Emission spectroscopy on a supersonically expanding argon/silane plasma
Meeusen, G.J.; Ershov-Pavlov, E.A.; Meulenbroeks, R.F.G.; van de Sanden, M.C.M.; Schram, D.C.

Published in:
Journal of Applied Physics

Published: 01/01/1992

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 author's 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

Citation for published version (APA):

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?

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Download date: 05. Dec. 2018
Emission spectroscopy on a supersonically expanding argon/silane plasma

G. J. Meeusen, E. A. Ershov-Pavlov,a) R. F. G. Meulenbroeks, M. C. M. van de Sanden, and D. C. Schram
Department of Physics, University of Technology Eindhoven, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

(Received 9 September 1991; accepted for publication 24 January 1992)

Results from emission spectroscopy measurements on an Ar/SiH4 plasma jet which is used for fast deposition of amorphous hydrogenated silicon are presented. The jet is produced by allowing a thermal cascaded arc plasma in argon (I = 60 A, V = 80 V, Ar flow = 60 scc/s and pressure 4 × 104 Pa) to expand to a low pressure (100 Pa) background. In the resulting plasma SiH4 is injected in front of the stationary shock front. Assuming a partial local thermal equilibrium situation for higher excited atomic levels, emission spectroscopy methods yield electron densities (∼1018 m−3), electron temperatures (∼5000 K) as well as concentrations of H+, Si+, and Ar+ particles. The emission spectrum of the SiH radical, the A 2Δ − X 2Π electronic transition, is observed. Numerical simulations of this spectrum are performed, resulting in upper limits for the rotational and vibrational temperatures of 4000 and 5600 K, respectively. The results can be understood assuming that, in the expansion, charge exchange and dissociative recombination are dominant processes in the formation of species in excited states, notably Si+.

I. INTRODUCTION

The deposition of thin films of hydrogenated amorphous silicon (a-Si:H) is one of the steps in the production of devices such as solar cells and large liquid crystal displays. Common deposition techniques are chemical vapor deposition (CVD) plasma enhanced CVD (PECVD), photon enhanced, CVD, and sputtering. The PECVD technique is used in nearly all technological applications where a high quality semiconductor material is desired, whereas the other techniques are applied in more exploratory research. The deposition rate is usually low (<0.1 nm/s), due to the fact that the transport of particles responsible for deposition is mainly diffusion determined.

The new method described here uses a directed particle beam to overcome this problem: a plasma jet is created by allowing a thermal cascaded arc plasma in argon to expand supersonically. The vacuum chamber is a cylindrical vessel (1.15 m length and 0.5 m diameter) with a substrate support at one end. The substrate support extends 0.5 m into the vacuum vessel. The system is pumped by two roots blowers and a large turbomolecular pump is used to attain high basic vacuum conditions (∼10−4 Pa). A large turbomolecular pump is used to attain high basic vacuum conditions (∼10−4 Pa). At the other end of the cylindrical vessel, a wall stabilized cascaded arc is mounted. In this arc, a thermal argon plasma is produced with a temperature of about 104 K at subatmospheric pressures (4 × 104 Pa). The arc consists of three cathodes and an anode separated by a stack of electrically isolated copper plates. The arc channel has a diameter of 4 mm. The argon carrier plasma is allowed to expand supersonically into the vacuum vessel through a conically shaped nozzle. After several centimeters a stationary shock front occurs, where the velocity of the plasma is reduced to a subsonic level. The subsonic beam reaches the substrate with a velocity of approximately 600 ms−1, and a temperature of about 2000 K. Just after the nozzle, an argon/silane (10:1) mixture is injected in the beam. The silane is dissociated and partially ionized. The standard arc settings during the measurements are: Iarc = 60 A, Varc = 80 V, Ar flow = 60 scc/s, SiH4 flow = 0.5 scc/s, background pressure ≈100 Pa. One measurement is carried out using different arc conditions: Iarc = 30 A, Varc = 65 V. More detailed information concerning the silicon deposition apparatus can be found in Meeusen et al. 3

A spectroscopic setup for side-on observations of the...
plasma jet in the wavelength range of 350–700 nm was constructed, as sketched in Fig. 2. An optical system images the plasma 1:1 on the entrance slit of the monochromator. A parallel beam is created between the lenses \(L_1\) and \(L_2\), both with a focal length of 500 mm. Four aluminum coated mirrors, three of which are sketched in Fig. 2, are arranged in a way that a positioning system (which holds lens \(L_1\) and mirrors \(M_1, M_2\)) can be moved in the vertical plane without disturbing the light ray path. The surface of the first lens \(L_1\) and the size of the pinhole (radius 0.5 mm) determine the size of the detection volume: the part of the plasma from where radiation can pass through the optical system to reach the monochromator. A final biconvex glass lens \(L_3\) images the pinhole on the monochromator entrance slit. \(L_3\) has a radius of 22 mm and a focal length of 100 mm. Due to the vessel window size, lateral scans are limited to a region of about 100 mm.

A Czerny-Turner HR 640 monochromator (Jobin-Yvon) with a focal length of 640 mm and variable slits (10 μm–3 mm) is used. Apparatus profiles have been measured using a low pressure Hg lamp in front of the pinhole; the dispersion of the monochromator is about 1.2 nm/mm. A photomultiplier with a borosilicate window (EMI 9698B; sensitive wavelength region about 300–800 nm) is mounted on the monochromator exit slit. The data acquisition system consists of a Keithley 409 picomammeter (“pA” in Fig. 2) with its 3 V outlet connected to a Hewlett-Packard HP7101B strip chart recorder (SCR) and an RC damping network with an integration time of about 25 ms, averaging the noise from the photomultiplier output to make the signal fit for sampling by a personal computer (PC). The A/D converter sampling the picoammeter output is controlled by the same computer software that drives the stepping motor of the monochromator grating. The system was calibrated for absolute measurements, using a tungsten ribbon lamp in the vessel.

III. RESULTS

The emission spectra were used to study excited state densities for various plasma components (i.e., silicon, hydrogen, argon atoms and ions, and the SiH radical), to determine important plasma parameters. The side-on spectroscopic measurements reveal that, in the 350–700 nm region, the plasma radiation is mainly due to spectral lines of Si I. In the near UV (385.6, 386.3 nm) and near IR (634.7, 637.1 nm) regions Si II lines are observed. Furthermore, some argon lines are present, along with the hydrogen Balmer series, up to levels with \(n = 9,10\). The molecular spectrum of SiH in the region 405–430 nm [the \(A^2\Delta - X^2\Pi\) electronic transition, including the (0,0) and (1,1) vibrational bands] is not very intense in comparison to the strong emission of this radical observed using certain glow discharges. Some faint lines could not be identified, but are probably caused by impurities. The continuum part of the spectrum is weak.

A study of the spectra for different working conditions shows that they do not depend strongly on the silane input conditions, as long as the total SiH\(_4\) flow remains constant. Input conditions could vary due to gradual obstruction of the silane injection ring by deposition on the ring. Some (rather small) spectral intensity changes were noticed due to vessel pressure variations up to 15% from one experimental run to another. Drastic changes in the spectrum were observed, however, when the working cascaded arc current was lowered to 30 A. In this case, only the strongest lines of the hydrogen Balmer series, some Si I lines (4s–3p transitions), the strong 696.5 nm Ar I line and the SiH molecular spectrum remain.

It is appropriate to point here to an important difference in radiation characteristics between rf plasmas and expanding cascaded arc plasmas. In the rf case the plasma
is ionizing, i.e., the electron temperature is in the several eV range, and, hence, electron excitation and ionization of atomic and molecular species dominates. The present method uses a recombining plasma beam. From experiments in pure argon, argon–CH₄, and argon–H₂ in similar setups, it is known that the electron temperature is relatively low (around 0.3 eV) whereas the heavy particle temperature is relatively high (also around 0.3 eV), compared to glow discharge conditions. This has considerable consequences for atomic spectroscopy: in the present situation, electron excitation and ionization can totally be ignored in view of an extremely small Boltzmann exponent. The density of excited levels arises from higher lying states, either by dielectronic recombination (high lying levels in all systems) or by charge exchange and dissociative recombination (specific levels). As a consequence, high lying levels are in Saha equilibrium with their respective continuum and, hence, level population density measurements can be used to obtain information about plasma parameters.

The analysis of the side-on measurements on spatial distribution shows no noticeable gradients along the jet axis for distances of 120–190 mm from the nozzle. The lateral profile measurements showed rather smooth, Gaussian-like intensity distributions. The lateral measurements were Abel inverted in order to obtain the plasma emissivity as a function of the radial position. The measurements discussed here were performed at a distance of 135 mm from the nozzle.

### A. Atomic spectroscopy results

Relative intensity measurements using lines of silicon, argon, and hydrogen for different upper levels show that the plasma is recombining. Lower excited levels are strongly depopulated by radiation processes, whereas the uppermost levels are in Saha equilibrium with the adjacent ion ground state. The extent of this Saha region was estimated to be about 0.5 eV from the continuum for an electron density (nₑ) of 10¹⁸ m⁻³ and an electron temperature (Tₑ) of 5000 K. Electron collisions probably are the dominant process in excited-state destruction and creation in this Saha region, making it possible to use these levels to determine plasma parameters using absolute measurements. The lines selected for absolute intensity measurements are presented in Table I. Most of the Si I lines originating from higher excited levels (5p, 6p), are most likely in the Saha region.

Due to rather small plasma jet radial gradients, only 15 lateral points were taken. Emission spectra were registered for wavelength regions of interest at each lateral position. From these spectral data the radial profiles were presented in the same figure. Only averaged data for several lines originating from the same spectral region where the system is not very sensitive, making it possible to use these data to determine plasma parameters using absolute measurements. The lines selected for absolute intensity measurements are presented in Table I. Most of the Si I lines originating from higher excited levels (5p, 6p), are most likely in the Saha region.

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>Transition</th>
<th>Eₚ (eV)</th>
<th>Aₚₑ (10⁹ s⁻¹)</th>
<th>εₚ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si I</td>
<td>390.6</td>
<td>4s ¹P-3p ²S</td>
<td>5.08</td>
<td>0.118</td>
</tr>
<tr>
<td></td>
<td>410.3</td>
<td>4s ¹P-3p ²S</td>
<td>4.93</td>
<td>0.0016</td>
</tr>
<tr>
<td></td>
<td>564.6</td>
<td>5p ¹P-3p ¹P</td>
<td>7.12</td>
<td>0.0097</td>
</tr>
<tr>
<td></td>
<td>568.4</td>
<td>5p ₁S-4s ₁P</td>
<td>7.13</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td>569.0</td>
<td>5p ₁P-4s ¹P</td>
<td>7.10</td>
<td>0.012</td>
</tr>
<tr>
<td></td>
<td>570.1</td>
<td>5p ₁P-4s ¹P</td>
<td>7.10</td>
<td>0.037</td>
</tr>
<tr>
<td></td>
<td>570.8</td>
<td>5p ₁D-4s ¹P</td>
<td>7.12</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td>578.0</td>
<td>5p ₁D-4s ¹P</td>
<td>7.06</td>
<td>0.0098</td>
</tr>
<tr>
<td></td>
<td>579.3</td>
<td>5p ₁D-4s ¹P</td>
<td>7.07</td>
<td>0.013</td>
</tr>
<tr>
<td></td>
<td>579.8</td>
<td>5p ₁D-4s ¹P</td>
<td>7.09</td>
<td>0.018</td>
</tr>
<tr>
<td></td>
<td>474.8</td>
<td>6p ₁S-4s ²P</td>
<td>7.54</td>
<td>0.0057</td>
</tr>
<tr>
<td></td>
<td>475.3</td>
<td>6p ₁S-4s ²P</td>
<td>7.53</td>
<td>0.0073</td>
</tr>
<tr>
<td></td>
<td>477.3</td>
<td>6p ₁S-4s ²P</td>
<td>7.53</td>
<td>0.0057</td>
</tr>
<tr>
<td></td>
<td>478.3</td>
<td>6p ₁S-4s ²P</td>
<td>7.54</td>
<td>0.017</td>
</tr>
<tr>
<td></td>
<td>480.5</td>
<td>6p ₁S-4s ²P</td>
<td>7.50</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>494.8</td>
<td>6p ₁S-4s ²P</td>
<td>7.36</td>
<td>0.044</td>
</tr>
<tr>
<td></td>
<td>672.2</td>
<td>6d ₁P-6p ¹D</td>
<td>7.71</td>
<td>0.034</td>
</tr>
<tr>
<td></td>
<td>665.5</td>
<td>7d ₁P-7p ¹D</td>
<td>7.87</td>
<td>0.0069</td>
</tr>
<tr>
<td>Si II</td>
<td>385.6</td>
<td>4p ¹P-3p ²D</td>
<td>10.07</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>386.2</td>
<td>4p ¹P-3p ²D</td>
<td>10.07</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>634.7</td>
<td>4p ¹P-3s ²S</td>
<td>10.07</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>637.1</td>
<td>4p ¹P-3s ²S</td>
<td>10.07</td>
<td>0.69</td>
</tr>
<tr>
<td>HI</td>
<td>656.3</td>
<td>3-2</td>
<td>12.09</td>
<td>0.441</td>
</tr>
<tr>
<td></td>
<td>486.1</td>
<td>4-2</td>
<td>12.75</td>
<td>0.0842</td>
</tr>
<tr>
<td></td>
<td>434.0</td>
<td>5-2</td>
<td>13.06</td>
<td>0.0253</td>
</tr>
<tr>
<td>ArI</td>
<td>696.5</td>
<td>4p ¹S-4s ³s</td>
<td>13.33</td>
<td>0.067</td>
</tr>
<tr>
<td></td>
<td>525.3</td>
<td>7d ₁P-6p ¹D</td>
<td>15.45</td>
<td>0.0056</td>
</tr>
</tbody>
</table>

The absolute calibration of the experiment was performed with an accuracy of about 10%. Hence, the uncertainties in the transition probabilities for silicon (up to 50%) determine the accuracy of the calculations of the level number densities per statistical weight (n/g). Using averaged data for several lines originating from the same upper levels (e.g., 5p, 6p levels for Si I) probably eliminates part of the uncertainties introduced by inaccurate transition probabilities and possible plasma variations.

Some results for (n/g) calculations are given in Fig. 3 for excited states of Si, H, and Ar atoms, as well as Si ions—all at the center of the plasma jet. A simplified scheme of the energy level structure for different species is presented in the same figure. Only averaged data for 5p, 6p levels for Si I are given: the error bars indicate the data scattering due to errors mentioned before. The population number densities for 6d, 7p levels of Si I were evaluated using single lines (672.2 and 655.6 nm, respectively) in a spectral region where the system is not very sensitive, making these data less reliable. Furthermore, lines originating from the 4s level of Si I were not used because this level is too far from the continuum to be in Saha equilibrium. If we use the 4s, 5p, and 6p levels for temperature determini...
Relative ion concentrations of different plasma species can be evaluated starting from Saha-Boltzmann equations for different species:

$$\frac{n_{Si^+} + n_{H^+}}{(n/g)_{Si^+} + (n/g)_{H^+}} \approx K_{Si^+},$$  \hspace{1cm} (3)

defining the symbol $K$. By doing so, we suppose that all electrons originate from atomic ionization processes, i.e., that the abundancies of molecular ions, negative ions, and doubly ionized species are small. We note, that this does not mean that these ions cannot be important as an intermediate in kinetic processes.

If we use Eq. (3), we can evaluate the electron temperature more accurately using $(n/g)$ values for Si atoms and ions. We write the Saha–Boltzmann equation for silicon as follows:

$$\frac{((n/g)_{Si^+} + n_{H^+})^2}{(n/g)_{Si^+}} \approx K_{Si^+},$$  \hspace{1cm} (4)

In Eq (4), we suppose that, in the ion system, there is a Boltzmann-like equilibrium. Due to the strong influence of the electron temperature in Eq. (4) (the energy sum in the exponent is large), the temperature determination can be quite exact, even though there may be considerable uncertainties in $K$ and $(n/g)$. The validity of (4) is determined also by the presence of Saha equilibrium for the levels concerned.

The temperatures evaluated in this way can be used to determine ion and electron concentrations, using Eqs. (1) and (3):

$$n_{Si^+} = CT_{ie}^{3/2} \left( \frac{N}{g_{Si^+}} \right) \frac{u_{Si^+}}{K} \times \exp \left( - \frac{(E_i - E_g)_{Si^+}}{kT_e} \right) \left[ \frac{1}{2} \right].$$  \hspace{1cm} (5)

Note that $n_e$ can actually be evaluated using only Eq (1), with $(n/g)_{Si^+} + n_{H^+}$ instead of $n_{Si^+}/u_{Si^+}$, but that approach would have several disadvantages. First, the temperature would have a large influence (large energy difference $\left(E_p + E_i - E_g\right)$ in the exponent). Furthermore, the assump-

---

**FIG. 3.** Excited levels population for different species in the expanding Ar-SiH$_4$ plasma jet. Schematic energy levels diagrams are presented below the Boltzmann plots. The slope of the lines in the Boltzmann plots correspond to an electron temperature of about 5000 K. Full circles denote averaged data for several lines with error bars indicating the data scattering; open circles indicate single line measurements.
tion of a Boltzmann equilibrium for the ion state would have to be satisfied. The value of $n_{Si+}$, as determined using Eq. (4), is less dependent on the electron temperature (small energy difference in exponent), but depends on the calculation of the factor $K$.

The following lines were used for the $(n/g)$ determination to apply the above theory:

- Si: $6p$, $\lambda = 474.8-494.8$ nm; $E_p(6p) = 7.53$ eV;
- Si$^+$: $4p$, $\lambda = 634.7,386.3$ nm; $E_p(4p) = 10.07$ eV;
- Ar: $7d$, $\lambda = 525.3$ nm; $E_p(7d) = 15.45$ eV;
- H: $5$, $\lambda = 434.1$ nm; $E_p(5d) = 13.06$ eV.

Transition probabilities were taken from Wiese, Smith, and Miles;\(^1\^4\) partition function values were obtained from Drawin and Felenbok.\(^1\^5\)

The electron temperature, determined in this way, proved to be about 5000 K and equal for all radial positions up to 40 mm from the center of the plasma, within 100 K. The charged particle concentration distributions are presented in Fig. 4. The ion concentration ratios appeared to be constant over the studied volume of the plasma: $n_{H^+}/n_{Si+} \approx 10^{-2}$; $n_{Ar^+}/n_{Si+} \approx 2$.

It is possible to obtain information about the heavy particle temperature by investigating the line profiles of hydrogen lines. As the electron concentration (Fig. 4) in our case is below $10^{19}$ m$^{-3}$, we may expect the Doppler broadening to be dominant. The registred line profiles of H$\alpha$, H$\beta$, and H$\gamma$ show no dependence on distance from the jet axis. This shows that the electron density does not influence the line profile and that, hence, Stark broadening may be neglected in our case. This is also indicated by the fact that line profile half-widths are about the same for the hydrogen lines mentioned, whereas, in the case of Stark broadening, the effect should increase from H$\alpha$ to H$\gamma$.\(^1\^6\)

The monochromator apparatus profile, registred using a low-pressure H$_2$ lamp, appeared to have a full width at half maximum (FWHM) of 0.038 nm, for 20 $\mu$m slits. The H$\alpha$ line profile turned out to have a FWHM of about 0.06 nm. Unfortunately, both the apparatus profile and the line profiles were asymmetric and could not be approximated by either Lorentzian or Gaussian forms. Nevertheless, the H$\alpha$ FWHM value can be used to obtain a rough estimate for the hydrogen heavy particle temperature, which appeared to be about 4000-5000 K.

**B. SiH radical emission spectrum simulations and measurements**

The simulation of a molecular spectrum that cannot be fully resolved has proven to be a powerful technique to obtain values for parameters such as vibrational and rotational temperatures ($T_{vib}$, $T_{rot}$). This technique has been explored for SiH by Perrin and Delafosse;\(^*\) the very analogous case of CH is treated by Koulidiati et al.\(^1\^7\)

The full procedure to simulate the spectrum is described in literature\(^1\^8-2\^2\) and only a brief review will be given here. The steps to simulate the spectrum are the following:

1. The calculation of energy level positions of electronic, rotational, and vibrational levels for the $A^2\Delta$ and the $X^2\Pi$ state for $J<29.5$, using formulas as given by Klynning, Lindgren, and Sassenberg.\(^2\^2\)

2. Calculation of the transition wavelengths in vacuo using the appropriate selection rules; correction to wavelengths in air (a correction in the order of 0.1 nm).

3. Calculation of line strengths using the Franck-Condon factors,\(^1\^8\) HönI-London factors,\(^1\^9\) and the exponential (Boltzmann-like) laws governing the vibrational and rotational population in the equilibrium case, using $T_{vib}$ and $T_{rot}$ as parameters.

4. Convolution of the theoretical spectrum with an apparatus profile, of triangular or Gaussian form, with adjustable FWHM value.

The simulations thus have a set of three free parameters: FWHM, $T_{rot}$, and $T_{vib}$. The resulting simulations are identical to those obtained by Perrin and Delafosse\(^8\) if the same set of parameters is used.

The measured spectra were recorded using 200 or 100 $\mu$m monochromator slits (FWHM = 0.24 and 0.12 nm, respectively). Because of low intensities, smaller slits could not be used, whereas larger slits would have resulted in a very poor resolution.

Figure 5 shows the registred SiH spectrum and its simulation. The latter is performed using the appropriate FWHM value (0.12 nm) and $T_{rot} = 4000$ K, and $T_{vib} = 5600$ K. A comparison of the measured and simulated spectra shows the problems associated with the measured SiH spectra in our case. To begin with, SiH emission intensities (e.g., compared with H Balmer lines) are small in our case. In glow discharges,\(^8\)^5 the SiH spectrum is the main feature in the spectrum, facilitating comparison with
simulations. This, again, may be caused by the low electron temperature and the absence of electron excitation in the present case.

Furthermore, with the arc burning on argon some persistent argon lines (present at 415.9, 416.4, 418.2, 419.1, and around 420.0 nm), together with the Hg-Si I combination at 410.1/410.2 nm, are present in the SiH region. Especially the argon lines near 420.0 nm and the (very strong) combination around 410.1 nm make comparison difficult, as they coincide with prominent features [the (0,0) R branches heads around 410.0 nm and the (1,1) Q2 branch head at 419.8 nm] of the SiH spectrum.

Some bandlike features not present in the simulations are observed around 411.7 and 420.4 nm, the 411.7 system being fairly strong. These might be attributed to impurities: the presence of the SiN molecule, for example, might explain the bands and also the blurred appearance of the system around 417.2 nm (however blurred). As the disturbing Ar lines increase the peak heights of all the peaks mentioned but the (0,0) Q2 band head, the values for $T_{\text{rot}}$ and $T_{\text{vib}}$ (4000, 5600 K, respectively) as used in the simulation in Fig. 5 (the best fit) should be regarded as upper limits for their true values. This is a consequence of the specific dependence of band head strengths on $T_{\text{rot}}$ and $T_{\text{vib}}$.

IV. DISCUSSION

The results, obtained using the spectroscopic techniques described above, can be summarized as follows. The expanding SiH$_4$–Ar plasma jet can be characterized as having an electron temperature of about 5000 K and an electron density of about $2 \times 10^{18}$ m$^{-3}$ at the plasma jet center, decreasing to about $8 \times 10^{17}$ m$^{-3}$ at a distance of 40 mm from the plasma jet axis. The ion concentration ratios appear to be constant over the plasma volume studied: $n_{\text{He}}^+ / n_{\text{Si}}^+ \approx 10^{-2}, n_{\text{Ar}}^+ / n_{\text{Si}}^+ \approx 2$. Upper limits for the rotational and vibrational temperatures of the SiH radical are found to be 4000 and 5600 K, respectively.

From other experiments in pure argon it has been verified that the electron density decrease with axial position is mainly due to the expansion process (the plasma beam widens). From these measurements it has become clear, that the total ion fluence (i.e., integrated over the beam cross section) does not depend on the axial position. This is to be expected, as dielectronic and radiative recombination can be ignored in first approximation. In argon–hydrogen mixtures the situation is changed drastically: the total ion fluence decreases steeply with axial position. In view of the insignificance of atomic recombination, it has been concluded that the recombination is via a molecular channel.

In the present experiment, the emission from higher excited species (especially the Si$^+$ emission) cannot be explained in terms of excitation by electron collisions, as in our case the silane is injected in the expansion where $n_e$ and $T_e$ values are rather low. Because the rate constants for ionization and dissociation become very small for low $T_e$ values (around 5000 K in the expansion), we can neglect the effect of electron collisions in the dissociation and ionization processes.
The effect, then, of the presence of metastable (4s) argon atoms has to be considered, as they may cause dissociation by Penning-like ionization of SiH₄ molecules. The argon (4s) levels originate from dielectronic recombination of argon ions coming out of the arc. The amount of metastables can be estimated in our case, as a numerical/analytical collisional radiative model for argon by Benoy et al.[26] turns out to describe the level population density distribution accurately for the pure argon case. From this model, we can derive the total (4s) state density, as well as, for example, the 4p [3s] state density, for given electron density, neutral particle density, and electron temperature. The 4p [3s] state population can be measured by investigating the 696.5 nm radiation of a pure argon plasma. We have done this, and found n(4p [3s]) = 5 × 10¹² m⁻³. Using the model, the total (4s) metastable concentration can then, be estimated to be about 10¹⁷ m⁻³.

Now, if we consider the case with silane injected in the jet, the argon 4p [3s] level density drops drastically to about 5 × 10⁸ m⁻³. We suppose the metastable density to be a factor 10⁴ higher than this value, as indicated by the pure argon case. The metastable density, then, would be in the order of 10¹³–10¹⁴ m⁻³, for our argon/silane plasma jet. Therefore, a major contribution to ionization by Penning-like processes is not very likely, as the concentration of metastables is much less than the ion concentration.

These arguments indicate that we will have to find other processes to account for the observed ion concentration ratios (n(H⁺): negligible, n(Si⁺)/n(Ar⁺) ~ 1:2). We may explain the results by considering the following charge exchange/dissociative recombination reactions:

\[
\begin{align*}
\text{Ar}^+ + \text{SiH}_4 & \rightarrow \text{SiH}_4^+ + \text{Ar} & (6a) \\
\text{SiH}_4^+ + e^- & \rightarrow \text{SiH}_3 + \text{H} \\
\text{Ar}^+ + \text{SiH}_3 & \rightarrow \text{SiH}_3^+ + \text{Ar} & (6b) \\
\text{SiH}_3^+ + e^- & \rightarrow \text{SiH}_2 + \text{H} \\
\text{Ar}^+ + \text{SiH}_2 & \rightarrow \text{SiH}_2^+ + \text{Ar} & (6c) \\
\text{SiH}_2^+ + e^- & \rightarrow \text{SiH} + \text{H} \\
\text{Ar}^+ + \text{SiH} & \rightarrow \text{SiH}^+ + \text{Ar} & (6d) \\
\text{SiH}^+ + e^- & \rightarrow \text{Si} + \text{H} \\
\text{Ar}^+ + \text{Si} & \rightarrow \text{Si}^+ + \text{Ar} & (6e) \\
5\text{Ar}^+ + \text{SiH}_4 + 4e^- & \rightarrow \text{Si}^+ + 4\text{H} + 5\text{Ar}. \\
\end{align*}
\]

In the sequence 6(a)–6(e) one or more steps may be skipped (dissociative charge exchange), as indicated by the dashed arrows. This is most certainly the case for the first reaction, as indicated by rate coefficients by Haaland[28] and Bowers and Elleman.[29] Each charge exchange process is followed by a dissociative recombination process, in which the formed molecule dissociates. It is likely, that the main source of radiation is dissociative recombination, ending in excited levels.

Cross sections for the charge exchange reactions with Ar⁺ are usually very large, and these processes are expected to be faster (rate coefficients typically a few 10⁻¹⁵ m³/s if there is a good energy match between the exchanging levels) than electron processes in the expansion. Penning-like ionization processes are also neglected, because the ion concentration is a factor 10⁶–10⁹ higher than the metastable concentration. The dissociative recombination processes following the charge exchanges have even larger rate constants (a few times 10⁻¹⁴ m³/s for Tₑ ≈ 5000 K). The radicals and atoms, formed in the above processes (6) can appear in excited states, and probably explain the very existence of the observed Si I and Si II emission spectra at such low electron temperatures and electron densities.

A comparison of the energy level positions in the Si + and the hydrogen system[24] explains why Si + ions are formed through charge exchange channels and H⁺ protons are not. The position of the argon ion ground state (15.76 eV) in the Si + system makes a near-resonance process possible between Si atoms and Ar⁺ ions, leaving the formed Si⁺ ion in one of the excited states nearby the Ar ionization potential. We observed the emission originating from the (3p)²(4p) excited state of Si⁺, giving us confidence in this view: emission from other nearby levels, notably (3s)²(4s), lies in the vacuum ultraviolet region,[14,30] not observable in our case.

Charge exchange between H and Ar⁺ is more difficult as the proton has no electronic energy levels and the energy match is poor. This makes resonant processes impossible, resulting in lower rate coefficients for the following reaction:

\[
\text{Ar}^+ + \text{H} \rightarrow \text{Ar} + \text{H}^+. \quad (7)
\]

If we assume the argon cascaded arc plasma to have an initial ionization degree of about 10% (Ref. 4) (i.e., at the start of the expansion), and we inject about 0.8% SiH₄, this results in 0.8% silicon ions if the above reactions (6) are dominant, at the cost of 3 to 5 Ar⁺ ions per Si⁺ ion. This leaves a minimum Ar⁺ ion fraction of about 10⁻⁵ × 0.8 = 6%, if no other recombination occurs (radiative and dielectronic recombination are too slow). As we find an n(Si⁺)/n(Ar⁺) ratio of 1/2, while the H⁺ fraction is negligible, some additional Ar⁺ losses are to be expected. A possible recombination channel is a direct charge exchange with hydrogen molecules:[23]

\[
\text{H}_2 + \text{Ar}^+ \rightarrow \text{ArH}^+ + \text{H}, \quad (8)
\]

Rate constants for the reactions (8) are about 10⁻¹⁵ m³/s for the first step and very large, about 10⁻¹³ m³/s, for the second step. As the hydrogen, produced in the second step of (8), may appear in excited states, the reactions (8) may well account for the hydrogen emission observed. This is confirmed by measurements on a pure argon plasma, using the same machine: the strongest Balmer lines were distinctly present in these argon spectra. The hydrogen molecules necessary for the reactions (8) may origi-
nate from the walls of the steel vacuum vessel, as the machine produces hydrogen by the reactions (6) during operation, and it is known that hydrogen may stick to the steel walls and enter the plasma again as a molecule, causing recombination by the above process.

Any hydrogen ions produced by (unlikely) charge exchange with argon ions [reaction (7)] will disappear, in the presence of vibrationally excited hydrogen molecules, by the following charge exchange/dissociative recombination process:

\[
H^+ + H_2(v > 3) \rightarrow H^+ + H, \\
H^+_2 + e^- \rightarrow 2H. 
\]  

(9)

This reaction can also produce excited hydrogen atoms. It is, however, unlikely that it is responsible for the hydrogen emission as we observe low H^+ concentrations.

V. CONCLUSIONS

The expanding plasma jet in argon with silane injected in the expansion is an example of a recombining plasma, with electron densities (for an arc current of 60 A and at a distance of 155 mm from the nozzle) in the order of \(10^{18}\) m^-3 and emission by Si, Si^+, H, Ar, and SiH particles.

The electron temperature is about 3000 K in the 60 A case. Estimates for the vibrational temperatures of the emitting SiH radical seem to confirm this value.

To explain the observed density ratio for silicon and argon ions (1:2) a reaction chain (6) leading to the production of Si^+ ions by charge exchange and dissociative recombination may be used. In this view, the argon ions coming out of the arc are some kind of an “ionization reservoir” for charge exchange processes with silane reaction products and silicon atoms. Some extra loss of ionization may be explained by molecular processes with hydrogen molecules coming from the vessel walls. A change in ionization degree also may result from volume effects.

Emission spectroscopy, however simple in our case, can give a first characterization of the plasma jet and, thus, may be considered a valuable plasma diagnostic.

ACKNOWLEDGMENTS

We would like to thank A. B. M. Hüsken, M. J. F. van de Sande, and H. de Jong for their fine technical assistance and D. K. Otorbaev (Institute of Physics, Kirghiz Academy of Physics, Frunze, 720071, USSR) for his contributions to the molecular spectroscopy part. This work is part of the research program of the “Stichting voor Fundamenteel Onderzoek der Materie (FOM),” which is financially supported by the “Nederlandse organisatie voor wetenschappelijk onderzoek (NWO).”


