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EMISSION SPECTROSCOPY ON A SUPERSONICALLY EXPANDING ARGON/SILANE PLASMA

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ABSTRACT

Results from emission spectroscopy measurements on an expanding thermal Ar–SiH_4 plasma jet which is used for fast deposition of a–Si:H are presented. Analysis of the spectroscopic data yields electron densities ($\sim 10^{18}$ m^{-3}), electron temperatures ($\sim$5000 K) as well as ion concentrations. The spectrum of the $A^2\Delta - X^2\Pi$ transition of the SiH radical is measured and simulated. Charge exchange and dissociative recombination appear to be dominant processes in the formation of Si^+ ions and excited species.

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 can produce high quality material, but deposition rates are low ($\approx$ 0.1 nm/s) due to the fact that the transport of particles responsible for deposition is diffusion determined.

To overcome this problem a machine has been built which makes use of a directed particle beam by allowing a thermal cascaded arc plasma in argon to expand towards vacuum. This method has been succesfully applied to a–C:H, graphite, and diamond deposition /1/. For a–Si:H deposition, *silane* (SiH_4) is injected and dissociated in the expanding plasma jet and transported towards a heatable substrate support where deposition takes place. Optimization of the three deposition phases (dissociation, transport, and deposition) can be performed independently from each other because of good spatial separation. With this method a–Si:H films have been produced with a refractive index similar to PECVD produced a–Si:H while transmission interferometry shows no other than SiH vibrations /2/.

In order to characterize the plasma jet and to investigate the dissociation chemistry, emission– and absorption spectroscopy are suitable diagnostics. Until now the emission spectroscopic set up has been realized. In this paper results of spectroscopic measurements on the plasma jet are presented and discussed.

EXPERIMENTAL

In figure 1 the deposition apparatus is depicted schematically. 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.
Various vacuum pumps are used to obtain high basic vacuum conditions (10^{-4} Pa). At the other end of the cylindrical vessel, a wall stabilized DC cascaded arc is mounted. In this wall stabilized arc a thermal argon plasma is produced at temperatures of about 10^4 K and at sub–atmospheric pressures ($\simeq$ 0.4 Bar). The arc consists of three cathodes and an anode separated by a stack of electrically isolated copper plates. The construction of this arc is treated in detail in Kroesen *et al* /3/. The arc parameters in the case under

consideration are: $I_{tot} = 60$ A, V = 80 V. The argon carrier plasma is allowed to expand supersonically into the vacuum vessel through a conically shaped nozzle in the anode. The argon flow through the arc was 60 scc/s during the measurements. After several centimeters a shock occurs /3,4/: the velocity of the plasma is reduced to a subsonic level. Just outside the nozzle an argon/silane (10:1) mixture is injected into the beam (resulting SiH_4 flow: 0.5 scc/s): the silane is dissociated and partially ionized.

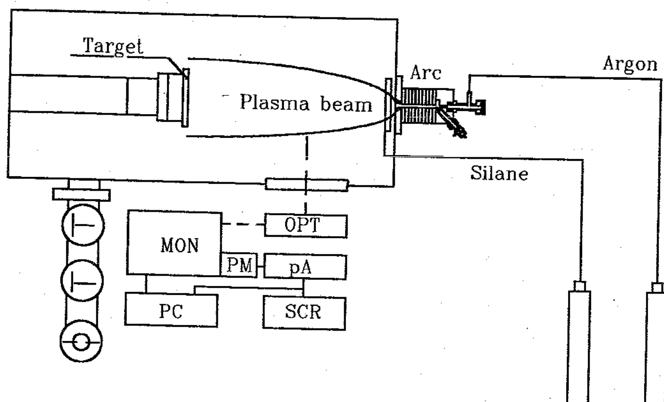


Figure 1. The experimental set up.

An emission spectroscopy set up for side–on observations of the plasma jet in the region of 350–700 nm was constructed, as indicated in figure 1. The observations take place through a glass vessel window (diameter 120 mm) positioned at 150 mm from the nozzle: this limits the volume that can be investigated. The optical part of the system (OPT) is a combination of glass lenses and mirrors arranged in a way that the light ray path is undisturbed when a spatial scan is made /5,6/. A 1:1 image of the plasma is obtained at the entrance slit of a Czerny–Turner monochromator (MON) with a focal length of 640 mm. The spectra are registrated using a photomultiplier (PM, sensitivity range about 300–800 nm) and a picoammeter (pA) connnected to a strip chart recorder (SCR) and a personal computer (PC).

The system was calibrated in an absolute way using a tungsten ribbon lamp.

RESULTS

Emission spectroscopy methods have been used to study the density distribution of excited particles for various plasma components including silicon, hydrogen, argon atoms and ions, and the SiH radical to determine important plasma parameters. The side–on spectroscopic measurements reveal that in the studied wavelength region (350 – 700 nm) the plasma radiation is mainly due to spectral lines of Si I. In the near UV and near IR regions Si II lines are observed. Some argon lines are present, along with the hydrogen Balmer series, up to the very weak lines resulting from transitions from 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) is not very intense in comparison to that observed using certain glow discharges /5/. The spectrum continuum is very weak.

The analysis of the side–on registrations showed, that in the observed spatial region no noticeable gradients along the jet axis occurred. The lateral radiation intensity distribution profiles appeared to be a rather smooth and Gaussian–like, with the maximum at the center of the plasma jet. According to the experimental conditions we limited the measurements to a single plane of observation perpendicular to the jet axis at a distance of 150 mm from the nozzle.

Atomic spectroscopy results

Intensity distribution measurements using lines from different upper levels show that the plasma state resembles the recombining case, where lower excited levels are strongly depopulated by radiation processes, while 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 /7/. Collisions with electrons may be the dominant process in this Saha region, making it possible to use these levels to determine plasma parameters. In view of the rather small plasma jet radial gradients only a few lateral measuring points were taken at intervals of 1 cm. Spectra of the plasma jet were registrated for wavelength regions of interest at each lateral position. From these spectral data the plasma emissivity radial profiles were calculated using Abel inversion /8/.

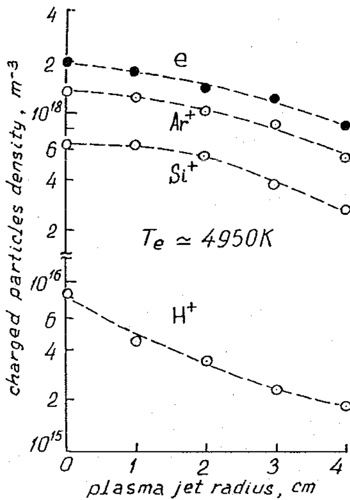


Figure 2. Charged particles density distributions.

As the absolute calibration of the experiment was performed with an accuracy of about 10 % and transition probabilities introduce inaccuracies up to 50 % our calculations of absolute level population number densities per statistical weight (n/g) should be regarded as having an inaccuracy of 60%. This level of errors could be decreased using averaged data for several lines originating from the same upper levels (e.g. 5p, 6p levels for Si I). The population number densities for 6d, 7p levels of Si were evaluated using single lines (672.2 nm and 655.6 nm, respectively) in a spectral region where the system is not very sensitive. This makes these data less reliable when determining plasma parameters. The lines originating from the 4s level of Si were not used because this level is probably too far from the ionization border to be in Saha equilibrium /7/. Using only the 5p, 6p levels, a value for the temperature of T ~ 4500 K is obtained for the jet axis. The same situation is found at radial positions up to 4 cm from the center of the jet.

Using this value as a first approximation of the electron temperature T_e, relative ion concentrations of different plasma species can be evaluated by dividing Saha–Boltzmann equations for different species /5/.

$$\frac{n_{Ar^+}}{n_{Si^+}} = \frac{(n/g)_{Ar,q}}{(n/g)_{Si,q}} \cdot \frac{u_{Ar^+}}{u_{Si^+}} \cdot \exp\left[-\frac{(E_i-E_q)_{Ar}-(E_i-E_q)_{Si}}{kT_e}\right]. \tag{1}$$

The index q refers to the emitting level in the atomic system concerned while u^+ is the ion partition function. The other symbols are common. A formula analogous to (1) can be written for n_{Ar^+}/n_{H^+}. Note that the temperature dependence of the ratio in equation (1) can be made very small by using energy levels (close to the continuum) such that the difference $[(E_i-E_q)_{Ar}-(E_i-E_q)_{Si}]$ is as small as possible.

With the plasma quasineutrality condition the electron density can be expressed as: $n_e = n_{Si^+} \cdot (1 + [n_{Ar^+}/n_{Si^+}] + [n_{H^+}/n_{Si^+}]) \equiv K \cdot n_{Si^+}$, defining the symbol K. By doing so, we suppose that the ions are atomic, i.e. that the molecular ion density and negative ion density can be neglected. This assumption is justified as molecular ions forming processes are slower than destruction by dissociative recombination (cf. discussion).

Inserting K and the (n/g) values for Si^+ and Si in the Saha–Boltzmann equation, we can evaluate T_e:

$$\frac{[(n/g)_{Si^+,p}]^2}{(n/g)_{Si,q}} \cdot u_{Si^+} \cdot K = C \cdot T_e^{3/2} \cdot \exp(-(E_i+2E_p-E_q)/kT_e). \tag{2}$$

The index p refers to an ion excited level; C is a constant ($C = [2\pi m_e k/h^2]^{3/2}$). In eq. (2) a Boltzmann–like equilibrium is assumed also for the Si^+ system.

The values of T_e and K can be used together with the (n/g) values for Si atoms to determine n_{Si^+} (and, hence, n_e) using the Saha–Boltzmann equation:

$$n_{Si^+} = \left[C \cdot T^{3/2} \cdot \left[\frac{n}{g}\right]_{Si,q} \cdot \frac{u_{Si^+}}{K} \cdot \exp(-(E_i - E_q)/kT_e)\right]^{1/2}. \qquad (3)$$

The following lines were used for the (n/g) determination to apply the above theory: **Si**: $\lambda = 474.8$–494.8 nm, $E_q(6p) = 7.53$ eV; **Si⁺**: $\lambda = 386.3$, 634.7 nm, $E_q(4p) = 10.07$ eV; **Ar**: $\lambda = 525.3$ nm, $E_q(7d) = 15.45$ eV; **H**: $\lambda = 434.1$ nm, $E_q(5d) = 13.06$ eV. The electron temperature determined in this way appeared to be about 4950 K and constant within ± 100 K for all radial positions up to 4 cm from the center of the plasma. The charged species concentration distributions are presented in fig. 2. The ion concentration ratios (determined using eq. (1)) appeared to be about constant over the studied volume of the plasma: $n_{H^+}/n_{Si^+} \simeq 10^{-2}$; $n_{Ar^+}/n_{Si^+} \simeq 2$.

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}). The full procedure to simulate the spectrum is described in literature /5,9–13/ and will not be repeated here. Energy levels and line intensities were calculated for the (0,0), (1,1), and (2,2) vibrational bands of the $A^2\Delta - X^2\Pi$ transition using data by Klynning *et al* /12,13/. The simulations thus have a set of three free parameters: the HWHM (Half Width Half Maximum) value of the apparatus profile, T_{rot}, and T_{vib}. The resulting simulations are identical to those obtained by Perrin *et al* /9/ if the same set of parameters is used.

The measured spectra were recorded using 100 μm monochromator slits. Because of low intensities, smaller slits could not be used. Larger slits would have resulted in a very poor resolution.

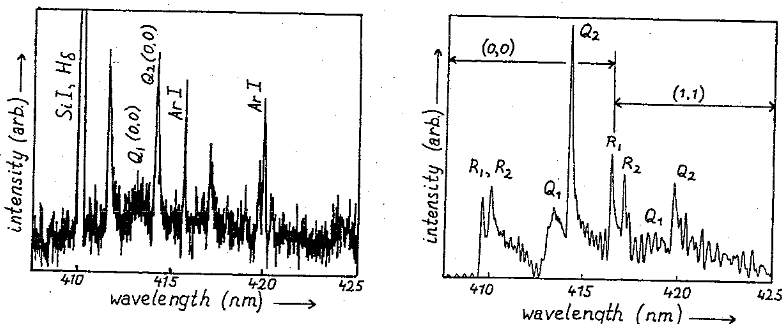


Figure 3. SiH molecular spectrum measurement (left) and simulation (right).

Figure 3 shows the registrated SiH spectrum and its simulation, using the appropriate HWHM value (0.06 nm) and $T_{rot} = 4000$ K, and $T_{vib} = 5600$ K. Several factors caused comparison between measured and simulated spectra to be difficult. First, the signal–to–noise ratio is rather poor. Furthermore, atomic lines of Ar I, Si I, and H I are present in the SiH region. Especially the argon lines near 420.0 nm and the very strong Si I/Hδ combination around 410.0 nm make comparison difficult as they coincide with prominent features (the (0,0) R–branches heads around 410.0 nm and the (1,1) Q_2 branch head at 419.8 nm) of the SiH spectra. Some band–like features not seen in the simulations are measured around 411.7 and 420.4 nm. These might be attributed to impurities: e.g. SiN. One general reason for differences between simulations and measurements may be the absence of a Boltzmann–like distribution over the rotational

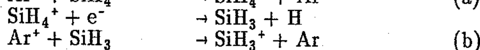
and vibrational energy levels in the first excited state of the molecular system.

The above discussion is a summary of the problems associated with the comparison of calculations with the measurements, and thus with the determination of T_{vib} and T_{rot}, as these temperatures are determined using *relative peak heights* within one simulation or measurement /9/. As the disturbances *increase* the heights of the band heads, the values for T_{rot} and T_{vib} as used in the simulation in figure 3 (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_{rot} and T_{vib} /5/.

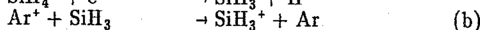
DISCUSSION

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 (fig. 2). Because the rate constants for ionization and dissociation become very small for these low T_e values /14/ we can presumably neglect the effect of electron collisions in the dissociation and ionization processes. The results can be explained by considering the following *charge exchange/ dissociative recombination* reactions:

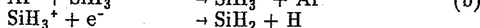
$Ar^+ + SiH_4 \rightarrow SiH_4^+ + Ar$ (a)



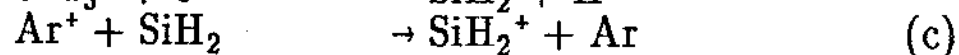
$SiH_4^+ + e^- \rightarrow SiH_3 + H$



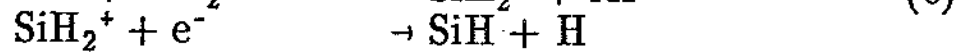
$Ar^+ + SiH_3 \rightarrow SiH_3^+ + Ar$ (b)



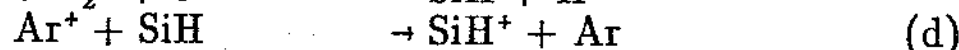
$SiH_3^+ + e^- \rightarrow SiH_2 + H$



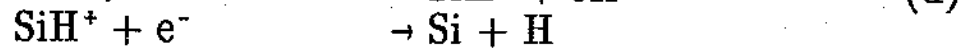
$Ar^+ + SiH_2 \rightarrow SiH_2^+ + Ar$ (c)



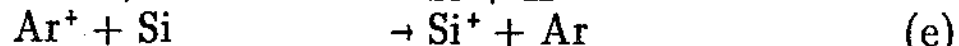
$SiH_2^+ + e^- \rightarrow SiH + H$



$Ar^+ + SiH \rightarrow SiH^+ + Ar$ (d)



$SiH^+ + e^- \rightarrow Si + H$



$Ar^+ + Si \rightarrow Si^+ + Ar$ (e)

+

$$5\,Ar^+ + SiH_4 + 4\,e^- \rightarrow Si^+ + 4\,H + 5\,Ar \qquad (4)$$

Rate coefficients for the charge exchange reactions with Ar^+ are usually very large (typically a few $10^{-15}\ m^3/s$ if there is a good energy match between the exchanging levels) and these processes are expected to be much faster than electron processes in the expansion. The dissociative recombination processes following the charge exchanges have even larger rate constants (a few times $10^{-14}\ m^3/s$). Furthermore, the radicals, atoms, and ions formed by these reactions can appear in excited states and this probably explains *the very existence* of the observed emission spectra from Si and Si^+ particles at such low electron temperatures and electron densities.

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 ($(3s)^2(4s)$) nearby the Ar ionization potential. We observed the emission originating from the $(3s)^2(4p)$ excited state of Si^+, giving us confidence in this view. As the proton has no electronic energy levels, resonant processes are impossible, resulting in low rate coefficients for the reaction $Ar^+ + H \rightarrow Ar + H^+$.

If we assume the expanding arc plasma in argon to have an initial ionization degree of about 10 % /6/ and we inject about 0.8 % SiH_4, this results in 0.8 % silicon ions if the above reactions (4) are dominant, at the maximum cost of 5 Ar^+ ions per Si^+ ion, i.e. when the reaction chain (4) does not skip any steps. This leaves an Ar^+ ion fraction of about $10 - 5 \cdot 0.8 = 6$ %, that is if no other ionization losses occur. As we find an n_{Si^+}/n_{Ar^+} ratio of 1/2, while the H^+ fraction is negligible, some additional losses are to be concluded. A possible Ar^+ loss process is a direct charge exchange with hydrogen molecules, i.e. (a) $H_2 + Ar^+ \rightarrow ArH^+ + H$, followed by (b) $ArH^+ + e^- \rightarrow Ar + H^*$ /15/. Rate constants for these reactions are about $10^{-15}\ m^3/s$ for step (a) and very large, about $10^{-13}\ m^3/s$, for step (b). As the hydrogen produced in step (b) may appear in excited states, these reactions may well account for the hydrogen emission observed. The hydrogen molecules necessary for reactions (a,b) may originate from the walls of the steel vacuum vessel, as the machine produces hydrogen by the reactions (4) during operation and it is known that hydrogen may stick to the steel walls and enter the

plasma again. Similar reactions could also occur with argon ions and radicals, e.g. $Ar^+ + SiH_2 \rightarrow SiH^+ + H + Ar$. Another cause for a decrease in ionization degree may be found in volume effects (expansion). This is observed in a pure argon expanding arc plasma by Thomson scattering measurements /4/.

CONCLUSIONS

The expanding argon arc plasma jet 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 150 mm from the nozzle) in the range of $1\text{–}2 \cdot 10^{18}\ m^{-3}$ and emission by Si, Si^+, H, Ar, and SiH particles. Electron temperatures are about 5000 K. Estimates for the vibrational/rotational temperatures of the emitting SiH radical ($T_{rot} \lesssim 4000$ K, $T_{vib} \lesssim 5600$ K) seem to confirm this value.

To explain the observed density ratio for silicon and argon ions (1:2) a reaction chain (4) leading to the production of Si^+ ions by charge exchange and dissociative recombination may be considered. In this view, the argon ions coming out of the arc are some kind of a "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.

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