OPTICAL SPECTROSCOPIC DIAGNOSTIC OF AN ARGON-HYDROGEN RF INDUCTIVE THERMAL PLASMA TORCH USED FOR SILICON HYDROGENATION

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Abstract

The hydrogenation of silicon material proves great advantages concerning its photovoltaic properties and secure a key for the elimination of crystalline defects during the basaltic growth of the crystal. It is therefore interesting to characterise the plasma by Optical Emission Spectroscopy in order to study the hydrogenation of silicon particles during their treatment by an inductive thermal plasma burning in Ar-H₂ mixture.

Highly excited states of atomic hydrogen, responsible for the silicon hydrogenation, have been detected in the plasma. These hydrogen lines have been used to determine the electronic density on the plasma axis. Furthermore, the Ar I lines were used to estimate the electronic temperature.

Then, the deviation from the Local Thermodynamic Equilibrium (LTE) of the plasma has been estimated.

Introduction

Previous works have shown that the highly excited states of atomic and molecular hydrogen produced by an inductive thermal plasma burning in Ar-H₂ mixture, react with the melted silicon leading to a photovoltaic grade silicon. The measurement of physical properties of the silicon deposit shows a long diffusion length (200 μm) despite a high dislocation density (10⁶ cm⁻²). This is due to the high hydrogen content in the silicon (2×10¹⁵ at.cm⁻³) measured by the exodiffusion technique.

It is clear that there is a correlation between the excited states of hydrogen in the plasma and the final hydrogen content in the material. The aim of this work is the characterisation of the used inductive plasma torch by Optical Emission Spectroscopy (OES).
Experimental set-up

The spectroscopic study has been realised with the plasma torch described in Figure 1. The plasma jet is generated by a RF generator (5.2 MHz) operating with a fixed power in the range 5-7 kW. The torch, composed of a quartz tube (internal diameter $d_{in} = 30 \text{ mm}$), is placed in the centre of four water cooled copper coils spaced of 4 mm. The gas mixture (Ar + H$_2$), controlled by mass-flow meters, is introduced tangentially at the atmospheric pressure in the upper part of the torch, and flows in the quartz tube with a swirling trajectory. The average residence time of the gaseous species in the plasma is close to 5 ms on the axis.

The emission spectrum of the plasma is simultaneously side-on recorded in three points of the axis by three optical fibres placed in a teflon support. That allows to reduce the acceptance angle of the optical fibre, calculated equal to 0.044 st. This means that the measurements are well spatially localised. The volume of plasma covered by each optical fibre is $94 \text{ mm}^3$. This localisation allows the characterisation of the plasma all along the jet axis.

The signal is transmitted to a spectrometer (grating: 1200 lines/mm, resolution $\Delta \lambda = 0.108 \text{ nm}$ for $\lambda = 400 \text{ nm}$) equipped with a CCD detector (1024×128 pixels).

The origin of the plasma jet length ($Z=0$) was fixed in the centre of the inductive coils between the second and the third turn, where the temperature of the plasma is supposed maximum [6]. Three successive measurements are performed along the axis in order to cover the entire plasma length, from $Z=0$ mm to $Z=96$ mm by step of 12 mm.

The used experimental conditions (power, mass flows...) will be given with the experimental results.
Determination of the electronic density

A previous study of the plasma\textsuperscript{[3]} has revealed the presence of excited atomic hydrogen species (Balmer series from H\textsubscript{c} to H\textsubscript{a} at atmospheric pressure. These Balmer lines (notably H\textsubscript{a}) have been used to determine the electronic density through the estimation of the stark broadening\textsuperscript{[3]}. The electronic density is given by the equation\textsuperscript{[4]}:

\[ N_e = \frac{C(N_e, T_e)}{\Delta \lambda_s^{3/2}} \]

where \( \Delta \lambda_s \) is the Stark broadening (full width at half maximum) of the atomic line and \( C(N_e, T_e) \) is a coefficient given by Griem\textsuperscript{[4]} for different temperatures \( T_e \). In our case, its dependence with \( T_e \) is weak.

It is important to remark that this method is completely independent of the equilibrium state of the plasma.

The apparatus function \( \Delta \lambda_{app} \) of the optical set-up, supposed gaussian, was determined as a function of the wavelength \( \lambda \), using low-pressure calibration lamp. So, we have verified that it was negligible compared to the Stark broadening of the hydrogen lines, and we have not taken it into account. So, the Stark broadening of the atomic hydrogen line is assumed to be equal to the full broadening of the line.

The obtained electron densities \( N_e \) as a function of the axis length \( Z \), are shown on Figure 2 for the experimental conditions summarised in the Table 1.
The results show a decrease of the electronic density from $N_e = 1.5 \times 10^{10}$ cm$^{-3}$ in the middle of the inductive coils ($Z \approx 0$ mm), to $N_e = 8.0 \times 10^{9}$ cm$^{-3}$ at $Z = 96$ mm from the coils [cf. Figure 2]. This confirms that the inductive coils are the most reactive zone of the plasma.

When we increase the hydrogen content in the plasma, it is necessary to increase simultaneously the power applied in order to stabilise the plasma. Then, the higher observed electron density is probably due to the increasing of power and not to the higher hydrogen concentration.

The argon spectrum has been recorded between 400 and 800 nm and revealed many intensive Ar I lines, but no Ar II line. So, we have tried to compare these preceding results with electron density obtained from the Ar I lines. But they were very thin, and apparatus function was close to their Stark width. So the accuracy of the method was quite bad and without significance.

**Measurement of the electronic temperature**

The intensive Ar I lines can be efficiently used to determine the electronic temperature. Two different methods were applied: the atomic Boltzmann plot and the ratio of the intensity line to the continuum.

4.1 Boltzmann plot method
Assuming the LTE state, the plasma temperature can be obtained using the equation [1]:

\[
\ln\left(\frac{\varepsilon_{mn}}{A_{mn} \nu_{nm} g_m}\right) = \ln K - \frac{E_m}{kT_e}
\]

where \(\varepsilon_{mn}\), \(\nu_{nm}\) and \(A_{mn}\) are respectively the emission coefficient, the frequency and the transition probability of the transition; \(E_m\) and \(g_m\) are the energy and the statistical weight of the upper state of the transition, respectively; \(k\) is the Boltzmann constant, and \(K\) is a constant for all the ArI lines.

Seven ArI lines have been chosen in order to cover the maximum energy area so as to increase the precision of the method. The slope of the obtained straight lines is inversely proportional to the electronic temperature. A typical Boltzmann plot obtained for a pure argon plasma is presented on the Figure 3.

![Boltzmann plot](image)

\(T_e = (8950\pm450)\ \text{K}\)

Figure 3: Typical Boltzmann plot obtained with argon lines

The influence of the power injected to the plasma and the hydrogen content has been studied [Cf. Table 2]. The obtained variation of the electronic temperature along the plasma axis for different power (4.4–6.4 kW) and different hydrogen content (0–2% \(\text{H}_2\)) are shown in the Figure 4. The difference of temperature between the middle of the coils and the end of the plasma plume (Z=90 mm) is around 1000-1500 K, depending on the power injected to the plasma. These results are in good agreement with calculations obtained by numerical modelling [10].

The electronic temperature of the plasma seems to be directly proportional with the power and independent of the hydrogen content.
The addition of hydrogen in an argon plasma modifies significantly the plasma properties (thermal conductivity, enthalpy, diameter of the plasma) but doesn’t seem to have any influence on the plasma temperature. The presence of hydrogen, increases the thermal conductivity, which is responsible of the improvement of the thermal treatment of the silicon particles in the deposition process with a high evaporation phenomenon.

The accuracy of this method is quite sensitive to the determination of the line intensity that were sometimes bad resolved. Particularly, the measurement made at the extremity of the plasma plume correspond to a non-intense plasma zone, with a bad signal-to-noise ratio. Nevertheless, this method gives a first idea on the equilibrium plasma state, because the points in Boltzmann plots were generally well aligned.

<table>
<thead>
<tr>
<th>Argon</th>
<th>Hydrogen</th>
<th>Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>29.4 L min⁻¹</td>
<td>0.6 L min⁻¹ (2.0 % Arg)</td>
<td>6.3 kW</td>
</tr>
<tr>
<td>29.6 L min⁻¹</td>
<td>0.4 L min⁻¹ (1.3 % Arg)</td>
<td>5.9 kW</td>
</tr>
<tr>
<td>29.8 L min⁻¹</td>
<td>0.2 L min⁻¹ (0.6 % Arg)</td>
<td>5.6 kW</td>
</tr>
<tr>
<td>30.0 L min⁻¹</td>
<td>0 L min⁻¹</td>
<td>4.5 kW</td>
</tr>
<tr>
<td>30.0 L min⁻¹</td>
<td>0 L min⁻¹</td>
<td>5.4 kW</td>
</tr>
<tr>
<td>30.0 L min⁻¹</td>
<td>0 L min⁻¹</td>
<td>6.4 kW</td>
</tr>
</tbody>
</table>

Table 2: Experimental Plasma conditions used for the evaluation of the temperature

![Graph showing axial variation of T_e as a function of the power (with and without H₂)](image)

Figure 4: Axial variation of $T_e$ as a function of the power (with and without H₂)

4.2 Line-to-continuum ratio method

The second method used for the determination of the $T_e$ is based on the equation [3]:

$$ y = \frac{h^4 C}{8\pi C^2 (2\pi m e)^{3/2}} \frac{g_{me}}{g_i} \frac{\lambda}{\Delta \lambda} \frac{\exp[(E_m - E_e)/kT_e]}{T_e \xi(\lambda, T_e)} \left(1 - \frac{\Delta E_e}{kT_e}\right) $$

where $h$ is the Planck’s constant; $C$ is the light velocity; $m_e$ is the electronic weight; $g_i$ is the statistical weight of the fundamental level of ArII ion, $E_m$ and $\Delta E_e$ are the ionisation energy and the lowering of ionisation potential, respectively; and $C_i$ is a constant for all the ArII lines.
This equation can be theoretically solved using the Biberian factor $\xi(\lambda, T_e)$ given by \cite{7} for each ArI line. It gives the value of $T_e$ versus the ratio of a line’s intensity at the wavelength $\lambda$ to the adjacent continuum intensity in a given spectral range $\Delta \lambda = 1$nm. This ratio has been determined from the experimental data for three ArI lines: 415.86, 430.01 and 451.07 nm. The obtained results are presented in the Figure 5.

![Figure 5: Influence of power and hydrogen in the argon plasma on the electronic temperature measured by the line to continuum ratio method](image)

The accuracy of this method is quite good. The obtained plasma temperature distributions are similar to this obtained by the Boltzmann plot method. But a constant gap of temperature of about 1000 K which is probably due to the difference of accuracy between the spectroscopic data used in these two cases.

Then, the validation of the Local Thermodynamic Equilibrium assumption has been verified comparing the $N_e$ determined experimentally from the Stark broadening of the hydrogen lines (independent of any equilibrium assumption) with the electron density calculated from the plasma composition at the equilibrium with temperature $T_e$ given by the line-to-continuum ratio. In any case, we can consider that the plasma is very close to the thermodynamic equilibrium.

**Conclusion**

The energetic characterisation of an inductive thermal plasma torch burning in Ar-H$_2$ mixture, has been obtained by Optical Emission Spectroscopy. The electronic density and temperature have been determined for a power varying from 4.4 to 6.4 kW with different hydrogen contents. The maximum of temperature of the plasma is around 10000-11000 K in the middle of the inductive coils for an electronic density $N_e=1.5 \times 10^{16}$ cm$^{-3}$.

The introduction of hydrogen in an argon plasma doesn’t modify the temperature repartition in the plasma which is only related to the power injected to the plasma gas.

The Local Thermodynamic Equilibrium assumption, which is supposed to be reached in the numerical modelling, has been verified.
References

(16th European Photovoltaic Solar Energy Conference, 1-5 May 2000, Glasgow, UK)

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