Deposition of a-C:H Thin Films:
Material Characteristics and Plasma Chemistry
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Introduction
It is a known fact that a-C:H can be deposited at high rates by injecting acetylene (or other precursor gases) in an expanding thermal plasma created by means of a cascaded arc. Injected hydrocarbons are dissociated and react differently for various plasma parameters. Using Cavity Ring Down Spectroscopy (CRDS), CH and C2 radicals were identified and quantified in the gas phase above the substrate for different plasma parameters. Though not spectrally resolved, C2H is thought to be responsible for the broad band absorption around 270 nm. In this study, the gas phase absorption by C2, CH and C2H radicals are correlated with the material characteristics, that is to say index of refraction and growth rate as measured by in-situ real time ellipsometry. We will propose a model for the growth of a-C:H. It is established that C2H is a primary dissociation product of the C2H2 dissociation leading in some conditions to the creation of secondary products like CH and C2. Competition between these radicals explains the variations in material quality (in our case characterized by the index of refraction) and deposition rate. The best conditions are reached at high C2H flux. This coincides well with recent in-situ real time Fourier Transform Infrared absorption measurements of species present on the surface during growth.

Experiments and Discussion
Plasma is created in the cascaded arc at a pressure of around 0.4 bar. The DC current is applied between three cathodes and the arc nozzle. By variation of the arc current it is possible to change and control the amount of Ar ions emanating from the cascaded arc. Typical power is in the range of 1 to 5 kW. The plasma expands into a low-pressure vessel (typically 0.3 mbar) where supersonic and after a shock, subsonic expansion takes place. Into the plasma beam, acetylene is injected[1],[2] (Fig. 1). Because the temperature of electrons is low (around 0.3 eV in the expansion), electron driven processes may be neglected. Thus ion chemistry plays the most important role in the expansion zone. The proposed dissociation reactions are:

\[ \text{Ar}^+ + \text{C}_2\text{H}_2 \rightarrow \text{Ar} + \text{C}_2\text{H}_2^{+,.r,v} \quad k \approx 10^{-16} \text{ m}^3/\text{s} \quad \{1\} \]
\[ \text{e}^- + \text{C}_2\text{H}_2^{+,.r,v} \rightarrow \text{C}_2\text{H}^{r,.v} + \text{H}^+ \quad k \approx 3 \times 10^{-13} \text{ m}^3/\text{s} \quad \{2\} \]
\[ \rightarrow \text{CH}^* + \text{CH}^* \quad \{3\} \]
\[ \rightarrow \text{C}_2^* + \text{H} \quad \{4\} \]

(so-called primary reactions)

\[ \text{Ar}^+ + \text{C}_2\text{H}_2^{r,.v} \rightarrow \text{Ar} + \text{C}_2\text{H}_2^{+.r,v} \quad k = ? \quad \{5\} \]
\[ \text{C}_2\text{H}_2^{+.r,v} + \text{e}^- \rightarrow \text{CH}^* + \text{C} \quad k = ? \quad \{6\} \]
\[ \rightarrow \text{C}_2^* \quad \text{H} \quad \{7\} \]

(using second Ar$^+$ to secondary reactions)
Deposition takes place on the substrate at a distance of 60 cm from the cascaded arc. The substrate is crystalline silicon (111) and its temperature can be controlled and is kept at 250 °C. During deposition the vessel is pumped by two mechanical booster pumps (Edwards EH2600, 2600 m³ h⁻¹; Edwards EH500A, 500 m³ h⁻¹) and one rotary piston pump (Edwards, 240 m³ h⁻¹). A turbomolecular pump (Leybold Turbvac 1500, 90 m³ h⁻¹) and a rotary pump (Edwards, 40 m³ h⁻¹) are used to maintain a base pressure (10⁻⁶ mbar) before deposition.

Two experimental techniques are applied. First the Cavity Ring Down Spectroscopy [3],[4] is used for measuring concentrations of radicals 3 cm above the substrate. A schematical view of the experimental apparatus used for detection of CH radical is depicted in Fig. 2.

![Schematic view of a CRD experimental apparatus for CH radical detection](image)

The two high reflectivity plano-concave mirrors are placed 78 cm apart and create an optical cavity. The light used for CRD experiment is produced by a 10 Hz repetition rate Nd:YAG pumped dye laser (Spectra Physics DCR11/PDL2 combination) operating on Coumarin 440. Light pulses with length 5ns, with wavelength around 430 nm and with a bandwidth of about 0.4 cm⁻¹ are used. The light that leaks from the cavity is detected by a photomultiplier tube (Hamamatsu R928) connected to an oscilloscope (Tektronix TDS 340A, 8 bit, 350 MHz bandwidth, 500 Ms s⁻¹ sampling rate). A narrow band filter in front of the photomultiplier tube blocks the emission of the plasma. A LabView program controls the stepping of the dye laser and reads out the recorded transients via a GPIB interface. At every frequency typically 64 transients are averaged on the on-board 16-bit memory of the oscilloscope. The averaged transient, read out by the PC, is fitted with a standard least-squares fitting routine to an exponentially decaying function. The decay time \( \tau \) of the transient is stored together with the frequency of the light and can be written as:

\[
\tau(\nu) = \frac{d}{c(1 - R_{\text{eff}} + \sigma(\nu) \int_0^d n(x) dx)}
\]

where \( d \) is the length of the cavity, \( c \) is the speed of light, \( R_{\text{eff}} \) is the effective reflectivity of the mirrors, \( \sigma(\nu) \) the frequency-dependent cross-section of the absorbing species and \( \int_0^d n(x) dx \) the line-integrated number density. If the species is homogeneously distributed over a path length \( L \) in the optical cavity, the integral can be written as \( \sigma(\nu) nL \).
With CRDS CH and C₂ radicals were successfully identified. The spectrum of C₂H radical is still spectrally not resolved and only broad band absorption, which can be most probably ascribed to this radical, was observed. In Fig. 3 the example of absorption is shown as a function of acetylene flow at the arc current I_{arc} = 48 A.

![Figure 3: CRDS measurements of absorption of CH, C₂ radicals and absorption at 276 nm (“C₂H”) as a function of acetylene flow. The arc current is 48 A.](image1)

Second in-situ real time Ellipsometry was used to measure a refractive index (at 632.8 nm) and a growth rate of the films. The principle of ellipsometry is the measurement of the polarization change of light due to the reflection on a surface. This polarization can be expressed in terms of the ellipsometric parameters Ψ and Δ: \( R_p/R_s = \tan(\Psi) \exp(i\Delta) \), where \( R_p \) and \( R_s \) are the Fresnel reflection coefficients parallel and perpendicular, respectively, to the plane of incidence including interference effects\(^{[5],[6]}\). The Ψ-Δ plot is recorded during deposition and obtained curve is afterwards fitted with a simulation program. Fitting parameters are refractive index and extinction coefficient of the growing film. The thickness of the film can be deduced from the fitting curve too and because the deposition time is known it gives growth rate of the deposition. The value of refractive index for silicon substrate is taken from the literature and a thin film of native silicon oxide at the top of the substrate is taken into account. It is possible to simulate influence roughness at the top of the film. The measurements were performed using a homemade HeNe ellipsometer in the PCSA configuration. The results of measurements of refractive index and growth rate for the arc current I_{arc} = 48 A are presented in Fig. 4. From previous measurements the dependence of the hardness of the films on the growth rate (Fig.5) and on the infrared refractive index is known\(^{[7]}\).

![Figure 5: The hardness of the films as a function of the growth rate. Similar dependence of hardness is also observed for IR refractive index.](image2)

Thus with high acetylene flow most of the Ar ions are consumed in primary reactions (\{1\}-\{4\}). On the other hand with low acetylene flow there are enough Ar ions for primary and subsequently for secondary reactions (\{5\} – \{7\}).
From Fig. 3 it is clear that CH and C₂ radicals are produced mainly at low acetylene flow, thus in secondary reactions \{6\} and \{7\}. In the case of high acetylene flows amounts of CH and C₂ radicals in the reactor are below the detection limit (reactions \{3\} and \{4\} are negligible) and only the C₂H radical is produced via primary reactions \{1\} and \{2\}. The boundary value between these two regimes (only primary reactions x secondary reaction) is acetylene flow of about six sccs. This flow approximately matches with the argon ion flow from the cascaded arc\[2\].

The impact of different radicals in the beam on the quality of the film is seen in Fig. 4. At high acetylene flow films are hard (see growth rate and Fig. 5) and at low flow (smaller than six sccs of acetylene) are soft. From this the conclusion is drawn that the C₂H radical is responsible for hard amorphous DLC films and CH together with C₂ and most probably atomic hydrogen are responsible for soft polymerlike films. The measurements in high and low arc current show the same dependence only the boundary region is shifted to the higher acetylene flow, if the arc current is higher (more argon ions) and vice versa if the arc current is lower (less argon ions). This is in agreement with the proposed reaction scheme \{1\}–\{7\}.

References