Argon ion-induced dissociation of acetylene in an expanding Ar/C2H2 plasma

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Hydrogenated amorphous carbon (a-C:H) is well known for its favorable properties like high hardness, chemical inertness, and infrared transparency. \(^1\)\(^2\) These properties make the material very suitable for use as a protective coating on optical devices, e.g., bar-code laser scanners and flat panel displays, and as a wear resistant coating. For industrial applications however, high growth rates are desirable. It was shown in previous work \(^3\) that with an expanding thermal argon plasma into which acetylene (C\(_2\)H\(_2\)) is injected downstream, a-C:H films can be deposited at rates as high as 70 nm s\(^{-1}\). Moreover, it was demonstrated that the quality in terms of hardness and infrared refractive index increases with increasing growth rate. \(^3\) The maximum hardness obtained is approximately 14 GPa. \(^3\) In earlier studies, it was argued that the dissociation of acetylene is ion induced since the electron temperature in the expansion is too low (<0.3 eV) for significant electron-induced dissociation or ionization. \(^3\) Note that this is a main difference with most other remote plasma deposition sources in which the dissociation of the precursor gases is by electron impact. The proposed dissociation mechanism consists of a charge exchange reaction of an argon ion with an acetylene molecule directly followed by the dissociative recombination of the (rovibrationally excited) acetylene ion with an electron, i.e.,

\[
\text{Ar}^+ + \text{C}_2\text{H}_2 \rightarrow \text{Ar} + \text{C}_2\text{H}_2^{+.,.v}.
\]

\(^{(1a)}\)

\[
\text{C}_2\text{H}_2^{+.,.v} + e \rightarrow \text{products}.
\]

\(^{(1b)}\)

The typical rate \(k_{\text{CE}}\) for the charge exchange reaction \((1a)\) is \(10^{-16}\) m\(^3\) s\(^{-1}\), a value close to the Langevin limit. \(^4\) The overall rate coefficient \(k_{\text{DR}}\) for the dissociative recombination reaction \((1b)\) was measured to be around \(3 \times 10^{-13}\) m\(^3\) s\(^{-1}\). \(^5\) The dissociation rate will be limited by the lowest rate, which is the rate \(k_{\text{CE}}\) for the charge exchange reaction \((1a)\). The cross sections for electron-induced ionization or dissociation of acetylene are in the same order of magnitude (~\(10^{-20}\) m\(^2\)) as the cross section for the charge exchange reaction \((1a)\), but have a typical threshold at an electron energy of \(\approx 10\) eV. \(^6\) Therefore, the dissociation rate of these processes will be considerably smaller than \(k_{\text{CE}}\) at mean electron energies below this threshold. The ion-induced dissociation will be thus much more effective than electron-induced processes, especially at lower electron temperatures. Results from particle flow rate and arc current studies \(^7\) and recently also from cavity ringdown spectroscopy and optical emission spectroscopy measurements \(^8\) suggest that the C\(_2\)H radical and atomic hydrogen are the dominant dissociation products in reaction \((1b)\). Till now the dissociation products could not be directly measured, and the suggested dissociation mechanism and predominant production of C\(_2\)H and H radicals downstream of the arc source could not be verified. Using Langmuir probe and mass spectrometry measurements the plasma chemistry of the expanding Ar/C\(_2\)H\(_2\) plasma can be addressed in more detail.

The plasma deposition setup is extensively described elsewhere. \(^3\) It consists of a vertically positioned, cylindrical expansion vessel (diameter 36 cm, length 65 cm) at low pressure (25–30 Pa). In a cascaded arc, which is mounted on top of the vessel on a moveable holder, a thermal argon plasma is generated. Typical parameters in the arc are a pressure of 40–60 kPa, an arc current \(I_{\text{arc}}\) of 30–90 A (1–5 kW), and an argon particle flow rate \(\Phi_{\text{Ar}}\) of 50–100 sccs. The argon plasma expands into the low-pressure vessel where 0–20 sccs of acetylene is supersonically injected downstream by means of a gas injection ring. The produced radicals are transported with the flowing plasma towards the temperature-controlled substrate holder, which is positioned at 60 cm from the arc outlet. The Langmuir probe measurements were performed in a pure argon plasma at approximately 30 cm from the arc exit. The cylindrical Langmuir probe with a length of 0.5 cm and a radius of 0.1 mm is made out of tungsten and can be moved in radial direction to obtain radial profiles of the ion flux passing and the plasma beam area. The probe characteristic is analyzed using conventional methods. \(^9\) The deposition rate is measured \textit{in situ}\(^9\).
FIG. 1. Depletion of acetylene as a function of the acetylene particle flow injected for different arc currents. Plasma settings: \( \Phi_{Ar} = 100 \text{ sccs, } p = 25 \text{ Pa.} \) Solid lines are fits using Eq. (4).

This means that if the reaction time \( t \) is long enough and if the initial ion particle flow rate is larger than the injected acetylene particle flow rate full consumption \( (D=1) \) can be reached. In Fig. 1 the solid lines represent the fits of the consumption of acetylene following from Eq. (4). The measurement at 89.3 A was fitted using Eq. (4), varying \( k_{Qt} \) and \( \Phi_{Ar+}(t_0) \). For the other arc current settings, only \( \Phi_{Ar+}(t_0) \) was varied keeping the value for \( k_{Qt} \) fixed at the value found at \( I_{arc} = 89.3 \text{ A.} \) The value obtained for \( k_{Qt} \) is 2.8 \( \times 10^{-19} \text{ m}^3 \). At a velocity of 1000 m s\(^{-1}\) a distance of 0.65 m from the arc exit to the mass spectrometer, and a (constant) plasma beam radius of 0.1 m, this corresponds to a \( k_{CE} \) of \( 4.3 \times 10^{-16} \text{ m}^3 \text{s}^{-1}. \) The value for \( k_{CE} \) is in good agreement with the typical values \((\approx 10^{-14} \text{ m}^3 \text{s}^{-1})\) reported for the charge exchange reaction of Ar\(^+\) and C\(_2\)H\(_2\).\(^{11}\) suggesting that the plasma chemistry is indeed dominated by this reaction.

The expanding thermal plasma is a remote plasma which means that the downstream region is decoupled from the arc source due to the large pressure difference of approximately
In conclusion, mass spectrometry and Langmuir probe measurements clearly demonstrate that in an expanding Ar/C$_2$H$_2$ plasma acetylene is consumed by argon ions and electrons emanating from the arc. The good agreement found between a simple model describing the consumption of acetylene and independent measurements with a Langmuir probe points to a one-to-one reaction between argon ions and acetylene molecules. Under certain conditions, a dissociation degree of 100% was reached, indicating that the ion-induced dissociation is more efficient than dissociation by electron impact, for which full dissociation has never been reported. The fact that the growth rate is proportional to the depletion shows that the dissociation products are also very efficiently used in the deposition.

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