

# Argon ion-induced dissociation of acetylene in an expanding Ar/C<sub>2</sub>H<sub>2</sub> plasma

**Citation for published version (APA):**

Graaf, de, A., Hest, van, M. F. A. M., Sanden, van de, M. C. M., Letourneur, K. G. Y., & Schram, D. C. (1999). Argon ion-induced dissociation of acetylene in an expanding Ar/C<sub>2</sub>H<sub>2</sub> plasma. *Applied Physics Letters*, 74(20), 2927-2929. <https://doi.org/10.1063/1.123968>

**DOI:**

[10.1063/1.123968](https://doi.org/10.1063/1.123968)

**Document status and date:**

Published: 01/01/1999

**Document Version:**

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

**Please check the document version of this publication:**

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

**General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

[www.tue.nl/taverne](http://www.tue.nl/taverne)

**Take down policy**

If you believe that this document breaches copyright please contact us at:

[openaccess@tue.nl](mailto:openaccess@tue.nl)

providing details and we will investigate your claim.

## Argon ion-induced dissociation of acetylene in an expanding Ar/C<sub>2</sub>H<sub>2</sub> plasma

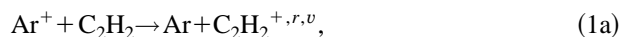
A. de Graaf,<sup>a)</sup> M. F. A. M. van Hest, M. C. M. van de Sanden,<sup>b)</sup> K. G. Y. Letourneur, and D. C. Schram

*Department of Applied Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands*

(Received 23 November 1998; accepted for publication 17 March 1999)

Mass spectrometric and Langmuir probe measurements reveal that the plasma chemistry of an expanding Ar/C<sub>2</sub>H<sub>2</sub> plasma which is used for deposition of hydrogenated amorphous carbon is dominated by argon ion-induced dissociation of the precursor gas. The ion-induced dissociation is very efficient leading to complete depletion under certain conditions. The ion fluence as determined from modeling the mass spectrometry results is in good agreement with Langmuir probe measurements suggesting a one-to-one relation between the argon ion and acetylene consumption. The good correlation found between the growth rate and the acetylene consumption rate expresses the efficient use of the dissociation products. © 1999 American Institute of Physics. [S0003-6951(99)02820-X]

Hydrogenated amorphous carbon (*a*-C:H) is well known for its favorable properties like high hardness, chemical inertness, and infrared transparency.<sup>1,2</sup> 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<sup>3</sup> that with an expanding thermal argon plasma into which acetylene (C<sub>2</sub>H<sub>2</sub>) is injected downstream, *a*-C:H films can be deposited at rates as high as 70 nm s<sup>-1</sup>. Moreover, it was demonstrated that the quality in terms of hardness and infrared refractive index increases with increasing growth rate.<sup>3</sup> The maximum hardness obtained is approximately 14 GPa.<sup>3</sup> 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.<sup>3</sup> 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.,



The typical rate  $k_{\text{CE}}$  for the charge exchange reaction (1a) is  $10^{-16} \text{ m}^3 \text{ s}^{-1}$ , a value close to the Langevin limit.<sup>4</sup> The overall rate coefficient  $k_{\text{DR}}$  for the dissociative recombination reaction (1b) was measured to be around  $3 \times 10^{-13} \text{ m}^3 \text{ s}^{-1}$ .<sup>5</sup> 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 ( $\sim 10^{-20} \text{ m}^2$ ) as the cross section for the charge exchange reaction (1a), but have a typical threshold at an electron energy of  $\approx 10 \text{ eV}$ .<sup>6</sup> 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<sup>7</sup> and recently also from cavity ringdown spectroscopy and optical emission spectroscopy measurements<sup>8</sup> suggest that the C<sub>2</sub>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<sub>2</sub>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<sub>2</sub>H<sub>2</sub> plasma can be addressed in more detail.

The plasma deposition setup is extensively described elsewhere.<sup>3</sup> 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.<sup>9</sup> The deposition rate is measured *in situ*

<sup>a)</sup>Electronic mail: a.degraaf@phys.tue.nl

<sup>b)</sup>Corresponding author; electronic mail: m.c.m.v.d.sanden@phys.tue.nl

with a home-built HeNe (632.8 nm) rotating compensator ellipsometer. A residual gas analyzer (K. J. Lesker Company, AccuQuad 200D) samples background gas approximately at the position of the substrate holder through a 30  $\mu\text{m}$  pinhole. The mass peak at 26 amu was used as a fingerprint for the presence of  $\text{C}_2\text{H}_2$  gas in the background. The full mass spectrum in the regions 12–16 and 24–30 amu was analyzed using measured cracking patterns of  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$  to correct for the contribution of ethene ( $\text{C}_2\text{H}_4$ ) and ethane ( $\text{C}_2\text{H}_6$ ). For the conditions presented here, the contribution of ethene and ethane to the signal was smaller than 4%. These results were independently confirmed by gas phase infrared absorption spectroscopy.<sup>10</sup> From the mass spectrometer data, the consumption of the precursor gas can be calculated. The depletion  $D$  of acetylene is defined as

$$D = 1 - \frac{I_{\text{on}}(m/Z=26)}{I_{\text{off}}(m/Z=26)}, \quad (2)$$

where  $I_{\text{on}}(m/Z=26)$  and  $I_{\text{off}}(m/Z=26)$  are the signals at 26 amu in plasma on respectively plasma off situation. It was verified that the gas temperature in the background does not change considerably when the plasma is switched on, which is logical considering the long residence time in the background. Therefore, no temperature correction is made in Eq. (2). Because the precursor injection is supersonic and the residence time of acetylene ( $\sim 0.4$  s) is much longer than its diffusion time from wall to wall ( $\sim 0.01$  s), both in the plasma off and plasma on situation the reactor is expected to be fully mixed. In this case the depletion as defined in Eq. (2) is a good measure for the acetylene consumption.

As can be seen in Fig. 1, where the depletion is shown as function of the injected acetylene particle flow rate for different arc currents, the depletion increases with decreasing acetylene particle flow rate and increasing arc current (higher ion and electron fluence). Notice that under high reactivity conditions the depletion is complete, indicating a very efficient dissociation mechanism and a good mixing. The consumption of acetylene at the position of the mass spectrometer can be described by a simple zero-dimensional model assuming that the acetylene molecules and argon ions are

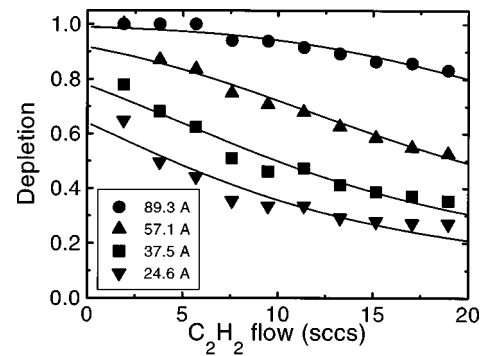


FIG. 1. Depletion of acetylene as a function of the acetylene particle flow injected for different arc currents. Plasma settings:  $\Phi_{\text{Ar}}=100$  sccs,  $p=25$  Pa. Solid lines are fits using Eq. (4).

only consumed by the charge exchange and subsequent dissociative recombination reaction (1a) and (1b), i.e.,

$$\frac{\partial}{\partial t} \Phi_{\text{C}_2\text{H}_2}(t) = \frac{\partial}{\partial t} \Phi_{\text{Ar}^+}(t) = -k_{\Phi} \Phi_{\text{C}_2\text{H}_2}(t) \Phi_{\text{Ar}^+}(t). \quad (3)$$

Here  $\Phi_{\text{C}_2\text{H}_2}(t)$  is the acetylene particle flow rate and  $\Phi_{\text{Ar}^+}(t)$  the ion particle flow rate. To compare  $k_{\Phi}$  to the (densities balance) dissociation reaction rate  $k_{\text{CE}}$  following from Eqs. (1a) and (1b), i.e.,  $(\partial/\partial t)n_{\text{C}_2\text{H}_2}(t) = -k_{\text{CE}}n_{\text{C}_2\text{H}_2}(t)n_{\text{Ar}^+}(t)$ , the diffusion profile and the directed velocity of both species should also be considered. Assuming that both species have the same constant beam area  $A$  and forward velocity  $v$  and that the gases in the vessel are well mixed, the particle flow rate  $\Phi$  can be related to the density  $n$  by the relation  $\Phi = nvA$ . The equation above can then be rewritten as:  $(\partial/\partial t)\Phi_{\text{C}_2\text{H}_2}(t) = -(k_{\text{CE}}/vA)\Phi_{\text{C}_2\text{H}_2}(t)\Phi_{\text{Ar}^+}(t)$ , which relates  $k_{\Phi}$  of Eq. (3) to  $k_{\text{CE}}$  by  $k_{\Phi} = k_{\text{CE}}/vA$ . The radicals formed in the dissociative recombination reaction (1b) may either deposit on the walls, or react in the gas phase and at the walls. Their lifetime is generally much shorter than the residence time of the gases in the expansion vessel (typically 0.4 s), and therefore the residence time does not need to be included in the model. The time-dependent solution of Eq. (3) can be expressed in the initial particle flow rates of argon ions  $\Phi_{\text{Ar}^+}(t_0)$  and acetylene  $\Phi_{\text{C}_2\text{H}_2}(t_0)$  injected:

$$\Phi_{\text{C}_2\text{H}_2}(t) = \frac{\Phi_{\text{Ar}^+}(t_0) - \Phi_{\text{C}_2\text{H}_2}(t_0)}{(\Phi_{\text{Ar}^+}(t_0)/\Phi_{\text{C}_2\text{H}_2}(t_0)\exp[(\Phi_{\text{Ar}^+}(t_0) - \Phi_{\text{C}_2\text{H}_2}(t_0)k_{\Phi}t]) - 1}. \quad (4)$$

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  $k_{\Phi}t$  and  $\Phi_{\text{Ar}^+}(t_0)$ . For the other arc current settings, only  $\Phi_{\text{Ar}^+}(t_0)$  was varied keeping the value for  $k_{\Phi}t$  fixed at the value found at  $I_{\text{arc}}=89.3$  A. The value obtained for  $k_{\Phi}t$  is  $2.8 \times 10^{-19} \text{ m}^3$ . At a velocity of  $1000 \text{ m s}^{-1}$ ,<sup>11</sup> 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  $k_{\text{CE}}$  of  $4.3 \times 10^{-16} \text{ m}^3 \cdot \text{s}^{-1}$ . The value for  $k_{\text{CE}}$  is in good agreement with the typical values ( $\approx 10^{-16} \text{ m}^3 \text{ s}^{-1}$ ) reported for the charge exchange reaction of  $\text{Ar}^+$  and  $\text{C}_2\text{H}_2$  (1a),<sup>4</sup> 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

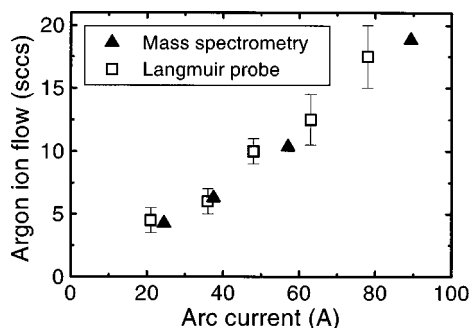


FIG. 2. Ion particle flow emanating from the arc as function of the arc current as obtained from Langmuir probe measurements and from modeling the mass spectrometry results. Plasma settings:  $\Phi_{Ar}=100$  scs,  $p=25$  Pa.

$10^4$  Pa.<sup>12</sup> Therefore, the chemical reactivity emanating from the arc can be characterized by measuring the ion or equally electron particle flow rate in a *pure* argon plasma, i.e., without  $C_2H_2$  injection. Figure 2 shows the ion fluence (expressed in equivalent particle flow rate) as function of the arc current at 30 cm from the arc exit. It was determined from the radial integrated ion density profile measured with a Langmuir probe assuming a directed velocity of approximately  $1000$  m s<sup>-1</sup> for the ions.<sup>11</sup> As can be seen, at 50 A about 10% of the total injected argon particle flow rate is ionized, which is in good agreement with arc modeling.<sup>13</sup> In Fig. 2 also the results for  $\Phi_{Ar^+}(t_0)$  obtained from the fits of Eq. (4) are shown. The good agreement strongly suggests that the proposed acetylene consumption mechanism is a one-to-one reaction, i.e., each argon ion (plus electron) consumes exactly one acetylene molecule and vice versa. In previous work it was shown that the best material is obtained at high growth rates or under conditions where the ion particle flow rate emanating from the arc is approximately equal to the injected acetylene particle flow rate (so-called critical loading).<sup>3</sup> This suggestion which was based on indirect particle flow rate and arc current variations can now be confirmed considering the measured consumption of acetylene. Moreover, the deposition rate as determined from ellipsometry measurements shows a good correlation with the consumed acetylene particle flow rate indicating that the deposition is a very fast and efficient process. From the proportionality between the consumed carbon particle flow rate and the deposition rate an effective deposition area of approximately  $0.3$  m<sup>2</sup> can be deduced assuming an *a*-C:H density of  $1.6$  g cm<sup>-3</sup> and a hydrogen content in the film of 40%.<sup>3</sup> This is about ten times the beam area suggesting that the largest fraction of the dissociation products ends up at other positions than the substrate.

In conclusion, mass spectrometry and Langmuir probe measurements clearly demonstrate that in an expanding Ar/ $C_2H_2$  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.

The skillful technical assistance of M.J.F. van de Sande, A.B.M. Hüsken and H.M.M. de Jong is greatly appreciated. The financial support from the foundation of Fundamental Research on Matter (projects FOM-RG and 95BR1406) and from the EC (INCO-Copernicus project IC15-CT96-0730) is thankfully acknowledged.

- <sup>1</sup>J. C. Angus and Y. Wang, in *Diamond and Diamond-like Films and Coatings*, NATO ASI Series B, Vol. 266, edited by R. E. Clausing, L. L. Horton, J. C. Angus, and P. Koidl (Plenum, New York, 1991), p. 173.
- <sup>2</sup>J. C. Angus, P. Koidl, and S. Domitz, in *Plasma Deposited Thin Films*, edited by J. Mort and F. Jansen (CRC, Boca Raton, FL, 1986), p. 89.
- <sup>3</sup>J. W. A. M. Gielen, W. M. M. Kessels, M. C. M. van de Sanden, and D. C. Schram, *J. Appl. Phys.* **82**, 2643 (1997); J. W. A. M. Gielen, P. R. M. Kleuskens, M. C. M. van de Sanden, L. J. van Ijendoorn, D. C. Schram, E. H. A. Dekempeneer, and J. Meneve, *ibid.* **80**, 5986 (1996); J. W. A. M. Gielen, M. C. M. van de Sanden, P. R. M. Kleuskens, and D. C. Schram, *Plasma Sources Sci. Technol.* **5**, 492 (1996); J. W. A. M. Gielen, M. C. M. van de Sanden, and D. C. Schram, *Appl. Phys. Lett.* **69**, 152 (1996).
- <sup>4</sup>W. B. Maier, *J. Chem. Phys.* **42**, 1790 (1965).
- <sup>5</sup>P. M. Mul and J. W. McGowan, *Astrophys. J.* **237**, 749 (1980).
- <sup>6</sup>S.-H. Zheng and S. K. Srivastava, *J. Phys. B* **29**, 3235 (1996).
- <sup>7</sup>M. C. M. van de Sanden, R. J. Severens, J. W. A. M. Gielen, R. M. J. Paffen, and D. C. Schram, *Plasma Sources Sci. Technol.* **5**, 268 (1996).
- <sup>8</sup>M. C. M. van de Sanden, M. F. A. M. van Hest, A. de Graaf, A. H. M. Smets, K. G. Y. Letourneur, M. G. H. Boogaarts, and D. C. Schram, *Diamond Rel. Mater.* (to be published).
- <sup>9</sup>F. F. Chen, in *Plasma Diagnostic Techniques*, edited by R. H. Huddleston and L. L. Stanley (Academic, New York, 1965), Chap. 4.
- <sup>10</sup>A. de Graaf, M. F. A. M. van Hest, M. C. M. van de Sanden, and D. C. Schram (unpublished).
- <sup>11</sup>G. M. W. Kroesen, D. C. Schram, A. T. M. Wilbers, and G. J. Meeusen, *Contrib. Plasma Phys.* **31**, 27 (1991).
- <sup>12</sup>M. C. M. van de Sanden, R. J. Severens, W. M. M. Kessels, R. F. G. Meulenbroeks, and D. C. Schram, *J. Appl. Phys.* **84**, 2426 (1998).
- <sup>13</sup>K. T. A. L. Burm, W. J. Goedheer, J. A. M. van der Mullen, G. M. Janssen, and D. C. Schram, *Plasma Sources Sci. Technol.* **7**, 395 (1998).