Influence of hydrogen on the structure and properties of tetrahedral amorphous carbon films obtained by the filtered cathodic vacuum arc technique

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Influence of hydrogen on the structure and properties of tetrahedral amorphous carbon films obtained by the filtered cathodic vacuum arc technique

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ABSTRACT

Hydrogenated tetrahedral amorphous carbon (ta-C:H) films prepared by filtered cathodic vacuum arc at different hydrogen partial pressures (0.0008–0.5 mTorr) were studied in terms of their structure and properties. It is shown that a single Breit–Wigner–Fano (BWF) line shape is appropriate to fit the Raman spectra acquired from the ta-C:H films deposited at a hydrogen partial pressure of 0.0008–0.08 mTorr. However, the single BWF fit shows a residual near 1350 cm⁻¹ for the film deposited at a higher hydrogen partial pressure. This indicates the presence of graphitic clusters in the corresponding film. The data from infrared spectroscopy show that the hydrogen in the ta-C:H films is associated with triply bonded sp³, CH₂, sp² and CH₃, sp³ bonding. The absorption for the CH₃, sp³ is maximum for ta-C:H at a hydrogen partial pressure of 0.008 mTorr. It was observed that the film hardness and compressive stress are about 70 GPa and 12 GPa respectively corresponding to the hydrogen partial pressure from 0.0008 to 0.02 mTorr. When the hydrogen partial pressure further increases from 0.02 to 0.5 mTorr, the hardness and compressive stress decrease to about 50 GPa and 8 GPa respectively. The optical bandgap is about 3.0 eV for the ta-C:H film deposited at hydrogen partial pressure of 0.008 mTorr compared with 2.7 eV for the hydrogen free ta-C films. A lower intraband absorption coefficient of the ta-C:H sample (hydrogen partial pressure, 0.008 mTorr) indicates that the defect states are lower in this sample.

§1. INTRODUCTION

Tetrahedral amorphous carbon (ta-C) films mainly contain sp³ hybridized bonds (up to 88% sp³ bonded carbon) and more resemble diamond in their properties. They can be deposited by the vacuum arc, mass-selected ion beam and laser ablation techniques (Lifshitz 1996, Shi et al. 1996). The high sp³ content of ta-C films is desirable for tribological applications, such as high hardness and Young’s modulus, smooth surface, low friction and chemical inertness (McKenzie et al. 1991, Veerasamy et al. 1993). The optical properties such as a high optical bandgap (about 2.7 eV) and low absorption coefficient make ta-C films potentially useful for optical applications (Shi et al. 1998, Tay et al. 1997a). All the deposition techniques apply high-energy C⁺ species to deposit the ta-C films (Lifshitz et al. 1990). It
is now well established that, for the room-temperature deposition, the threshold energy is needed to penetrate to the subsurface and to facilitate the formation of the sp\(^3\) configuration (Lifshitz et al. 1990). Thus, the energy of the high-energy species is a crucial parameter for the formation of sp\(^3\) bonding (Shi et al. 1996, 1997, Tay et al. 1997b). The properties of ta-C films may be further influenced by the concurrent bombardment of high-energy particles from a secondary-ion source. For instance, the optical and electronic characterization of ta-C films concurrently bombarded by the high-energy N\(^+\) particles showed that the optical and electronic properties of these films are strongly dependent on the nitrogen partial pressure (Cheah et al. 1997). The effect of the Ar\(^+\)-ion energy on the surface morphology, optical and mechanical properties of the ta-C films was also investigated in a previous study (Cheah et al. 1998a).

In this investigation hydrogenated tetrahedral amorphous carbon (ta-C: H) films are deposited by a filtered cathodic vacuum arc (FCVA) system under different hydrogen partial pressures. Raman spectroscopy and Fourier transform infrared (FTIR) spectroscopy are used to investigate the structure of these films. The optical and mechanical properties of these films are related to their structure.

§ 2. EXPERIMENTAL DETAILS

2.1. Sample preparation

The ta-C films were deposited by a FCVA system similar to that described by Shi et al. (1996, 1997). During deposition, the C\(^+\) ions left the self-sustaining arc and were then accelerated by a dc bias to the out-of-sight silicon substrate. The arc current was kept constant at 60 A. A toroidal magnetic field was employed to steer the plasma. An electrical duct bias was also used. Films with thickness about 80 nm were deposited. The substrates used were polished Si (100) wafers. The ion beam sputtering (500 eV and 20 mA Ar\(^+\) ions) with a pre-fixed duration (2 min) was used to remove the native oxide layer on the silicon wafer surface. ta-C: H films were produced by introducing the hydrogen gas into the cathode arc region. The hydrogen gas was then dissociated and ionized by the high-energy ions and electrons of the plasma stream. The chamber background pressure was 5 \times 10^{-7} \text{ Torr}, and the hydrogen partial pressure was varied from 0.0008 to 0.5 mTorr for the deposition of ta-C: H films. All depositions were carried out at room temperature.

2.2. Film characterization

The film thickness was measured with a surface profiler (Tencor P10). The structure of the ta-C: H was determined by micro-Raman spectroscopy (Renishaw Ramascope) operated with a 514.5 nm Ar\(^+\) ion laser at 5 mW in the range 500–4000 cm\(^{-1}\) and FTIR spectroscopy (Perkin–Elmer Spectrum 2000) in the range 750–3500 cm\(^{-1}\). Surface morphology was determined by atomic force microscopy (AFM) operated in the tapping mode (Digital Instruments Dimension 3000). The hardness was determined using a nanoindenter (Nano Instruments Nano Indenter II). A surface profiler was also used to determine the internal stress of the films. The optical properties such as the optical bandgap and absorption spectra were measured with a phase modulated spectral ellipsometer (ISA Jobin Yvon UNISEL).
3. EXPERIMENTAL RESULTS

3.1. Structure of hydrogenated tetrahedral amorphous carbon

Raman spectroscopy is a widely used technique to characterize the amorphous carbon materials. The Raman spectra of the ta-C:H films deposited at different hydrogen partial pressures are shown in figure 1. In general, there are broad peaks at about 1560 cm\(^{-1}\). The Raman spectra were fitted with a Breit–Wigner–Fano (BWF) line shape (Yoshikawa, 1989, Prawer et al. 1996) described by

\[
I(\omega) = \frac{I_0[1 + 2(\omega - \omega_0)/\Gamma]^2}{1 + [2(\omega - \omega_0)/\Gamma]^2},
\]

where \(I(\omega)\) is the intensity as a function of frequency, \(I_0\) is the maximum peak intensity, and \(\omega_0\) and \(\Gamma\) are the peak position and full width at half-maximum (FWHM) respectively. \(Q\) is the BWF coupling coefficient, which essentially measures

\[
\begin{align*}
\text{Raman Shift (cm}^{-1}) & \\
1800 & 1700 & 1600 & 1500 & 1400 & 1300 & 1200 & 1100 \\
0.5 \text{ mTorr} & 0.08 \text{ mTorr} & 0.02 \text{ mTorr} & 0.008 \text{ mTorr} & 0.002 \text{ mTorr} & 0.0008 \text{ mTorr} \\
\end{align*}
\]

Figure 1. Raman spectra and BWF lineshape fits of ta-C:H films deposited at different hydrogen partial pressures (a.u., arbitrary units).
the 'skewness' of the peak (Prawer et al. 1996). Prawer et al. (1996) have demonstrated that the $Q$ factor is sensitive to the present of sp$^2$ bonding of the hydrogen free ta-C films. The vibration modes of sp$^3$ photons in the ta-C:H films do not tend to show up in the Raman spectra because of their low scattering cross-sections. The Raman spectrum monitors the state of sp$^2$-bonded structure within the sp$^3$ matrix. The BWF fitting of the Raman spectra ranging from 1100 to 1850 cm$^{-1}$ are shown in figure 1. The single BWF line shape is sufficient to fit the Raman spectra for the ta-C:H films deposited at a hydrogen partial pressure in the range 0.0008–0.08 mTorr. However, a single BWF fit could not be obtained from the film deposited at a hydrogen partial pressure of 0.5 mTorr. The single BWF fit shows a residual near 1350 cm$^{-1}$ which is associated with the disordered carbon (D peak). This implies the presence of graphitic clusters in the film at a higher hydrogen partial pressure. The existence of the D peak was also noted by Prawer et al. (1996) in the hydrogen-free diamond-like carbon films containing a high content of sp$^2$ bonding. Figure 2 shows the $Q$ factor as a function of hydrogen partial pressure. The $Q$ factor decreases from $-20$ to $-39$ with increasing hydrogen partial pressure from 0.0008 to 0.008 mTorr and then increases to $-3.4$ as the hydrogen partial pressure further increases to 0.5 mTorr. It appears that the Raman spectrum becomes more symmetrical at the hydrogen partial pressure of 0.008 mTorr. The BWF line position shows a minimum value for the ta-C:H film deposited at hydrogen partial pressure of 0.008 mTorr (figure 3).

The local bonding of carbon and hydrogen sites can be deduced from the infrared (IR) data. The variation in the intensity of these modes as a function of hydrogen partial pressure is shown in figure 4. Table 1 lists the IR peak assignments in molecules according to Dischler et al. (1983), McKenzie et al. (1983), Silva et al. (1992) and Lin-Vien et al. (1991) (see also Robertson (1986)). The intensity of the C–H sp$^1$ absorption at around 3200 cm$^{-1}$ increases as the hydrogen partial pressure increases. Silva et al. (1992) attributed this observation to the formation of a triple bond by the carbon atom with another carbon atom as in acetylene (H–C≡C–H) and the presence of an intermediate 'carbyne' phase between graphite and diamond. We
also found absorption for CH₃ sp³ bonding from 2960 to 2850 cm⁻¹. The absorption for CH₃ sp³ is a maximum for the ta-C:H with the hydrogen partial pressure of 0.008 mTorr. The absorption peaks appearing between 1800 and 1510 cm⁻¹ are assigned to olefinic or aromatic C=C stretches. Stretching modes characteristic of sp² hybridized CH₃ groups give rise to absorption peaks at 3080 and 3010 cm⁻¹.
Table 1. IR absorption bands observed in the ta-C:H films and their assignments according to Dischler et al. (1983), McKenzie et al. (1983), Silva et al. (1992) and Lin-Vien et al. (1991) (see also Robertson (1986)).

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>≈3200</td>
<td>=C≡C—H sp⁻¹</td>
</tr>
<tr>
<td>3080</td>
<td>CH₂ olefinic sp²</td>
</tr>
<tr>
<td>3010</td>
<td>CH olefinic sp²</td>
</tr>
<tr>
<td>2960</td>
<td>CH₃ sp³</td>
</tr>
<tr>
<td>2925</td>
<td>CH₂ sp³</td>
</tr>
<tr>
<td>2915</td>
<td>CH sp³</td>
</tr>
<tr>
<td>2850</td>
<td>CH₂ sp³</td>
</tr>
<tr>
<td>1800</td>
<td>C=C</td>
</tr>
<tr>
<td>1700</td>
<td>C=C</td>
</tr>
<tr>
<td>1680</td>
<td>C=C</td>
</tr>
<tr>
<td>1650</td>
<td>C=C</td>
</tr>
<tr>
<td>1620</td>
<td>C=C olefinic sp³</td>
</tr>
<tr>
<td>1590</td>
<td>C=C aromatic stretch sp²</td>
</tr>
<tr>
<td>1510</td>
<td>C=C aromatic stretch sp³</td>
</tr>
<tr>
<td>1430</td>
<td>C=C aromatic stretch sp³</td>
</tr>
<tr>
<td>1355</td>
<td>Amorphous C</td>
</tr>
<tr>
<td>1280</td>
<td>CH₂ (out-of-plane) sp²</td>
</tr>
<tr>
<td>1205</td>
<td>C—H aromatic ring (out of plane)</td>
</tr>
<tr>
<td>1150</td>
<td>Microcrystalline-amorphous diamond</td>
</tr>
<tr>
<td>990</td>
<td>—CH—CH₂</td>
</tr>
</tbody>
</table>

absorption peaks appearing at 1280, 1205 and 990 cm⁻¹ are attributed to CHₙ bending modes.

3.2. Properties of hydrogenated tetrahedral amorphous carbon

We observed a similar surface morphology (figure 5(a)) and roughness (rms of 0.14 nm) for the ta-C:H films deposited under the hydrogen partial pressure ranging from 0.0008 to 0.02 mTorr. The surface roughness (rms) measured by AFM increases from 0.15 to 0.23 nm when the hydrogen partial pressure increases from 0.05 to 0.5 mTorr. In comparison, the surface morphology of ta-C:H films obtained at 0.5 mTorr hydrogen partial pressure is shown in figure 5(b).

A continuous stiffness-measuring technique utilizing the Nano Indenter II was used to monitor continuously the film hardness and Young's modulus without the need for discrete loading and unloading cycles (Cheah et al. 1998a). For each film examined with the Nano Indenter II, several positions on the film were measured and the variation in the results gives the derivation. Figure 6 shows the dependence of the hardness on the hydrogen partial pressure. It is observed that the hardness is about 70 GPa as the hydrogen partial pressure changes from 0.0008 to 0.02 mTorr (figure 6). When the hydrogen partial pressure is further increased to 0.5 mTorr, the hardness decreases from about 70 to around 50 GPa.

Whenever thin films are employed, their mechanical stability and strong adhesion to the substrate are essential. A high internal stress in the ta-C films is induced during their growth. The thermal stress due to the difference between the coefficients of expansion of film and substrate can be negligible since the temperature during deposition was always controlled to be below 60°C. The stress has been determined by the radius of curvature technique which compares the radius curvature of the
Figure 5. Surface morphology of ta-C:H at hydrogen partial pressures of (a) 0.008 mTorr and (b) 0.5 mTorr.
silicon substrates and the substrates coated with the thin film. The stress is determined by Stoney’s equation

\[ \sigma_s = \frac{E_s}{6(1-\nu_s)} \frac{r_c^2}{t_c} \left( \frac{1}{R} - \frac{1}{R_0} \right), \]  

(2)

where \( E_s, \nu_s \) and \( t_s \) are Young’s modulus, Poisson’s ratio, and the thickness of the substrate respectively. \( R \) and \( R_0 \) are the radii of curvature of the film-substrate composite and the bare substrate respectively. For each film, the radius of curvature has average values measured at different locations. The internal stress was found to be compressive for the samples prepared under all deposition conditions. Figure 6 shows the dependence of the compressive stress on the hydrogen partial pressure. The compressive stress is about 12 GPa as the hydrogen partial pressure is varied from 0.0008 to 0.02 mTorr. When the hydrogen partial pressure is further increased from 0.02 to 0.5 mTorr, the compressive stress decreases from 12 to 8 GPa. A good correlation can be observed between the hardness and the compressive stress.

In contrast with crystalline materials, the optical absorption edge of amorphous semiconductors often varies significantly when subject to different preparation conditions. The optical absorption coefficient \( \alpha \) is related to the complex part \( \varepsilon_2 \) of dielectric constant by

\[ \varepsilon_2 = \frac{\alpha n_0 c \hbar}{E}, \]  

(3)

where \( n_0 \) is the refractive index, \( c \) is the speed of light, \( \hbar \) is the Planck constant and \( E \) is the photon energy. \( \varepsilon_2 \) of the ta-C:H films is extracted from the phase modulated spectroscopic ellipsometry measurement. The film structure model used for the simulation in the spectroscopic ellipsometry is based on a four-layer model (Shi et al. 1998, Tay et al. 1997a), and the ta-C:H layer is modelled by the optical dispersion relation obtained by Forouhi and Bloomer (FB) (1986) and the formulation given by Tauc and Menth (1972). There is no pronounced feature in the absorption edge, which can directly be related to an optical bandgap. Two popular methods can be
Figure 7. Absorption spectra for the ta-C:H films at different hydrogen partial pressures.

empirically used to define the bandgap.

(i) The optical bandgap corresponds to the photon energy with $\alpha = 10^4$ cm$^{-1}$.

(ii) With the transition between extended states the energy dependence of $\alpha$ often gives a linear dependence on the ‘Tauc plot’, written as (Shi et al. 1998)

$$\varepsilon_2(E) = \text{constant} \times \frac{(E - E_g)^2}{E^2},$$

where $E_g$ is the Tauc bandgap proposed on the assumption that the density of states has a parabolic-energy-band edge.

Figure 7 shows the absorption coefficient for ta-C:H samples deposited at different hydrogen partial pressures. Each amorphous material exhibits two regions in the optical absorption spectra: an interband region (slowly varying regime) usually for $\alpha \geq 10^4$ cm$^{-1}$, and an intraband region (shoulder regime) for $\alpha < 10^4$ cm$^{-1}$. The shape of the optical absorption edge is similar to the absorption edges found for hydrogenated amorphous silicon (Cody 1984). The observation concerns the overall trend of the absorption spectra for the investigated samples, that is the absorption values decreasing with the increasing hydrogen partial pressure from 0.0008 to 0.008 mTorr and then increasing with the increase in hydrogen partial pressure to 0.5 mTorr. Moreover the absorption edge is observed to shift to the highest energies, as the hydrogen partial pressure is 0.08 mTorr. The films become more transparent. As shown in figure 7, the absorption values in the shoulder region increase at the hydrogen partial pressure away from 0.008 mTorr.

The optical bandgap for the hydrogen-free ta-C is about 2.7 eV with the optimization of the C$^+$-ion energy (Shi et al. 1998). The optical bandgap increases from 2.7 to 3.0 eV as the hydrogen partial pressure increases from 0.0008 to 0.008 mTorr and decreases to 2.1 eV as the hydrogen partial pressure further increases to 0.5 mTorr, as shown in figure 8.
Figure 8. Optical bandgap as a function of the hydrogen partial pressure. The line is drawn as a guide to the eye.

§4. DISCUSSION

The structure of the ta-C:H films can be described in terms of their density-of-states spectrum. The $\sigma$ bonds form the skeleton of the network. They give rise to a valence band of filled bonding $\sigma$ states and a conduction band of empty antibonding $\sigma^*$ states, separated by a wide bandgap of at least 5 eV. The $\pi$ states are more weakly bound than the $\sigma$ states and therefore lie closer to the Fermi level $E_F$, than the $\sigma$ states do (Shi et al. 1998). Consequently, the filled $\pi$ states will form the valence band while the empty $\pi^*$ states form the conduction band, and they further determine the size of the gap. In the ta-C films, the majority atoms form the $sp^3$-bonded matrix and the remaining are $sp^2$ sites. It is possible to decouple the $\pi$ and $\sigma$ states and to treat their effects separately.

The $sp^3$-bonded matrix largely determines the mechanical properties such as the hardness and induced stress (Robertson 1992) of the films. The mechanical properties changed almost linearly with the $sp^3$ fraction and can be used as indicators of the $sp^3$ fraction in the hydrogen free ta-C films (Shi et al. 1997). It was observed that the hardness and compressive stress are about 70 GPa and 12 GPa respectively for the hydrogen partial pressure ranging from 0.0008 to 0.02 mTorr. This might imply almost no change for the $sp^3$ fraction in ta-C:H films. The amount of $\pi$ bonding clusters and the $sp^2$ ordering determine the Raman spectrum (Prawer et al. 1996), optical bandgap (Robertson 1995) and optical absorption edge (Robertson 1986). The optical bandgap has been correlated with the $sp^3$ fraction in hydrogen free ta-C films (Shi et al. 1998). The optical bandgap also changed almost linearly with the $sp^3$ fraction. However, in the ta-C:H films, the optical bandgap exhibits a different behaviour from the hardness and compressive stress and in general shows a maximum value of 3.0 eV for the ta-C:H film deposited at a hydrogen partial pressure of 0.008 mTorr. Davis et al. (1994) has demonstrated by electron-energy-loss spectroscopy (EELS) measurement that the ta-C:H films deposited at hydrogen flow rates of less than 0.05 sccm give rise to an increase in the film density and the $sp^3$ content. We believe that one way in which hydrogen might cause the increase in $sp^3$ bonding is that an $sp^2$ site bonded to three carbon atoms can convert to an $sp^3$ site bonded to...
three carbon atoms and one hydrogen atom. The FTIR measurement shows that the absorption for the CH$_n$ sp$^3$ is a maximum for the ta-C:H film deposited at a hydrogen partial pressure of 0.008 mTorr. Thus, it is believed that the increase in sp$^3$ bonding by hydrogen incorporation might be able to widen the optical bandgap by reducing the sp$^2$ bonding but the contribution to the compressive stress and hardness might not be significant.

In order to consider the effect of the localized valence band or defect states, in addition to the interband which is simulated by FB formulations, the localized states deep in the gap is formulated according to Tauc (Cody 1984):

$$N(Z) = \frac{\rho_D}{2} \delta(Z - E_d),$$

where $\rho_D$ is the volume density of deep states and $E_d$ can be obtained from the spectroscopic ellipsometry modelling (Cheah et al. 1998b). Equation (5) is used to simulate the optical absorption (intraband) shoulder region (Cheah et al. 1998b). As shown in figure 7, the intraband absorption coefficient increases at the hydrogen partial pressure away from 0.008 mTorr. Thus the localized states within the gap are a minimum for the ta-C:H under this partial pressure. The localized states are related to the disorder effects in $\pi$-electron systems (Robertson 1995). Therefore, the disorder in the $\pi$ bonds is observed to increase when the hydrogen partial pressure is away from 0.008 mTorr. When the small sp$^2$ clusters increase at the hydrogen partial pressure away from 0.008 mTorr, the Raman spectrum becomes more asymmetric and the $Q$ factor increases. It appears that the $Q$ factor arises from the localized modes, which is possibly attributed to the isolated sp$^2$-bonded atoms with little linkage between them. Therefore the $Q$ factor seems to be an indicator of isolated sp$^2$-bonded carbon atoms.

The hardness, compressive stress and optical bandgap of the ta-C:H films reduce significantly with increasing hydrogen partial pressure from 0.08 to 0.5 mTorr. The interband region of absorption spectra is observed to shift to the lowest energy, when the hydrogen partial pressure reaches 0.5 mTorr. The single BWF fit shows a residual near 1350 cm$^{-1}$ for the ta-C:H deposited under a hydrogen partial pressure of 0.5 mTorr. These imply the increase in graphitic (sp$^3$) clusters in the film at a higher hydrogen partial pressure. This is because, the higher the deposition pressure, the shorter is the C$^+$ free path length, which reduces the C$^+$ energy. As mentioned earlier in this paper, a threshold energy is needed to penetrate the subsurface and to facilitate the formation of the sp$^3$ configuration, and the C$^+$ energy is a crucial parameter for the formation of sp$^3$ bonding (Lifshitz et al. 1990). Therefore, if the C$^+$ energy is less than the threshold energy, an sp$^2$-rich film will probably be formed (Lifshitz et al. 1990).

§ 5. Conclusion

The effect of hydrogen gas on the structure and properties of ta-C:H films has been investigated. It is shown that a hydrogen partial pressure of 0.008 mTorr gives rise to a decrease in the sp$^2$ bonding in the sp$^3$ matrix. A more transparent film with a higher optical bandgap of about 3.0 eV can be obtained under this deposition condition and the hardness and compressive stress are around 70 GPa and 12 GPa respectively. A lower intraband absorption coefficient of the ta-C:H sample (hydrogen partial pressure, 0.008 mTorr) indicates that the defect states are lower in this
sample. The IR transmission data show that the absorption for the CH₃ sp³ is the maximum for the ta-C: H at a hydrogen partial pressure of 0.008 mTorr.

The hardness, compressive stress and optical bandgap of the ta-C: H films reduce significantly with increasing hydrogen partial pressure from 0.08 to 0.5 mTorr. The interband region of the absorption spectrum is observed to shift to the lowest energy when the hydrogen partial pressure reaches 0.5 mTorr. The single BWF fit to the Raman spectrum shows a residual near 1350 cm⁻¹ for ta-C: H deposited under a hydrogen partial pressure of 0.5 mTorr. This indicates that sp²-rich films are probably formed under this condition.

References


