures. With twofold, threefold, and fourfold coordinations, carbon forms not only crystalline diamond and graphite, but also a variety of metastable disordered solids, e.g., cokes, glassy carbon, evaporated carbon, and diamondlike carbon.

Hard amorphous carbon films have received much attention\textsuperscript{1–3} in the past decade due to their diamondlike properties, such as extreme hardness, chemical inertness, high electrical resistivity, good thermal conductivity, high infrared transparency, and tunable optical constants.\textsuperscript{4} Therefore, diamondlike carbon films have potential applications\textsuperscript{2,3} as a wear resistant coating, an optical coating, an antireflection coating, and as electronic materials.

Many film–growth techniques\textsuperscript{1} can be used for preparing carbon and hydrocarbon films, e.g., ion beam deposition, ion beam sputtering, and glow discharge decomposition of hydrocarbon gases. Generally speaking, carbon films prepared by argon sputtering a graphite target contain little hydrogen. On the other hand, a significant amount of hydrogen can be incorporated in the film by using hydrocarbons as the carbon source. These amorphous carbon films with a high hydrogen concentration are called hydrogenated amorphous carbon (a–C:H) films.

In this research, a–C:H films were prepared by plasma enhanced chemical vapor deposition (PECVD) where methane was used as a precursor
gas. We investigated their physical and optical properties. One of the aims of our study was to correlate the deposition conditions and the properties. We also wished to understand the atomic structure of this complex hydrocarbon system. In addition, the role of hydrogen, thermal stability, and the doping effect on optical gap are important for applications and have also been studied.

The first step in the investigation was to thoroughly understand the capability of our deposition system. A wide range of deposition parameters were used and the plasma kinetics were studied. The sample preparation and deposition system are described in the next chapter.

Secondly, the basic physical properties (density, hardness, and internal stress) of the films were characterized. The absorption coefficient in the range of photon energies between 1.46 and 4.96 eV were determined. These coefficients were used to evaluate the optical gap. The physical and optical properties of the as-deposited a-C:H films are discussed in chapter III and IV respectively.

The molecular structure of the films was also studied in order to provide further understanding of the macroscopic properties. Electron energy loss spectroscopy (EELS) and Raman scattering were used to characterize the structure. Three atomic structure models, the graphitic cluster two-phase (GCT) model, the random covalent network (RCN) model, and the all-sp² defect graphite (DG) model, proposed by different groups were studied. The differences between each model and their limitations are carefully considered. In chapter V, the atomic structure and modelling of a-C:H are described.
Some extended studies on the deposition rate, the hydrogen concentration, and thermal stability of a-C:H films are contained in chapter VI. The conclusions are stated in chapter VII and some suggestions for future work are given in chapter VIII.
II. PREPARATION OF a–C:H FILMS

2.1 OVERVIEW

Plasma enhanced chemical vapor deposition (PECVD) is a potentially important technique for fabricating new devices and synthesizing novel thin film materials.\textsuperscript{9–12} In the microelectronics industry a number of plasma deposition systems and etching reactors are used for making integrated devices. The basic principles and processes of the PECVD method have been studied by several groups.\textsuperscript{13–16} However, the details of the deposition mechanism which forms an a–C:H film are not yet completely understood. Based on the current knowledge, the apparatus setup, rf glow discharge, and plasma kinetics are described in this chapter.

2.2 APPARATUS AND PROCEDURE

All a–C:H films were prepared in a capacitively coupled rf glow–discharge deposition system using a hydrocarbon source gas. A schematic diagram of the system is given in Fig. 2.2.1.

The vacuum system consists of a 18" diameter, 13" high aluminum–stainless steel vacuum chamber and a 400 l/sec turbomolecular pumping system. A Varian VGA 100 quadrupole mass spectrometer was used for monitoring the residual gases and leakage. Up–stream gas flow rates were controlled by a set of Vacuum General series 80 thermal mass flow controllers. A manual–control gate valve was utilized as a down–stream pumping rate controller.
The electrodes are water-cooled 6" stainless steel disks. 13.56 MHz rf power is capacitively coupled to a powered electrode via a matching network. We were using a π type matching network, the schematic diagram of this network is shown in Fig. 2.2.2. Through the load and input tuning the input power was controlled. Both the forward and the reflected powers can be measured. The negative bias voltage \( V_b \) is measured by a mega-ohm input dc voltmeter isolated from the rf power by a milli-henry inductor. The powered electrode also serves as a substrate holder. The wall of the vacuum chamber serves as the grounded electrode for the purpose of achieving uniform deposition.

There are three possible locations where the substrate can be mounted for film deposition: on the powered electrode, on the grounded electrode, or suspended in the plasma. Usually, the films deposited on the powered electrode are harder and less transparent than those made at the other two locations. Almost all of our films were deposited on the powered electrode.

In a deposition process, the geometry of the reactor, gas flow rate, gas pressure, rf power, bias voltage, and substrate temperature all can affect the structure and properties of the deposited film. From a microscopic point of view, these deposition parameters are not completely independent. The basic factors which affect the structures are the types of incident particles, particle impact energy and flux, and substrate temperature. In order to systematically study and simplify the system, we chose the bias voltage, \( V_b \), and the gas pressure, \( P \), as the variables and fixed all other parameters as constants. The \( V_b \) and \( P \) are two independent variables but both influence the ion impact energy. The deposition rate as a function of the product
$V_bP$ is discussed in Sec. 6.1.

A range of available deposition parameters for the rf glow−discharge deposition system is summarized in Table. 2.2.1.

Prior to any deposition, the base pressure was always lower than $2 \times 10^{-6}$ Torr. Then, argon gas was introduced into the vacuum chamber for sputter cleaning the substrate at $V_b = -500$ Volts and $P = 25$ mTorr. Subsequently, methane was introduced into the system and a deposition conducted. Practically any hydrocarbon gas can be used as a source gas. In this work, we usually used methane as the source gas.

2.3 SUBSTRATE MATERIALS

a−C:H films have been deposited on many different substrates including insulators, semiconductors, and conducting materials. UV grade synthetic fused silica slides (1" x 2" x 1mm) were used for the purpose of optical transmission measurements. In the range of our spectrophotometer, 250 − 850 nm, these slides have transmissions $> 90\%$. Most of our films were deposited on p−type (111) silicon wafers. The resistivity is between 2 and 6 ohm−cm. The silicon oxide layer was etched off by hydrofluoric acid and a light argon sputtering performed just prior to deposition. For considering the doping effect on the different type silicon substrates, several n−type (111) silicon wafers were used with resistivities between 10 and 20 ohm−cm. No difference in the properties of the films deposited on these two types of silicon wafers was found.

Because of insufficient adhesion between carbon and many metals, a hard a−C:H film cannot be deposited on molybdenum, aluminum, and
stainless steel thicker than 200 nm. To overcome this problem of weak adhesion, either a silicon bonding layer or a low power deposition had to be used.

2.4 CAPACITIVELY COUPLED RF GLOW DISCHARGE

The deposition chamber has a highly asymmetric geometry in which the plasma is sustained between the small powered electrode and the counter electrode (grounded). The 13.56 MHz rf power supply and the excitation electrode are coupled by a 500 pf capacitor. In an rf low pressure cold plasma, the reaction of charged particles to the applied electrical field depends on the plasma frequency

$$f_p = \frac{1}{2\pi} \left( \frac{n}{m} \frac{e^2}{\varepsilon_0} \right)^{0.5},$$  \hspace{1cm} (2.4.1)$$

where $n$ and $m$ are the number density and mass respectively. Assuming both ions and electrons have the same number density, $10^{10}$ cm$^{-3}$, the calculated values of frequency for CH$_3^+$ and an electron are 5.4 and 895 MHz respectively. Therefore, methyl ions do not respond to the 13.56 MHz electric field. The primary dissociation and ionization in an rf glow discharge is initiated by electrons accelerated by the applied electric field.

The plasma characteristic I–V curve is shown in Fig. 2.4.1, which explains the phenomena of self-bias in a capacitively coupled rf glow discharge very clearly. Conversely, a directly coupled system does not have a dc self-bias. As the rf power is applied, electrons arrive at the powered electrode during the positive half cycle, while a much smaller number of
immobile positive ions arrive at the powered electrode during the other half cycle. Certainly electrons also arrive at the counter electrode during the negative half cycle. Since the counter electrode in our system is grounded, the potential of the counter electrode always remain at zero. However, the counter electrode does have a negative bias voltage with respect to the plasma. Owing to the large difference in mobility between electrons and ions, the capacitively coupled electrode acquires a negative charge until the net current reaches zero. In the steady state an average DC bias voltage appears on the powered electrode. The magnitude of the negative bias depends strongly on the size of the electrodes. The smaller the powered electrode the greater the bias.

The waveform voltage distribution is illustrated in Fig. 2.4.2, where the plasma potential $V_p$ (solid curve) and powered electrode voltage $V$ (dashed curve) are shown as functions of time. The cross-section drawing of the time averaged plasma potential distribution is shown in Fig 2.4.3. A typical plasma potential is around 20 volts. The bias voltage can be controlled by the rf power output and a matching network in the range from several tens of volts to 2000 volts.

2.5 PLASMA KINETICS OF METHANE

In PECVD, it is very important to understand the physical and chemical reactions in the plasma in order to prepare films having controllable properties and also improve the reproducibility. Reactant gases are passed through a low pressure (3–100 mTorr) plasma discharge where dissociation, ionization and recombination occur. The main sources of
electrons are from electron impact ionization of the neutral reactant and secondary electron emission across the plasma sheath. A steady state glow discharge is achieved when the electron production rate is sufficient to balance the losses due to recombination.

Methane is an important source gas for the deposition of carbon films using the glow discharge method. The kinetics in a methane plasma have been studied by different groups, and some good references\textsuperscript{18–20} are available. The topic of electron dissociation of methane was discussed by L.E. Kline and the references therein. A comparison between experimental data on methane plasma and theoretical modelling of the discharge has been made by K. Tachibana.

It is expected that in a cold plasma the electron energy distribution function is quite different from a Maxwellian distribution. The differences are shown in Figure 2.5.1. The experimental energy distribution function in a low pressure plasma is much closer to Druyvesteyn distribution. The Distribution function \( f(V) \) is given by Druyvesteyn\textsuperscript{21} as

\[
n_e f(V) = \frac{2}{Ae} \left( \frac{2mV_e}{e} \right)^{0.5} \frac{d^2 i}{d V^2}
\]

(2.5.1)

where \( A \) is the area of probe, \( e \) and \( m \) are the electron charge and mass respectively, \( i \) is probe current, \( n_e \) is the electron density, and \( V = V_{sp} - V_p \) is the difference between the plasma potential \( V_{sp} \) and the probe bias potential \( V_p \).

At the high energy range, \( f(V) \) decreases faster than the Maxwellian distribution. At 5 W rf power and 220 mTorr pressure the Druyvesteyn
distribution yields an electron mean energy of 4.4 eV. The equivalent
electron temperature is 5 x 10^4 °K. In our system, the rf power is higher
(100 W) and the pressure is lower (25 mTorr). Therefore the mean energy
of electrons can be higher than 4.4 eV.

In a plasma, the concentrations of radicals give important information
about thin film growth. From a study of the rates of electron impact,
neutral–neutral molecule reactions, and ion–molecule reactions, one can
determine the dominant species in the glow discharge plasma. L.E. Kline
et al. considered CH₃, CH⁺, C₂H₅, and C₂H⁺ as the most possible
contributors to the film growth. They found that CH₃ was the only species
with sufficient surface flux to explain the deposition rate.

H. Kojima et al.²² studied the sticking coefficient of CH₃ and CH₂
radicals. They reported that CH₃ has a much lower sticking coefficient
(S < 10⁻³) than that of CH₂ (S ~ 2.5 x 10⁻²) on the surface of a–C:H.
Although the CH₂ concentration is two orders of magnitude less than the
CH₃ concentration, the contribution of CH₂ to the growth of amorphous
carbon films cannot be neglected. CH₂ can undergo direct insertion
reactions with C–H bonds and therefore may be more easily incorporated
into the network.
Table 2.2.1  The Range of Available Deposition Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bias Voltage ($V_b$)</td>
<td>50 - 2000 Volts</td>
</tr>
<tr>
<td>Input Power</td>
<td>40 - 500 Watts</td>
</tr>
<tr>
<td>Pressure ($P$)</td>
<td>$3 - 10^3$ mTorr</td>
</tr>
<tr>
<td>Base Pressure</td>
<td>$&lt; 2 \times 10^{-6}$ Torr</td>
</tr>
<tr>
<td>Gas Flow Rate</td>
<td>10 - 100 sccm</td>
</tr>
</tbody>
</table>
Fig. 2.2.1 Schematic diagram of rf self-bias deposition system.
Fig. 2.2.2 RF matching network

rf power
input

load tuning
input tuning

to electrode
Fig. 2.4.1 Development of a negative self-bias on the powered electrode in contact with an rf glow discharge.
Fig. 2.4.2 Illustrative plasma potentials (solid curves) and powered electrode voltages (dashed curves).
Fig. 2.4.3 Spatial distribution of average potential in a flat parallel reactor.
Fig. 2.5.1 An example of measured electron energy distribution with the mean energy of 4.4 eV. in comparison with the Maxwellian distribution and Druyvesteynian distribution. (From K. Tachibana et.al., 1984)
III. PHYSICAL PROPERTIES

3.1 FILM DENSITY

The mass density of the films was determined by sink–float measurements. The a–C:H films about 200 nm thick were deposited on silicon wafers, then the substrate was etched off by hydrofluoric acid. A series of halogenated hydrocarbon compounds were carefully prepared as the liquid media with which the density was measured. Small flakes of the films were placed in the test tubes which were filled with liquid media of different densities. After these test tubes were centrifuged, the position of the flakes in the liquids of various densities was determined visually.

The sources of uncertainty for this sink–float density measurement are twofold. One is from the mass and volume measurements of the liquid media. The other source comes from the impurities trapped in or around the sample flake, e.g., a small air bubble may stick on the flake and cause a lower density reading. If the samples are not chemically inert, e.g., polymerlike a–C:H, error may arise during the etching step. The etchant could conceivably change the composition of the flakes. The known error is mostly from the measurement of the volume of liquid media, which is estimated to be less than 1%. The total percentage error of this method should not be higher than 2%.

The densities of a matrix of a–C:H films which were deposited in a wide range of $V_b$ and P are shown in Table 3.1.1. The density ranges from $< 1.4 \text{ g/cm}^3$ to $1.68 \text{ g/cm}^3$ for our samples and is significantly less than that
of crystalline carbons (diamond 3.51 g/cm³, graphite 2.26 g/cm³). The relation between the density and average ion impact energy \( \sim V_b/P^{0.5} \), is drawn in Fig. 3.1.1. The effect of hydrogen concentration on the density will be discussed in Chapter VI.

3.2 HARDNESS

The intrinsic hardness can be related to cohesive energy, bonding energy, and the coordination numbers of the bonding. The measurable hardness of thin film materials is not only determined by the strength of the interaction forces but also by the deformation mechanisms. The size of the indentation also affects the measured hardness. In all cases the hardness decreases as the depth of indentation increases. It is very easy to misread the hardness of a thin film because of the substrate effect, especially when a hard layer is coated on a soft substrate. In order to avoid this influence, the ratio of indentation depth to film thickness should be limited between 0.07 and 0.2. Therefore, for the hardness measurement of a thin film, which is only several hundred nanometers, a nanoindentation tester should be used.

In our study, an empirical scratch hardness/adhesion was obtained using a diamond Vickers microhardness indenter. The typical load was one gram and the drawing speed was a constant 0.6 cm/min. The width of each scratch was measured by using a scanning electron microscope and the Dektak IID stylus profilometer. Usually, the scratch width is not well defined. An average width has to be used. Other uncertainties in the scratch width measurement come from the accuracy of the magnification of SEM and the stylus diameter of the Dektak IID.
The scratch width of various materials is shown in table 3.2.1 to compare with that of a-C:H films. It can be seen that our hardest film is harder than \( \beta \) silicon carbide.

### 3.3 INTERNAL STRESS

The internal stress arising during film deposition is from both the differential thermal expansion and intrinsic stress mechanisms, such as impurities, structural reordering, and fast quench metastabilization. Therefore the gas composition, substrate temperature, and deposition rate are the determining factors for the internal stress of the deposited films.

The substrate deflection technique is the conventional method for measuring the stress of thin films.\(^{27,28}\) For a circular disk shaped substrate with an isotropic film on it, the stress can be determined by equation 3.3.1

\[
\sigma = \frac{EZh^2}{3t(1-\nu)L^2}
\]  

(3.3.1)

where \( E \) is Young's modulus of the substrate, \( \nu \) is the Poisson's ratio of the substrate, \( h \) is the substrate thickness, \( Z \) is the vertical bending, \( L \) is horizontal length from the center to the measured point, and \( t \) is the film thickness. Equation 3.3.1 is valid only when the vertical bending \( Z \) is less than one-tenth of the substrate thickness \( h \).

A set of the a-C:H films were deposited on 3" fused quartz with the same deposition conditions as those for density measurements. The fused quartz\(^{29}\) has a Young's modulus of \( 7.22 \times 10^{11} \) dynes/cm\(^2\) and a Poisson's ratio of 0.16. The results of the stress measurements are shown in Table
3.3.1. It is clear the films with high compressive stress were deposited at low power. The relation between internal stress and hydrogen concentration are discussed in Sec. 6.2.

<table>
<thead>
<tr>
<th>Bias Voltage (kV)</th>
<th>Pressure, (mTorr)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
<td>40</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>1.57</td>
<td>&lt;1.4</td>
<td>&lt;1.4</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>1.57</td>
<td>1.68</td>
<td>1.68</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>1.61</td>
<td>1.63</td>
<td>1.50</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>1.50</td>
<td>1.57</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Densities are shown in units of g/cm$^3$
Table 3.2.1  Scratch width for various materials using Vickers diamond indentor

<table>
<thead>
<tr>
<th>Material</th>
<th>Scratch width, microns</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>9.17</td>
</tr>
<tr>
<td>NaCl</td>
<td>7.68</td>
</tr>
<tr>
<td>Soft a–C:H film</td>
<td>6.0</td>
</tr>
<tr>
<td>Si (111)</td>
<td>4.02</td>
</tr>
<tr>
<td>Glass chipper</td>
<td>3.06</td>
</tr>
<tr>
<td>Fused quartz</td>
<td>2.31</td>
</tr>
<tr>
<td>Quartz</td>
<td>1.92</td>
</tr>
<tr>
<td>β–SiC 3.8μm thick on (100) Silicon</td>
<td>1.36</td>
</tr>
<tr>
<td>Hardest a–C:H film</td>
<td>1.0</td>
</tr>
<tr>
<td>Sapphire</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>
Table 3.3.1  Stress Measurements of Matrix Samples

<table>
<thead>
<tr>
<th>Bias Voltage (kV)</th>
<th>Pressure, (mTorr)</th>
<th>5</th>
<th>40</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td></td>
<td>-14</td>
<td>-19</td>
<td>-19</td>
</tr>
<tr>
<td>0.5</td>
<td></td>
<td>-12</td>
<td>-7.9</td>
<td>-9.5</td>
</tr>
<tr>
<td>1.0</td>
<td></td>
<td>-6.7</td>
<td>-6.6</td>
<td>-5.3</td>
</tr>
<tr>
<td>1.5</td>
<td></td>
<td>-4.0</td>
<td>-3.3</td>
<td></td>
</tr>
</tbody>
</table>

Stresses are shown in units of $10^9$ dynes/cm$^2$
Fig. 3.1.1 The relation between ion impact energy and the mass density of as-deposited a-C:H films.
IV. OPTICAL PROPERTIES

4.1 OPTICAL MEASUREMENT

The determination of the optical constants of a thin film coating is very important both for the characterization of the deposition process and for the determination of the electronic structure of the material. A variety of optical characterization methods have been developed in the past five decades. Spectrophotometry, ellipsometry, and the Brewster angle technique (Abelès method) are the techniques most used.

The instrument used in this study for transmittance measurements was a Cary 219 double beam spectrophotometer. The wavelength range of the light source in this instrument is from 187 nm to 875 nm, but we only used the data obtained between 250 nm and 850 nm (1.46 eV to 4.96 eV). The values of the measured percentage transmittance ranged from 80 % to 1 %. Since the precision of the spectrophotometer is only 0.1 %, the percentage error is ± 1.25 % at T = 80 % and ± 10 % at T = 1 %. The a–C:H films were deposited on 1 mm thick fused silica slides which have around 90 % total transmittance in the energy range we used. A list of the samples which were prepared by different deposition parameters and gas compositions for optical measurements is given in Table 4.1.1.

Dane Clark, at North America Coating Labs., measured the transmittance and reflectance on a–C:H films in the same energy range for us. However, The results have not been incorporated into this work.
4.2 OPTICAL CONSTANTS

The absorption coefficient for the intensity loss of a propagating wave is defined as

\[ \alpha = -\frac{1}{I} \frac{dI}{dt} \quad \text{or} \quad I(t) = I_0 e^{-\alpha t} \quad (4.2.1) \]

therefore

\[ T = \frac{I}{I_0} = e^{-\alpha t} \quad \text{or} \quad \alpha = (\ln \frac{1}{T})/t \quad (4.2.2) \]

where \( t \) is the film thickness. Since the intensity depends on the square of the electrical field,

\[ k = \frac{\alpha \lambda}{4\pi} \quad (4.2.3) \]

where \( k \) is the imaginary part of refractive index, called the extinction coefficient. Therefore, from a single transmittance measurement, the absorption and extinction coefficients can be obtained. If the refractive index, \( n \), can be accurately measured in the same energy range, one can deduce the dielectric constants, \( \varepsilon = \varepsilon_1 + i\varepsilon_2 \), by the following equations:

\[ \varepsilon_1 = n^2 - k^2, \quad \varepsilon_2 = 2nk \quad (4.2.4) \]

4.3 OPTICAL GAP

The optical gap, \( E_0 \), is a very useful parameter for the
characterization of amorphous semiconducting films such as a-C:H. But in contrast to crystalline semiconductors, the optical absorption edge of amorphous semiconductors is difficult to define experimentally. Since tail states and gap states exist in a disordered structure, there is no sharp absorption edge.

An amorphous solid interband optical absorption can be described by

$$
\alpha h\nu = B(h\nu - E_0)^m
$$

(4.3.1)

where \(\alpha\) is the absorption coefficient, \(h\nu\) is the incident photon energy, \(B\) is a material constant, \(E_0\) is the optical gap, and \(m\) is an experimental constant. Usually \(m\) is equal to 2 and the expression is called the semiempirical Tauc relation.\(^{31}\)

$$
\sqrt{\alpha h\nu} = B(h\nu - E_0)
$$

(4.3.2)

It is important to note that a pseudo gap, \(E_0\), does not necessarily imply the existence of a true energy gap.

There is another similar equation\(^{32}\) which can be deduced from the relation between the imaginary part of the dielectric function \(\varepsilon_2(\nu)\) and the density of states in the valence and conduction bands. The optical gap is extracted from the energy dependence of the imaginary part of the dielectric constant via the following relation:

$$
E\sqrt{\varepsilon_2} = C(E - E_0)
$$

(4.3.3)
where the photon energy $E = h \nu$, and the constant $C$ is given by
$C = 2h \sigma_{\text{min}}/\Delta E$. Here $\sigma_{\text{min}}$ is the minimum conductivity and $\Delta E$ is the
width of the tail states.

By comparing Eqs (4.3.2) and (4.3.3), we found

$$C = \left(\frac{\hbar c}{2 \pi}\right)^{0.5} B $$

(4.3.4)

where $c$ is the speed of light, and $n$ is the refractive index. Since the refractive index is not a constant in this energy range, these two equations will give us slightly different results for $E_0$.

4.4 EXPERIMENTAL DATA ON ABSORPTION EDGE

Table 4.1.1 shows three sets of prepared samples for three different purposes of study. In the first set, four a-C:H films were deposited at different bias voltages in a range from 0.1 kV to 1.5 kV at 25 mTorr. The film thickness was determined by nuclear reaction analysis. For the purpose of comparison, the absorption coefficients of these four samples vs incident photon energy was drawn on one figure, Fig. 4.4.1. The optical gap deduced by the Tauc relation is shown in Fig. 4.4.2 and also indicated in the last column of Table. 4.1.1. Clearly the film deposited by lower power has a higher optical gap. Fig. 4.4.3 shows the experimentally determined values of the extinction coefficients plotted as a function of the photon energy. The lower the power to deposit a film, the smaller the extinction coefficient.

The second set of samples is part of the thermal stability study. Three samples were annealed at 100° C, 200° C, and 300° C for 20 hours
respectively. The graphs of absorption coefficient, square root of \( \alpha \nu \), and extinction coefficient vs photon energy are shown in Fig. 4.4.4, Fig. 4.4.5, and Fig. 4.4.6 respectively. These optical measurements indicate that the structure of the film does not change very much under 300° C. The other method for studying the hydrogen effusion at high temperatures is discussed in Sec. 6.3.

In the third set of samples, the a-C:H films were doped with boron and sulfur. The results of the optical measurements are shown in Fig. 4.4.7, Fig. 4.4.8, and Fig. 4.4.9. The optical gap decreased after doping which may indicate that the impurity introduced extra states in the gap.
Table 4.1.1 The list of a–C:H samples for optical measurements and the measured optical gaps.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Gases</th>
<th>Vb (kV)</th>
<th>P (mTorr)</th>
<th>Thickness (nm)</th>
<th>Optical Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>329</td>
<td>100% CH4</td>
<td>0.5</td>
<td>25</td>
<td>180</td>
<td>1.1</td>
</tr>
<tr>
<td>330</td>
<td>100% CH4</td>
<td>1.0</td>
<td>25</td>
<td>160</td>
<td>0.9</td>
</tr>
<tr>
<td>331</td>
<td>100% CH4</td>
<td>0.1</td>
<td>25</td>
<td>180</td>
<td>1.4</td>
</tr>
<tr>
<td>344</td>
<td>100% CH4</td>
<td>1.5</td>
<td>25</td>
<td>200</td>
<td>0.8</td>
</tr>
<tr>
<td>329A</td>
<td>100% CH4</td>
<td>0.5</td>
<td>25</td>
<td>180</td>
<td>1.1</td>
</tr>
<tr>
<td>329B</td>
<td>annealed at 1000 C for 20 hrs</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>329C</td>
<td>annealed at 2000 C for 20 hrs</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>329D</td>
<td>annealed at 3000 C for 20 hrs</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>327</td>
<td>1% B2H6</td>
<td>0.5</td>
<td>25</td>
<td>220</td>
<td>0.9</td>
</tr>
<tr>
<td>328</td>
<td>1% B2H6</td>
<td>1.0</td>
<td>25</td>
<td>190</td>
<td>0.9</td>
</tr>
<tr>
<td>336</td>
<td>1% H2S</td>
<td>0.5</td>
<td>25</td>
<td>150</td>
<td>0.9</td>
</tr>
<tr>
<td>337</td>
<td>10% H2S</td>
<td>0.5</td>
<td>25</td>
<td>41</td>
<td>&lt;0.6</td>
</tr>
</tbody>
</table>
Fig. 4.4.1 Optical absorption coefficient α as photon energy for α-C:H films prepared from methane plasma decomposition with different bias voltage.
Fig. 4.4.2 The Tauc relation, $\sqrt{\alpha \Delta \nu}$ vs photon energy, for a-C:H films prepared from methane plasma decomposition with different bias voltage.
Fig. 4.4.3 Extinction coefficient $k$ vs photon energy for $\alpha$-C:H films prepared from methane plasma decomposition with different bias voltage.
Fig. 4.4.4 Optical absorption coefficient $\alpha$ vs photon energy for annealed $\alpha$-C:H films.
Fig. 4.4.5 The Tauc relation, $\sqrt{\alpha\nu}$ vs photon energy, for annealed a-C:H films.
Fig. 4.4.6: Extinction coefficient $k$ vs photon energy for annealed $\alpha$-C:H films.
Fig. 4.4.7: Optical absorption coefficient $a$ vs photon energy for boron and sulfur doped $a$-C:H films.
Fig. 4.4.8 The Tauc relation, $\sqrt{\alpha h\nu}$ vs phonton energy, for boron and sulfur doped a-C:H films.
Fig. 4.4.9 Extinction coefficient $k$ vs photon energy for boron and sulfur doped $a$-C:H films.
V STRUCTURE AND MODELLING

5.1 STRUCTURAL DETERMINATION

The optical and physical properties of a–C:H are macroscopic quantities which are related to the microscopic structure of the films. In order to understand the material and to predict methods for modifying its properties, one must know the microstructure. The a–C:H system is a complex amorphous material. The fact that carbon atoms can form sp, and sp$^2$ orbital hybridization in addition to sp$^3$ hybrids makes a–C:H much more complex than amorphous hydrogenated silicon, a–Si:H.

The structure of amorphous carbon has been studied by a variety of techniques. These include $^{13}$C nuclear magnetic resonance, $^{33-35}$ electron energy loss spectroscopy, $^{36-39}$ Raman scattering, $^{40-43}$ electron diffraction, $^{44,45}$ infrared spectroscopy, $^{46}$ electron spin resonance, $^{47,48}$ optical spectroscopy, $^{49-51}$ and photoelectron spectroscopy. $^{5,52-54}$ All these measurements are sensitive to structural changes.

R.O. Dillon and J.A. Woollam$^{40}$ investigated both as–deposited and annealed amorphous carbon films by using first order Raman scattering in terms of the I(D)/I(G) intensity ratio, line position, and linewidth. I(D) is the intensity of Raman scattering peak by the disorder zone edge phonons in small crystalline graphite$^{42}$ and I(G) is the corresponding Raman peak of single–crystal graphite. For both graphite and diamond the Raman spectra are well known. The first order Raman spectrum of diamond consists of a single peak at 1332 cm$^{-1}$. Large single crystal graphite also has a single
peak, the "G" line, at 1581 cm\(^{-1}\). Since Raman spectra are very sensitive to the translational symmetry, for small graphite crystallites (basal plane dimensions < 20 nm), there appears a disorder, or "D", line at 1355 cm\(^{-1}\). Dillon and Woollam suggested that the downshifted G line position of 1536 cm\(^{-1}\) and D line position of 1283 cm\(^{-1}\) in the as-deposited films indicated the presence of bond–angle disorder. They also found that the linewidth decreased and threefold sites increased at the expense of fourfold sites with increasing annealing temperature.

Extended x-ray absorption fine structure (EXAFS) has been used to investigate a–C and a–C:H films. But because of the limited EXAFS range available and the lack of experimental C–C phase shift data, a quantitative analysis of the data has not been performed. The EXAFS data on a–C:H of G. Comelli et al.\(^5\) yield a more precise structural picture. The C–C bond length in the annealed film was found to be within 2.5 pm from that of graphite (142.1 pm). In contrast, the bond length was shorter by more than 0.01 nm from that of diamond (154.4 pm). That means the film is more "graphitelike" than "diamondlike" in structure. Analysis of the EXAFS amplitude of the nearest-neighbor shell leads to a two-phase structural model consisting of a "graphitelike" network and a statically and dynamically disordered "random matrix". The "random matrix" is suggested to be a floppy network of single and double bonds.

J. Fink et al.\(^36\) studied a–C:H films which were prepared by plasma decomposition of benzene by electron energy loss spectroscopy (EELS). In all as-prepared films, about two thirds of the carbon atoms were found to be in the sp\(^3\) configuration, while one third was found to be in sp\(^2\)
configuration. For low energy deposition, most of the \( \pi \) electrons were localized in weakly bonded benzene rings, whereas for high energy deposition, \( \pi \) electrons were bonded in more graphitic rings. Upon annealing the films above 400 \(^\circ\)C, a delocalization of the \( \pi \) electrons was observed. The optical gap closed near 600 \(^\circ\)C. Above 600 \(^\circ\)C, a transformation of amorphous carbon to graphitic carbon was found.

Because the structure of a–C:H films is critically dependent upon its preparation conditions and subsequent thermal history, it is very difficult to compare the structure of films from different research groups. Therefore a complete picture of amorphous carbon cannot yet be formulated. However some useful guidelines about the deposition conditions and the microstructure of our films can be developed. The general picture for describing the structure of a–C:H films is as follows.

1. About 20 – 60 at.% hydrogen exist in a–C:H. Most of the hydrogen is bonded to sp\(^3\) sites.
2. Although this material has been called "diamondlike", it still contains a considerable amount of graphitic structure. The aromatic sp\(^2\) configuration may be very important in determining the mechanical properties of the film.
3. There is a wide range for the sp\(^2\) to sp\(^3\) ratio, from 0.5 to 1.6, in as–deposited films.
4. After heat treatment at \( T > 400 \) \(^\circ\)C, the hydrogen is released and sp\(^2\) sites dominate.

5.2 GRAPHITIC CLUSTER TWO–PHASE MODEL
Robertson and O'Reilly\textsuperscript{6} have calculated the electron states and atomic structure for both nonhydrogenated and hydrogenated amorphous carbon. In a carbon system, the total energy of the $\pi$ electrons favor the $sp^2$ sites in compact clusters of sixfold rings. An extended carbon network formed by disordered $sp^2$ and $sp^3$ bonds links these clusters together. They argue that the formation of finite clusters results in order to relieve internal stress. The width of the optical gap was found to vary inversely with cluster size. They confirmed that $\pi$ electron states both configure band edges in a-$C:H$ and play an important role in the optical properties. In addition the relation between the optical gap and the $I(D)/I(G)$ ratio of the Raman spectrum indicates that these optical properties are determined by compact $\pi$-bonded clusters.

M.A. Tamor et al.\textsuperscript{55} studied the correlation between the $I(D)/I(G)$ ratio, the optical gap $E_0$, and the bias voltage $V_b$. They found that the optical gap decreased while $I(D)/I(G)$ increased with increasing bias voltage during deposition. They also adopted Robertson's relation between the optical gap and the cluster size.

$$E_0 = 6.0/N^{0.5} \text{ (eV)} \quad (5.2.1)$$

where $N$ is the number of rings in the cluster and $10 < N < 100$. These relations indicate that $I(D)/I(G)$ increases as $N$ increases.

In the conventional Raman scattering from finite-size crystals of graphite, the $I(D)/I(G)$ ratio decreases with increasing cluster size. Clearly these two statements are not consistent. Therefore, Tamor et al. conclude
that the relative intensity of the D peak in amorphous carbon is not a useful indicator of graphitic cluster size.

After investigating this issue carefully, we found these two statements do not contradict each other. Because, in the conventional study on graphite, the domain sizes were varied from highly crystalline (HOPG) to 3 nm.\textsuperscript{56} Since the I(D) line is contributed by the vibration mode of the domain boundary, a lower limit of domain size must exist for supporting this mode. On the other hand, eq.(5.2.1) is only suitable for 10\textless N \textless 100. If one assumes the graphite rings are arranged in a square, the upper limit has 10 x 10 rings that gives a domain size of only 2.47 nm. Therefore, we propose that a maximum of the I(D)/I(G) ratio exists around $L_a = 2.5$ nm, where $L_a$ is the cluster domain size. When $L_a > 2.5$ nm, I(D)/I(G) decreases with increasing cluster size. When $L_a < 2.5$ nm, I(D)/I(G) increases with increasing cluster size.

5.3 RANDOM COVALENT NETWORK

The concept of random networks was first proposed by Zachariasen.\textsuperscript{57} He suggested that the number of nearest neighbors are the same in both crystalline and amorphous forms, but the variations in the interbond angles and lengths lead the system to a random structure.

The random covalent network (RCN) model for a–C:H was proposed by Angus and Jansen.\textsuperscript{7} They followed Döhler's\textsuperscript{58} arguments stating that a random covalent network is completely constrained when the number of constraints per atom is just equal to the number of degrees of freedom per atom.
Therefore, for a completely constrained system with several types of atoms and/or bindings, the condition can be written as

\[ \Sigma X_i N_{\text{co},i} = 3 \]  \hspace{1cm} (5.3.1)

where \( X_i \) are the atomic fractions and \( N_{\text{co},i} \) are the number of constraints. Döbler modified Phillips'\(^{59}\) idea in which the number of constraints are described by considering the effects of angular constraints and internal degrees of freedom. For a three dimension random network, \( N_{\text{co}} \) is given by

\[
N_{\text{co}}(m) = \begin{cases} 
\frac{m^2}{2} & \text{for } m \leq 2 \\
5m/2 - 3 & \text{for } m \geq 2 
\end{cases}
\]  \hspace{1cm} (5.3.2)

where \( m \) is the average coordination number.

In an a-C:H system three types of atoms are distinguished: hydrogen with \( m = 1 \); sp\(^2\) bonded carbon with \( m = 3 \); and sp\(^3\) bonded carbon with \( m = 4 \). Since not many other divalent atoms exist and the amount of sp\(^1\) bonded carbon is low, \( m = 2 \) is ignored. Angus\(^7\) had further comments about carbon sp\(^2\) bonding. He assumed that all sp\(^2\) carbon sites appeared as pairs, i.e., as C=C bonds. Each pair of sp\(^2\) atoms would then have four constraints (\( m = 4 \)) because each C=C pair has four bonds to the rest of the network. Equation (5.3.1) is therefore

\[ 0.5X_1 + 7.0(0.5X_3) + 7.0X_4 = 3 \]  \hspace{1cm} (5.3.3)
One also has

\[ X_1 + X_3 + X_4 = 1 \]  \hspace{1cm} (5.3.4)

Combining equations (5.3.3) and (5.3.4), the relation between the \( \text{sp}^3/\text{sp}^2 \) ratio and hydrogen atom fraction in a completely constrained random hydrocarbon network is achieved as follows.

\[ \frac{X_4}{X_3} = \frac{6X_1 - 1}{8 - 13X_1} \]  \hspace{1cm} (5.3.5)

Equation (5.3.5) indicates that there is a upper limit for the atomic fraction of hydrogen, \( X_1 \), above which the hydrocarbon system is incapable of constructing a completely constrained random network. The limit is obtained by setting the denominator of eq. (5.3.5) to zero. At this limit, \( X_1 = 8/13, \) (\( X_1 \approx 61.5 \% \)), the only way the system can remain completely constrained is if all carbon atoms are in \( \text{sp}^3 \) sites. When \( X_1 \) is higher than the limit, 61.5 \%, the whole system becomes "underconstrained," and it is expected to be mechanically soft.

At the other extreme, Angus suggested a theoretical lower limit exists when the numerator of eq. (5.3.5) is equal to zero. Below this hydrogen atom fraction, \( X_1 = 1/6 = 16.7 \% \), the random covalent network would be "overconstrained" even if all carbon atoms are \( \text{sp}^2 \) coordinated.

This RCN model is quite general. As long as the number of degrees of freedom and the number of constraints are properly defined, the model
can be used on many different amorphous systems.

Considering the physical meaning of eq.(5.3.1), it is clear that when \( \Sigma X_i N_{co,i} = 3 \), the random network is stable, \( \Sigma X_i N_{co,i} > 3 \), the network is overconstrained and unstable, whereas when \( \Sigma X_i N_{co,i} < 3 \), the random network is underconstrained and loose or floppy.

Therefore, if one knows the hydrogen atom fraction and the sp\(^3\)/sp\(^2\) ratio of a random hydrocarbon system, one should be able to tell how rigid the system is. The random network theory implies that there is a lower limit for the hydrogen concentration of the system only if the system remains random. In other words, when \( X_i < 16.7 \% \), the system is overconstrained only if the sp\(^2\) and sp\(^3\) sites remain randomly distributed.

When the number of constraints is too high, the network is unstable and may break down and reconstruct into more sp\(^2\) sites. Once small sp\(^2\) clusters exist in the system, the RCN model fails, and the two phase model should hold.

From the same point of view, the RCN model can suitably explain why a nonhydrogenated amorphous carbon film is very hard.

5.4 ALL–sp\(^2\) DEFECT GRAPHITE MODEL

The all–sp\(^2\) defect graphite (DG) model was proposed by Tamor and Wu.\(^8\) They got the idea from the experimental data of Raman scattering and electron energy loss spectroscopy which indicated large amounts of sp\(^2\) graphitic structure in a–C:H.

The approach of the DG model is completely different from that of the RCN model. The DG model begins with a single–layer of crystalline
graphite on which \( \pi \) electrons are delocalized. Defects are introduced by removing carbon atoms randomly and connecting hydrogen atoms to the dangling carbon bonds. The hydrogenated carbon are assumed to be \( sp^3 \) sites.

Percolation theory is used as a guideline for predicting how many carbon atoms can be removed and how many hydrogen atoms can be added. For a minimum hydrogen content of 20 at.\%, at least 42 \% of the carbons atoms must be deleted to induce \( \pi \) electron localization. No more than 30 at.\% of the carbon atoms can be deleted and still maintain a solid network. In this case, a maximum hydrogen content of 60 at.\% is achieved.

Although the DG model takes a very simple approach, it describes some properties of a–C:H films without using any free parameters. It is not a definitive structural model, and some ambiguities in the model are discussed below.

1. In the DG model, a hydrogen concentration lower than 20 at.\% is still allowed because the minimum was defined by the conductivity of \( \pi \) electrons. Following this model, an a–C:H sample is conductive when the atomic hydrogen concentration is lower than 20 at.\%. This is a major difference from the RCN model in which the minimum hydrogen content is defined by the bonding constraints.

2. At high hydrogen concentration, the DG model is limited by the percolation theory to the polymerlike (long chain) a–C:H structure which is supported by the results of many experiments.

3. Experimental data show that there are some quaternary all–carbon \( sp^3 \) sites in a–C:H. The all–sp\(^2\) model fails to describe the existence
of any carbon in this configuration, i.e., a carbon atom bonded to four other carbon atoms. (The DG model allows $sp^3$ sites only when carbon is bonded to hydrogen, the all–carbon quaternary $sp^3$ site is forbidden).

(4) Without any strong interlayer bonding, the material described by the DG model predicts a weak interplanar bonding like graphite, which is not supported by current knowledge of a–C:H.

(5) The DG model cannot be extended to describe non–hydrogenated amorphous carbon (a–C), because a–C films have high electrical resistivity\textsuperscript{60} and internal compressive stress.\textsuperscript{61}
VI. RESULTS AND DISCUSSION

6.1 DEPOSITION RATE

The deposition rate of an rf plasma system is assumed not to change with time. In our experiment, the film thickness was determined with a DEKTAK IID profilometer and nuclear reaction analysis. These two methods usually agree with each other within 15%. Then the deposition rate was determined by direct calculation (film thickness divided by deposition time).

If one assumes during the deposition that the sputtering rate is zero or proportional to $V_b$, the deposition rate will change linearly with $(V_b P)$. Fig. 6.1.1. shows this relation for films deposited with 100% methane. Most of the samples deposited at low power fit this linear relation very well. The two points far from the straight line were deposited at $V_b = -1 \text{ kV}$, $P = 78 \text{ mTorr}$ and $V_b = -1.5 \text{ kV}$, $P = 40 \text{ mTorr}$, respectively. Since there was neither an increase in the film density with increasing $(V_b P)$, nor an increase in the sputtering rate with increasing ion impact energy ($\sim V_b / P^{0.5}$), the decrease in the deposition rate at high bias voltage and high pressure must related to the glow discharge itself.

In some deposition processes, reactive gases were mixed with methane as the source gases. The results indicated that a small amount of certain additives had a great influence on the deposition rate, e.g., 1% $B_2H_6$ increased the deposition rate by 40% and 1% $H_2S$ reduced it by nearly 30%. The relation between the deposition rate and different additives is
shown in Table 6.1.1.

6.2 HYDROGEN CONCENTRATION

The hydrogen concentration of a-C:H films was determined by nuclear reaction analysis. When $^{15}$N ions with energy $> 6.35$ MeV are incident upon samples containing hydrogen, a resonant nuclear reaction takes place as follows:

$$^{15}\text{N} + ^1\text{H} = ^{12}\text{C} + ^4\text{He} + \gamma$$

The gamma ray yield at specific ion energies is a measure of the hydrogen concentration. Depth profiling is achieved by changing the energy of the incident $^{15}$N ion beam.

Our samples have an atomic percentage of hydrogen from 28 % to 44 %, which is within the range predicted by theory. The results of hydrogen concentration measurements are shown in Table 6.2.1. The relation between hydrogen concentration and other properties is critical for understanding the films.

The results indicated that the hydrogen content is not a clear function of the impact energy, $\sim V_b/P^{0.5}$, the deposition rate, $\sim V_b P$, or the mass density of the deposited film, see Fig. 6.2.1, 6.2.2, and 6.2.3. Of all the deposition parameters and their combinations, the bias voltage is the most sensitive parameter in determining the hydrogen content of the deposited films. The relation between bias voltage and hydrogen content is shown in Fig. 6.2.4.

As the hydrogen concentration increased, we found the optical energy gap increased as well as the internal compressive stress. On the other hand,
the hardness of the film decreased with increased hydrogen concentration. Similar results have been reported by other groups. The explanation is the hydrogen in the film reduces the average coordination number, therefore permitting more sp$^3$ carbon sites. Hydrogen atoms, being univalent, can only serve as network terminators. Therefore the optical gap is larger and the films become softer. Apparently a a–C:H film which is both hard and transparent does not exist.

6.3 THERMAL STABILITY

Thermal desorption spectroscopy (TDS)$^{62}$ is one of the simplest experiments for studying surface adsorption and chemical changes as a function of temperature. The method was adopted to determine hydrogen effusion from a–C:H films. The films were about 250 nm thick on molybdenum substrates. A K–type thermocouple was directly connected to the substrate. The sample was transferred into a UHV chamber and placed in front of the ionizer of the mass spectrometer.

During the experiment, the temperature was manually ramped from room temperature to 900 °C in five minutes using an electron bombardment heater. The results indicate that atomic and molecular hydrogen both start effusing at 400 °C and have a maximum effusion rate around 650 °C, see Fig. 6.3.1. In Fig. 6.3.2, the experiment was repeated and a similar spectra reproduced. In addition, a blank molybdenum substrate was tested under the same conditions to show that the hydrogen was effusing from a–C:H films not the substrate. Fig. 6.3.3 indicates the Mo substrate and the equipment itself released hydrogen at a rate at least an order of magnitude
less than that from the tested films. This result is consistent with the post annealing optical measurements. The a-C:H films are quite stable when the temperature is lower than 400 °C. At temperatures above 400 °C, the hydrogen effuses out of the film, and the remaining film reconstructs and becomes more graphitic.

Table 6.1.1 The deposition rate as a function of the different source gases combination

<table>
<thead>
<tr>
<th>Gases</th>
<th>D rate (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% CH4</td>
<td>18</td>
</tr>
<tr>
<td>1% B2H6 in CH4</td>
<td>22</td>
</tr>
<tr>
<td>1% SiH4 in CH4</td>
<td>20</td>
</tr>
<tr>
<td>H2S/CH4 = 1/100</td>
<td>15</td>
</tr>
<tr>
<td>H2S/CH4 = 1/10</td>
<td>4</td>
</tr>
<tr>
<td>N2/CH4 = 1/10</td>
<td>15</td>
</tr>
<tr>
<td>CO2/CH4 = 1/10</td>
<td>14</td>
</tr>
</tbody>
</table>
Table 6.2.1 Hydrogen Concentration of Matrix Samples

<table>
<thead>
<tr>
<th>Bias Voltage (kV)</th>
<th>Pressure, (mTorr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
</tr>
<tr>
<td>0.1</td>
<td>41 %</td>
</tr>
<tr>
<td>0.5</td>
<td>35 %</td>
</tr>
<tr>
<td>1.0</td>
<td>34 %</td>
</tr>
<tr>
<td>1.5</td>
<td>29 %</td>
</tr>
</tbody>
</table>
Fig. 6.1.1 The deposition rate vs. (bias voltage * pressure) for 100% methane rf plasma decomposition.
Fig. 6.2.1 Hydrogen content vs (bias voltage / sqrt(pressure))
Fig. 6.2.4 Hydrogen content vs bias voltage
Fig. 6.3.1 Thermal desorption spectrum of a-C:H film on a Mo substrate.
Fig. 6.3.2 Comparison sample for thermal desorption spectrum of a-C:H film on Mo substrate.
Fig. 6.3.3 Thermal desorption spectrum of a blank Mo substrate.
VII. CONCLUSIONS

The main results of this research on a–C:H films are the correlations between the parameters of rf plasma deposition, the physical and optical properties, and the structure of the films. The individual achievements of this study are listed as follows:

(1) The deposition process was accurately and reproducibly controlled by two parameters: negative self–bias $V_b$ and gas pressure $P$. The ranges of deposition parameters for achieving hard and semitransparent a–C:H films in our system are $-100 > V_b > -1000$ volts and $10 < P < 40$ mTorr.

(2) The non–hydrogen impurities in our films were examined by RBS and AES showed to be less than 1 %.

(3) High hydrogen content, $\sim 40$ %, films deposited at low power have high internal stress. Low hydrogen content, 28 %, films deposited at high power have low internal stress.

(4) Our studies do not agree with P. Koidl's\textsuperscript{23} result that the mass density of a film is proportional to the impact energy via $\sim V_b/P^{0.5}$. We found the mass density decreased at the high energies.

(5) The optical gap of a deposited film increases with decreasing bias voltage, i.e., the film with higher hydrogen concentration has bigger optical gap.

(6) The graphitic cluster two–phase (GCT) model, the random covalent network (RCN) model, and all–sp$^2$ defect graphite (DG) model were used for describing the relations between the structure, and the
mechanical and optical properties. According the GCT model the optical
gap is determined by $\pi$-electrons and the cluster size can be related to the
$I(D)/I(G)$ ratio in Raman spectra. The CRN model explained the
mechanical strength of a–C:H films by comparing the number of constraints
and the number of degrees of freedom. The DG model used a completely
different approach to this structural issue, the percolation theory. Many
aspects of this model need to be reconsidered.

(7) A significant amount of hydrogen started effusing through a–C:H
films at 400 °C. After heat treatment at a temperature higher than 400 °C,
the film became darker and graphitic, i.e., $sp^2$ sites increased.
VIII. FUTURE RESEARCH

Although many basic properties of the rf plasma deposited a-C:H films have been well studied, this is still an immature field. Either for basic science or for the purpose of application, there are many interesting areas that need to be explored.

In most other types of thin film deposition, the substrate temperature $T_s$ is always a major factor affecting the structure of the film. This important parameter has not yet been studied. The amorphous materials are usually formed by a fast quench. Therefore, by decreasing $T_s$, one could hope to grow films with different metastable structures. On the other hand, by increasing $T_s$ we may give adatoms some extra energy before they are trapped in potential wells resulting in structurally different materials.

For studying the hardness of thin films, a nanoindenter shall be used because the scratch width is only a comparative reference without any absolute meaning.

I regret not having the opportunity to study the optical properties of a-C:H films thoroughly. Since we were missing an important parameter, the refractance $R$, we could not get the dielectric constants from optical measurements. I hope that in the near future these measurements can be made. Then the energy loss function can be deduced from the dielectric constants and a comparison with the results from EELS can be made. If these results are reliable, the $sp^3/sp^2$ ratio can be determined from optical measurements. Also from the optical constants, the method of effective
media approximation\textsuperscript{50} (EMA) can be adopted and one can get some idea about both the percentage of \( sp^3 \) and \( sp^2 \) sites and the volume of microvoids present. The accuracy of this method can be checked by a positron annihilation study\textsuperscript{63} on microvoids.

The presence of hydrogen is not necessary for the formation of a hard amorphous carbon film. Non–hydrogenated amorphous carbon, (a–C), films have similar mechanical properties as a–C:H films, but much higher thermal stability.\textsuperscript{64} The only advantage hydrogenated films have over nonhydrogenated films is that they have a much wider optical gap. Therefore, for the fabrication of non–optical coatings, the a–C films may be better candidates.
REFERENCES


12. J.A. Thornton, the same as ref. 10. pp. 19–62.


64. Personal communication with Dr. P.H. Schmidt.