Hard amorphous hydrogenated carbon films deposited from an expanding thermal plasma

HARD AMORPHOUS HYDROGENATED CARBON FILMS DEPOSITED FROM AN EXPANDING THERMAL PLASMA

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ABSTRACT

Diamondlike amorphous hydrogenated carbon is deposited from an expanding thermal argon/acetylene plasma. It is observed that the film quality improves with increasing deposition rate. To obtain the best material quality the admixed acetylene flow has to be of comparable magnitude as the argon ion flow from the plasma source (critical loading). A new method to determine the ion density in an argon/acetylene plasma, by probe measurements, is presented. They reveal that the deposition during critical loading is governed by radicals. It is suggested that acetylene is dissociated once and that the C_2H radical is formed dominantly.

INTRODUCTION

Amorphous hydrogenated carbon (a-C:H) is a non-crystalline form of carbon containing up to 40 % of hydrogen. It is generally produced via a Plasma Enhanced Chemical Vapour Deposition (PECVD) technique. The properties of the deposited a-C:H films can be adjusted by variation of the plasma deposition parameters and may vary from soft-polymerlike to hard-diamondlike. The C-C bonding types, i.e. the sp^2 and sp^3 bonds, determine the actual properties. The sp^3 bonds are responsible for the beneficial mechanical properties, which are for diamondlike material: high hardness (10-20 GPa) and high elastic modulus, low friction, chemical inertness and transparency to infrared light. The optical and electronic properties are mainly due to the sp^2 bonded carbon sites, which decrease the optical bandgap by enhanced cluster formation. Possible applications of a-C:H films are protective- and anti reflection coatings on glass plates in e.g. bar-code laser scanner devices or in flat panel displays [1].

The deposition of a-C:H is performed by several PECVD techniques [2]. All techniques have in common that a substrate bias of at least 50 V per deposited carbon atom is needed to obtain diamondlike material [1]. This ion bombardment results in the displacement of hydrogen and carbon atoms. The hydrogen recombines with atomic hydrogen from the plasma and desorbs. On the surface dangling bonds are created. These may either recombine with each other or bond to hydrocarbon radicals from the plasma. Both effects result in more cross-linking and denser diamondlike material [3]. An interesting question now is whether this ion energy is always necessary to obtain diamondlike properties or that plasma-surface chemistry also could play a role. In e.g. the synthesis of diamond, atomic hydrogen from the plasma passivates and etches hydrogen and sp^2 bonded carbon from the growing film and is responsible for the diamond nature of the deposited films. In this paper the quality of diamondlike a-C:H will be discussed when films are grown without additional substrate bias. The quality will be related to the plasma chemistry, i.e. the dissociation mechanism of acetylene molecules will be described.

a-C:H FILM DEPOSITION

Deposition of the a-C:H films is performed with an expanding thermal plasma set-up. In a cascaded arc plasma source a flowing argon plasma (flow = 100 standard cm^3/s (scc/s); pressure

287

≈ 0.5 bar; electron density $\approx 10^{22}$ m^{-3}; electron temperature ≈ 1 eV) is created. The plasma expands into a vacuum chamber, which is at low pressure (0.25 mbar). The electron density and temperature in pure argon decrease to $\approx 10^{19}$ m^{-3} and ≈ 0.2 eV, respectively. In the expansion zone acetylene is admixed. The films are deposited on crystalline silicon and glass substrates, mounted on a grounded holder, at low temperature (≤ 100 °C); thicknesses are about 2 μm. Due to the low electron temperature (≈ 0.2 eV) the sheath potential is low, i.e. on the order of 1 V, and thus deposition takes place without additional ion acceleration. Two process parameters are varied. The electrical current through the plasma source is changed from 22 to 88 A. This implies that the ionisation degree of the argon flow varies from 5 to 25 %. Also the admixed acetylene flow is varied from 2 to 20 scc/s. An extensive description of the set-up is given elsewhere [4].

RESULTS

The deposited films are characterised by its hardness and infrared refractive index. Via Nano-indentation the hardness is determined. The refractive index and thickness of the films are obtained via infrared absorption spectroscopy. In Figure 1a the hardness, which is a measure for the film quality, is given as a function of the infrared refractive index. It clearly correlates with the infrared refractive index. The film quality changes from soft-polymerlike (4 GPa), at low refractive index, to hard-diamondlike (13 GPa), at higher indices. The maximum observed hardness of about 13 GPa is in the range known for diamondlike material [1]. However, note that our diamondlike properties are obtained without applying a substrate bias. At the best film quality other properties like the hydrogen content, carbon-hydrogen bonding structure and mass density are also found to be in the diamondlike material range [5,6].

As is obvious from Figure 1a film quality improvement is equivalent to maximising the refractive index. In Figure 1b the refractive index is given as a function of the process parameters varied, i.e. the arc current and admixed acetylene flow. For each arc current applied a similar trend is observed in the refractive index with respect to the acetylene flow: with increasing acetylene flow the refractive index first increases until a maximum is reached, then a decrease occurs. From Langmuir probe measurements in a pure argon plasma the argon ion density as a function of the radial position is determined for various arc currents. These densities are transformed into ion flows by integrating over the beam area assuming a beam velocity of 1000 m/s. For arc currents of 22, 48 and 75 A argon ion flows are calculated of about 5, 12 and 25 scc/s. The maximum in the refractive index is observed at those acetylene flows which are of
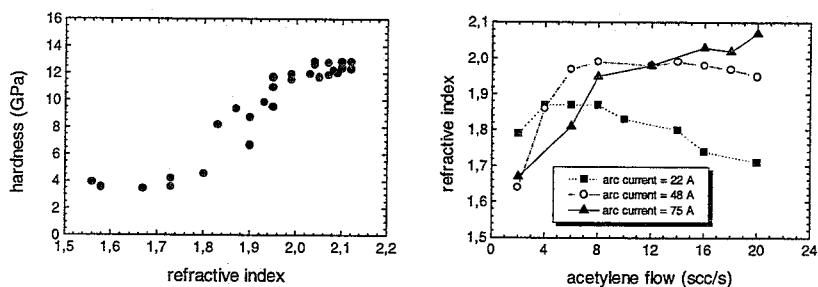

Figure 1 :   a.)   The film hardness vs. the refractive index.

b.)   The refractive index vs. the admixed acetylene flow at various arc currents.

the same magnitude as the argon ion flows appearing from the arc source. For the arc current of 75 A the maximum is not yet observed as the admixed acetylene flow is lower than 25 scc/s.

To understand the observed behaviour of the refractive index under plasma variation, the plasma chemistry has to be studied. Dissociation of the acetylene does not take place via electron induced processes as the electron temperature is too low (≈ 0.2 eV). Also dissociation by heating is excluded as it is slower than the here presented dissociation mechanism. The acetylene is dissociated in two steps. First a charge transfer reaction occurs between an argon ion and an acetylene molecule:

$$Ar^+ + C_2H_2 \rightarrow Ar + C_2H_2^+ \tag{1}$$

at a rate $k_{ce} \approx 10^{-16}$ m^{3}s^{-1} [7]. The formed acetylene ion rapidly recombines dissociatively with an electron:

$$
\begin{aligned}
C_2H_2^+ + e^- &\rightarrow C_2H + H \\
&\rightarrow CH + CH \\
&\rightarrow C_2 + H_2
\end{aligned} \tag{2}
$$
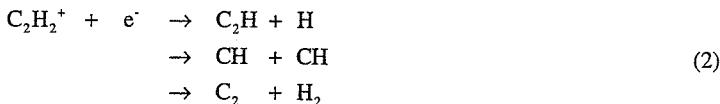
at a rate $k_{dr} \approx 3 \cdot 10^{-13}$ m^{3}s^{-1} [8]. In this recombination process many different radicals are formed. Depending on the argon ion density the formed radicals can be ionised and dissociated further. Note that the ionisation degree decreases as a result of the proposed dissociation mechanism.

In literature no branching ratios are presently known for the various reaction paths in Eq. (2). From emission spectroscopy it is determined that the creation of C_2H is far dominant. Von Keudell [9] has shown that this radical plays an important role in the deposition of diamondlike a-C:H from an argon/acetylene plasma. The C_2H radical is chemisorbed on the growing surface in an sp^2 hybridised bond, with each carbon atom either bonded to a hydrogen or carbon atom or containing a dangling bond. Impact of energetic ions or hydrogen atoms transform the layer into its diamondlike form. In our plasma hydrogen atoms are created too during the dissociation of acetylene into the C_2H radical. These hydrogen atoms can either passivate dangling bonds on the surface or abstract hydrogen from the surface, depending on the substrate temperature. The influence of the formed hydrogen molecules on the plasma will be discussed later. No energetic ions are available for surface modification as there is no substrate biasing. Nevertheless, diamondlike a-C:H is obtained. This suggests that plasma-surface interactions may be as important as surface modification by energetic ion bombardment.

Qualitatively, the effect of arc current variation and acetylene flow admixture on the plasma composition is best explained from Eq. (1) and (2). When at a fixed arc current the acetylene flow is smaller than the argon ion flow from the source (underloading), enhanced dissociation of the radicals formed in Eq. (2) occurs. When the acetylene flow is equal to the argon ion flow from the source (critical loading), the acetylene can be dissociated only once, as for each dissociation step one argon ion is needed. Further increment of the acetylene flow (overloading) results in non-dissociated acetylene as there are not enough ions for full dissociation. Therefore, Figure 1b suggests that critical loading of the argon plasma with acetylene is necessary for the highest film quality and results in a one step dissociation. Both underloading and overloading proof to be unbeneficial for film quality.

As is observed from Eq. (1) and (2) the ion density decreases with increasing acetylene flow. To determine the ion density Langmuir probe experiments [10] have been performed. Measuring complete probe characteristics (probe current vs. probe voltage) in an argon/acetylene

plasma by the method described by Flender at al. [11] is in our case not possible. On the probe an insulating film is grown at a high deposition rate (up to 75 nm/s), which changes the surface conditions continuously.

We have developed a new procedure to determine the argon ion density. We measure the ion saturation current (I_{ion}) which is related to the ion density (n_{ion}) by

$$I_{ion} \propto n_{ion} c_s.$$

(3)

In this equation c_s is the Bohm velocity which depends on the electron temperature and the mass of the collected ions. In our plasma the ion saturation current is dominated by argon ions as molecular hydrocarbon ions recombine fast into hydrocarbon radicals. By measuring the ion saturation current as a function of time we obtain time dependent information on the ion density. However, the measured current is influenced by variations in the probe conditions due to deposition of a-C:H.

In Figure 2 a typical example of the measured absolute ion saturation current as a function of time is given. At t_1 a pure argon plasma is ignited and a constant ion current is measured. At t_2 acetylene is admixed, which immediately decreases the current as ions are consumed by reaction Eq. (1). Although the plasma does not change, the probe current is observed to increase, which is caused by a change of the probe surface by deposition of a-C:H. At t_3 the acetylene is switched off and the ion saturation current increases. The plasma composition is the same as at t_1 but the measured ion saturation current is larger. This is due to the a-C:H film on the probe surface. It is observed that the ion current increases slightly with time. This might be due to changing probe conditions by either heating or modification by the argon plasma. Admixture of oxygen to the plasma (t_4) cleans the probe. When the current is constant, oxygen is switched off (t_5) and the ion saturation current in pure argon is again the same as at t_1. This demonstrates that the deposition of a-C:H does not change the probe irreversibly.

The argon ion density in an argon/acetylene environment is determined from the ion saturation current in argon/acetylene and pure argon under equal probe conditions: this is the case at t_3. In argon/acetylene the current is easily read from the measured current - time graph as the last current before switching off acetylene. As the current in a pure argon plasma is not immediately constant at t_3 a linear extrapolation to this point is performed. The ratio of the probe current for the argon/acetylene plasma and the pure argon plasma at t_3 is a measure for the argon ion density in an argon/acetylene environment. Multiplication of this ratio with the argon ion density in a pure argon plasma reveals the ion density in the argon/acetylene environment. The
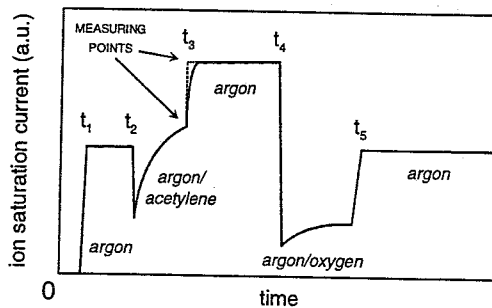

Figure 2 : The measured ion saturation current vs. time for various plasma conditions (t_1: argon; t_2: argon/acetylene; t_3: argon; t_4: argon/oxygen; t_5: argon).

only assumption made is that the electron temperature is constant in all cases and that only argon ions are collected.

Via the described procedure the argon ion density is determined as a function of the admixed acetylene flow, for one specific arc current (48 A). The probe is positioned half way the expansion vessel at 30 cm from the arc exit and at $x = 25$ cm from the acetylene injection point. The result is shown in Figure 3. The argon ion density decreases from 2×10^{19} m^{-3} to 2×10^{18} m^{-3} when the admixed acetylene flow increases from 0 to 10 scc/s. An approximation for the description of the argon ion density with varying acetylene density is given by an exponential decay:

$$ n_{ion}(n_{ac}) = n_{ion}(0) \exp\left[-\frac{k_{ce}x}{v} n_{ac}\right] \tag{4} $$

with n_{ion} the ion density and n_{ac} the acetylene density, which are calculated from their respective partial pressures; v is the beam velocity. The acetylene flow at which the ion density has decreased to 1/e times the original value, i.e. 7.4×10^{18} m^{-3}, is calculated from Eq (4) and is about 6 scc/s (a typical beam velocity of 1000 m/s is assumed). Comparing this result to Figure 3 the ion density is found to be about 7×10^{18} m^{-3} at an admixed acetylene flow of 6 scc/s.

The mean free path (v/nk_{ce}) for the acetylene molecules to react with argon ions for critical loading is about 20 cm ($v \approx 1000$ m/s, $n_{ion} = 6 \times 10^{19}$ m^{-3} at an acetylene flow of 12 scc/s). From Figure 3 it is determined that the ion density at 25 cm from the acetylene injection point has decreased more than 90 % for an acetylene flow of 12 scc/s. Enhanced dissociation of the formed radicals now is unlikely as no dissociative capacity is available anymore. This supports the suggestion that the acetylene needs to be dissociated once and that the formed radicals are responsible for good diamondlike material.

In the reasoning above it is assumed that only reactions with acetylene decrease the ion density. However, also molecular hydrogen, which is formed by abstraction of hydrogen from the growing film or via recombination of atomic hydrogen in the plasma with wall adsorbed hydrogen, can decrease the ion density. If this would be a dominant process, no full dissociation of acetylene occurs. But in this case the amount of hydrogen molecules formed is too low to explain the loss in ionisation observed in Figure 3. This observation supports the statement in [6] that full dissociation of acetylene occurs and that the formed C_2H radicals have a sticking probability of about 5 %.

More support for the suggestion that no surface modification by energetic ions is needed for the deposition of diamondlike a-C:H is obtained from a growth rate analysis. At increased
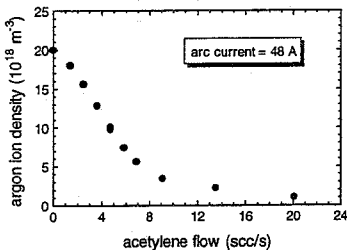

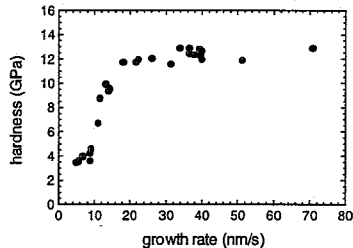Figure 3 : The argon ion density vs. the admixed acetylene flow.

Figure 4 :   The hardness of the a-C:H films vs. the growth rate.

acetylene admixture the growth rate is observed to increase. The ion density then decreases. In Figure 4 the quality of the a-C:H material, given by its hardness, is plotted as a function of the growth rate. The quality is found to increase at increasing growth rate. Especially remarkable is that the highest rates are obtained at the highest acetylene flows and the lowest ion densities. Growth rate increment just means an increment of the C_2H radical flux towards the growing film surface, which only influences the film quality marginally. Currently, a maximum growth rate of 75 nm/s is obtained.

CONCLUSIONS

The use of an expanding thermal plasma allows the deposition of high quality diamondlike a-C:H. It is observed that increment of the deposition rate is accompanied by quality improvement. The best diamondlike a-C:H material quality is obtained when the argon plasma is critically loaded with acetylene. Then a one step dissociation of acetylene occurs. Under these conditions primarily C_2H is formed and is considered to determine the film quality. The plasma-surface chemistry is suggested to determine the film quality which implies that no substrate bias is needed for surface modification.

ACKNOWLEDGEMENT

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