Spectral behavior of cascade arc plasma jet in Ar/H2/SiH4

SPECTRAL BEHAVIOR OF CASCADE ARC PLASMA JET IN $Ar/H_2/SiH_4$

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ABSTRACT

The emission of $Ar/H_2/SiH_4$ plasma jet is studied in the spectral range 380-760 nm at 32 cm distance from nozzle. The spectra are dominated by the H atomic lines but Si lines and in a smaller measure Ar lines are still detected. The molecular SiH radical bands are well developed. They are compared with computer simulated spectra and the rotational and vibrational temperatures in plasma expansion are found.

INTRODUCTION

In the last years many works outlined the advantages of expanding plasmas for deposition, etching, treatment. Particularly their use for a:C-H, graphite, diamond deposition /1/ has proved that the optimization of the three deposition phases (dissociation, transport, deposition) can be performed independently because of spatial separation. By instance high quality material at high growth rate (up to 1 μm/sec for graphite) has been obtained. In the same way a:Si-H films have been produced having refractive index similar to normal deposited films /2/. Nevertheless the mechanism of deposition is not well understood, as the expanding plasmas are generally recombining plasmas, very different from the usually ionizing plasmas to which the most works were devoted.

The present work is a step in the attempt to understand better the physico-chemical conditions in which deposition takes place. It must be seen correlated with the already performed spectral study on Ar/SiH_4 expanded plasmas /3/.

EXPERIMENTAL

The set up consists of a cascade arc plasma jet generator and a spectral measuring system.

The cascade arc was largely described before /3, 4/. An arc channel is created between three tungsten-thorium cathodes and an anode nozzle which are separated by a stack of cooled cooper disks having role in the stability of the arc. The thermal plasma generated in arc (T=10000K, p=0.1bar) expands supersonically into a vacuum vessel maintained at low pressure (p=0.1-1mbar) by a series of roots blowers and a roughing pump. After passing a shock wave appeared just downstream the nozzle, the plasma flow is subsonic/4/.

The gases are introduced in the plasma generator in different places. The discharge is sustained mainly in Ar and H_2 is added in the last part of the arc column. Downstream after the nozzle exit the SiH_4 is injected.

The spectral measuring system consisting of a focusing lens, optical fiber, monochromator ,photomultiplier works in the photon counting mode. By cooling the photomultiplier enough low dark counting levels were obtained (less than 10c/s). The dynamic range for the optical detection covers about 5 decades.

The spectra were recorded at 32 cm distance from the nozzle just in front of sample holder.

RESULTS AND DISCUSSION

The most results will be presented have been obtained in the following experimental conditions: arc current I=75A, background pressure in expansion p=0.5mbar, gases flux (in sccm) $Ar/H_2/SiH_4$=60/10.4/0.35.

A) Atomic lines

case a) Ar fed jet

Practically all atomic Ar lines present in the spectral tables are exhibited by the emitted spectrum of the expanded plasma when the arc is run only in Ar. Besides traces of H atomic lines (Hα, Hβ, Hγ) and Si (390.5nm) are evidenced, probably due to the H_2 molecules desorbed from the walls of the reactor and to the contamination with previously synthesized Si powder.

case b) Ar/H_2 fed jet

It is known that the effect of adding H_2 in the Ar column consists in the extinction of argon lines and emphasis of H atomic lines originating even from high quantum levels n>15. However in our case some Ar lines are still visible in the long wavelengths region of the spectra (at 696.5, 706.8, 714.7, 738.4, 750.4, 751.4 nm).

case c) Ar/SiH_4 fed jet

Results of spectral behavior of expanded plasma in Ar with SiH4 added have been already presented in the case of 15 cm distance from the nozzle /3/. In that paper the atomic emission of Si, Ar, H, from the recombining plasma was used to find ions $[Ar^+]/[Si^+]$ and $[H^+]/[Si^+]$ ratios.

The same general emission characteristics were found in our case at 32 cm distance from the nozzle (Figs. 1a, 1b):

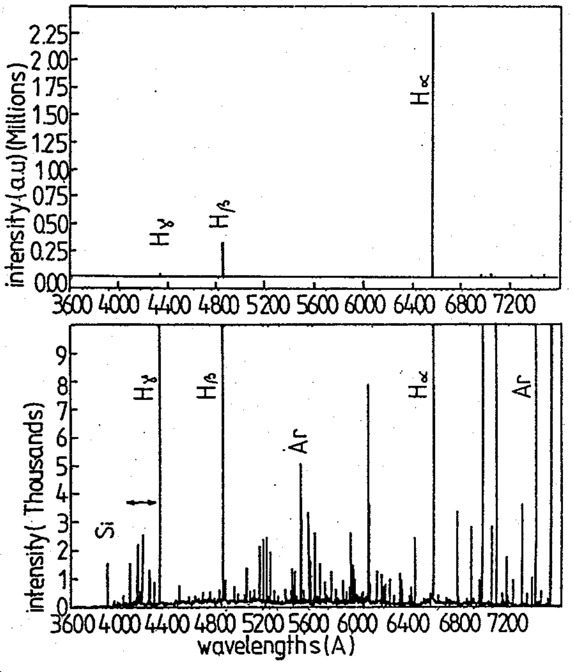

Fig.1 Spectra of Ar/SiH_4 plasma jet

a) Global view

b) Low intensity range

The spectrum is dominated by the atomic hydrogen emission consisting of Balmer series lines (n<10). The atomic Si lines are present, the most intense being Si at 390.5 nm. Nevertheless at this distance their intensity is generally small and sometimes their identification is difficult as they are closed to the strongest Ar lines in which the spectrum is abundant. In the spectral range 405.0-435.0nm the molecular spectrum of SiH radical corresponding to $A^2\Delta-X^2\Sigma$ electronic transition is observed, but is strongly polluted by the H-Si combination at 410.2 nm and the persistent Ar lines at 415.9, 416.4, 418.2, 419.1, 420.0 nm.

case d) $Ar/H_2/SiH_2$ fed jet

The spectra recorded from expanded plasma in $Ar/H_2/SiH_4$ mixtures (Figs. 2a and 2b) exhibits new features by comparing with previously presented cases. As a general observation the total intensity of spectrum diminishes approximately two orders of magnitude. The prominent fact is Ar atomic lines are considerably week and only the most intense can be observed where the transmission of the spectral system is high enough (λ>450nm).

By comparing spectra in cases c) and d) is to be notified that H_2 addition on Ar/SiH_4 mixture decreases considerably the H atomic line emission. The H lines begin to be observed starting with n=8 being comparable with their intensity in Ar/H_2. Thus it appears that H_2 addition on Ar/SiH_4 plasma has a quenching effect on the process responsible for excited H production.

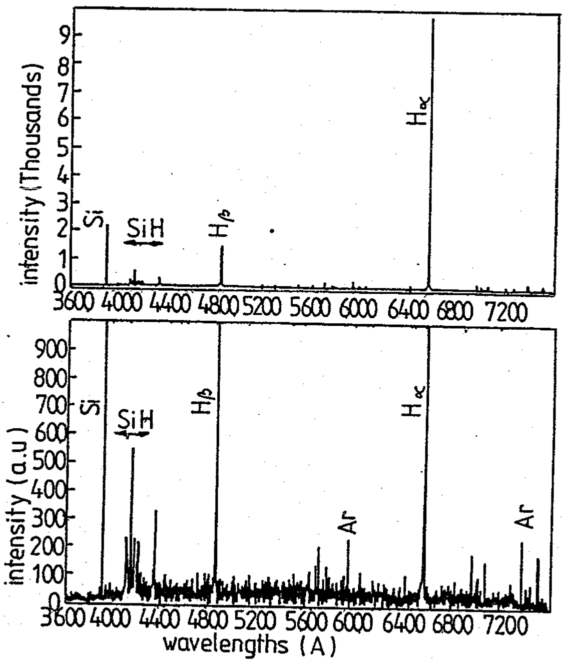

Fig.2 Spectra of $Ar/H_2/SiH_4$ plasma jet
a) Global view
b) Low intensity range

The same Si, Si^+ as in Ar/SiH_4 spectrum seems to be observed in the $Ar/H_2/SiH_4$ case having the intensities half the case before. Due to the weakness of Ar lines it is easier to be observed now. Nevertheless an atomic spectroscopy diagnostics based on SI, Si^+ lines is hardly to be done and probably needs large monochromator slits and long acquisition times.

B) Molecular bands

By comparing spectra in cases c) and d) in the 405.0-425.0 nm spectral range where the SiH radical radical emission appears, is observed that the molecular spectrum is cleaned of the polluting effect of Ar and H atomic lines. So the recorded molecular spectra of SiH radical from $Ar/H_2/Si_4$ plasmas can be used for diagnostic purposes. In the following the attention will be focused on this subject.

A detailed description of the characteristics of $SiH(A^2\Delta - X^2\Pi)$ molecular spectral system can be found in /5/. In the spectra are prominent the peaks (Fig. 3):

$R_1(0,0)$: 409.6 nm

$R_2(0,0)$: 410.1 nm

$Q_1(0,0)$: 413.4 nm

$Q_2(0,0)$: 414.2 nm

$R_1(1,1)$: 416.5 nm

$R_2(1,1)$: 417.2 nm

$Q_1(1,1)$

$Q_2(1,1)$: 419.8 nm

As the usual Boltzmann diagram method to determine rotational and vibrational temperatures cannot be used in cases of strong overlap of rotational lines combined with a moderate resolution of the spectrometer one appealed to the method of comparing the recorded spectra with computer simulated spectra.

The procedure to simulate the SiH spectra was similar to that used in /4/. The simulated spectra are dependent on three parameters: Trot, Tvib, HWHM (half width at half maximum).

How the changes of the values of parameters Trot and Tvib are reflected by the simulated spectra is shown in Figs. 4a and 4b only are normalized with respect to $Q_2(0,0)$ band height. The important fact arises is in the spectral range 405.0-416.0 nm the normalized simulated spectra ar quite independent on the vibrational temperature.

In practice the apparatus profile (HWHM) is given as a characteristic of the spectrometer. A method based on the so named "thermometric lines" /8/ can be used to compare the simulated and experimental spectra and to find the

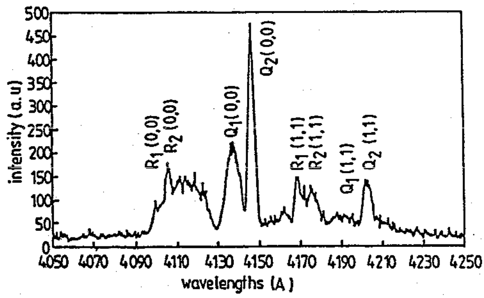

Fig.3 Molecular bands of SiH radical (from $Ar/H_2/SiH_4$: 60/10.4/0.35 sccm)

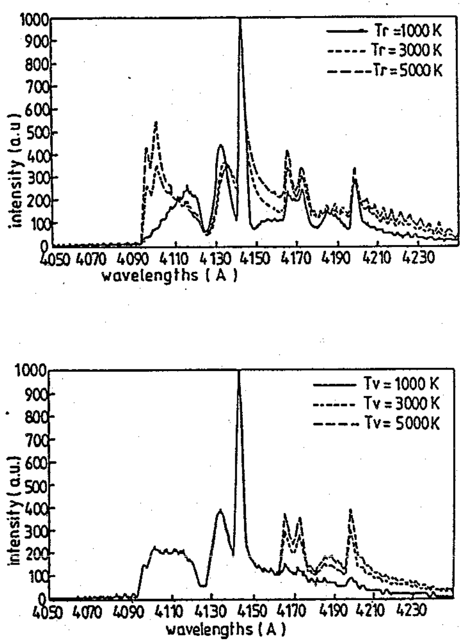

Fig.4 Simulated spectra of SiH radical emission

a) rotational temperature effect

b) vibrational temperature effect

rotational and vibrational temperatures.

On the basis of previous observation the normalized spectrum is dependent only on a parameter (Trot) on a limited spectral range one can use a χ^2 minimizing method to find Trot and Tvib.

One choose as input data values presumed (from visual inspection) for the parameters: Trot,o and Tvib,o. A χ^2 minimizing procedure, dependent only of one parameter (Trot or Tvib) was built up to fit, on a variable wavelength interval, the simulated spectra with the experimental ones. This procedure was first applied on the limited interval where spectra are dependent only on rotational temperature to find the best value for Trot. Afterwards it was applied on the whole wavelength interval to find the best value for Tvib. Subsequently these steps were repeated in an iterative manner.

As a typical example, for an expanded plasma having working parameters, I=75A, p=0.5mbar, Ar/H2/SiH4 flux values 62.0/10.4/0.35 sccm the values Trot=2500K, Tvib=4200K were found

The method has the advantage to use clean, free of disturbing foreign emissions, parts of spectra. Besides making use of large portions, instead of thermometric lines ,is less sensible to calibration and background errors and have to deliver the most reliable results in such situations. However because the simulated spectra are only slightly dependent on vibrational temperature, in the cases Tvib is high (Tvib>5000-5500K) the minimum of χ^2=f(Tvib) curve tends to become flat and the precision of the method decreases.

CONCLUSIONS

Regarding the mechanisms of excitation of atomic lines it is generally accepted that in Ar seeded recombined plasmas the main chemical source is argon ionization in the flow emerging from the arc.

In the case of H_2 seeded arc cascade Ar plasmas a charge exchange/dissociative recombination channel in which Ar^+ and H_2 species are involved (Ar^+-H_2 channel) can explain the emission of Balmer lines and extinction of Ar lines/3/.

In the case of SiH_4 seeded plasmas the emission of H lines is also strong and cannot be explained only by contribution of H_2 molecules desorbed from walls (this contribution is seen to be small in spectra obtained from Ar only). So a different channel of excitation of H lines in which are probably involved Ar^+ and SiH_4 species (Ar^+-SiH_4 channel) must be considered.

As the H_2 addition decreases the H emission of Ar/SiH_4 plasma the Ar^+-SiH_4 channel is more efficient in H excitation than the Ar-H_2 channel.More details on this mechanism could be obtained from a comparative study of intensity distribution of Balmer lines in Ar/H_2 and Ar/SiH_4 recombining plasmas.

The Si, Si^+ emission is only slightly dependent of H_2 addition. This fact suggests that excited H and Si production are based on on different mechanisms; probably Ar^+ is not directly involved in Si excitation, but a dissociative recombination channel for ionized radicals could be assumed.

The rotational and vibrational temperatures are correlated respectively with the translational temperature of heavy particles and the electron temperature in plasma. The values obtained are in good agreement with other measurement techniques used for the same type of plasma /7/ and with similar measurements performed on Ar seeded with CH_4 plasmas/8/. A nonequillibrium effect (Trot<Tvib) is to be noted. Nevertheless a complete and systematic study of the dependence of these plasma parameters on working conditions must be done.

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