IS VISIBLE SPECTROMETRY A RELEVANT DIAGNOSTIC IN SILANE PLASMAS ?

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ABSTRACT

Visible emission from a pure silane plasma was analyzed in a multipole discharge. Emission from H, Si, Si^+, SiH and SiH^+ was identified and is demonstrated to result from the dissociation of excited and superexcited states of silane produced by electron impact. Cross sections for the photoemissive processes were measured. The utility of emission spectroscopy is discussed.

1. INTRODUCTION

Reactive plasmas are widely used for amorphous silicon thin film deposition(1). Pure or diluted silane is used, occasionally with minority doping gases added. Plasma emission spectroscopy is a widely used (2-5) tool for characterizing the plasma state and correlating it with the thin film properties. Such a technique is non-intrusive, requiring only an observation window and a spectrometer. Furthermore, spectrum analysis allows ready identification of the emitting species, as well as the presence of impurities (2). However, interpretation of relative species densities from relative line amplitudes is fraught with difficulty. This paper reports an analysis of emission processes in a basic research oriented device : a multipole dc discharge (6) fed with pure silane.

2. EXPERIMENTAL CONDITIONS

A schematic of the experimental arrangement is shown in fig. 1. Typical experimental parameters (7) are : base pressure 5×10^{-7} Torr, operating pressure 0.1-3m Torr, plasma density $0\text{-}1 \times 10^{10}$ cm^{-3}, flow rate 1-50 cc/min. Besides sustaining stable discharges at low pressures, a unique feature of multipoles is their electron distribution function. The primary electrons emitted by the hot filaments are accelerated by the sum of the applied voltage and the plasma potential, thus acheiving energies from 17 eV up to 65 eV with less than 4 eV energy spread. The secondary electrons are rapidly cooled by inelastic collisions, hence, at least at low pressures (below 0.7 m Torr) they play a negligible role in the plasma activation processes. The emission spectrum in the visible and the near uv was recorded with a 70 cm focal length grating monochromator. The system spectral response was calibrated with a tungsten lamp. As already reported (2) the spectrum contains :

- The atomic hydrogen Balmer series.
- SiH, $A^2\Delta\text{-}X^2\pi$ band emission in the blue. Using a simulation technique(5), anomalous rotational temperature ($\sim 2000°$ K) and vibrational temperature ($\sim 4000°$ K) were inferred for the emitting SiH free radicals.

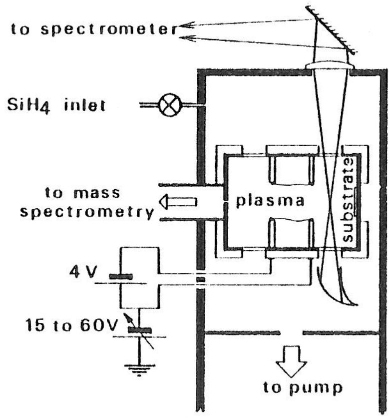

Fig. 1 - Experimental arrangement

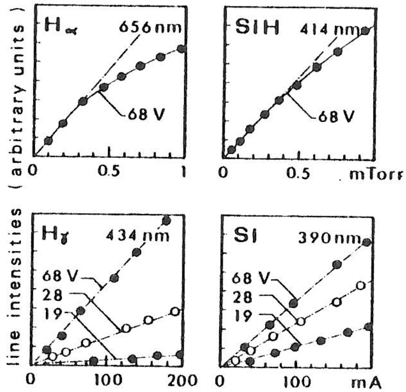

Fig. 2 - Various emission intensities as a function of pressure (60V-80mA) and current (0,5 mTorr)

- Various atomic silicon lines, in particular those emitted from the $4s\,^1P^o$ level.
- Various molecular hydrogen bands observed at low flow rate.
- The SiH^+ band system corresponding to the $A^1\pi - X^1\Sigma^+$ transition with anomalous rotational temperature ($\sim$ 700°K). Another SiH^+ band, heretofore not observed (8), is attributed to $B^1\Sigma - A^1\pi$ transitions.

This work has also identified emission from the $4p\,^2P^o_J$ states of the ion S_i^+.

3. EMISSION ANALYSIS.

In order to understand the physical processes leading to emission, the spontaneous light intensity was monitored as a function of primary electron current and silane partial pressure. Fig. 2 shows that measured line intensities are proportional to both current and pressure, for all lines exept the H_2 bands. This functional behaviour implies that Si, Si^+, SiH, SiH^+ and H emission stem from a primary excitation process involving only one primary electron and one silane molecule. This well known process has been widely studied for H_2(9-11) and various hydrocarbons (12-15), it relies on the creation, by electron impact, of an excited or superexcited state SiH_4^{**} (some of these states are known from uv absorption). These states are repulsive leading to molecular dissociation through many possible channels. Some dissociation fragments are produced in excited electronic states which subsequently emit one or a cascade of photons. It is claimed that all the lines observed in this silane plasma originate from such a process. This explains the high vibrational and rotational excitations of SiH and SiH^+. The H_2 band intensity varies as the current squared implying that i) SiH_4^{**} does not decay into H_2^* (ii) the emission is due to electron impact on stable H_2 resulting from the dissociation of silane. Indeed, high pumping rates reduce H_2 emission to negligible levels.

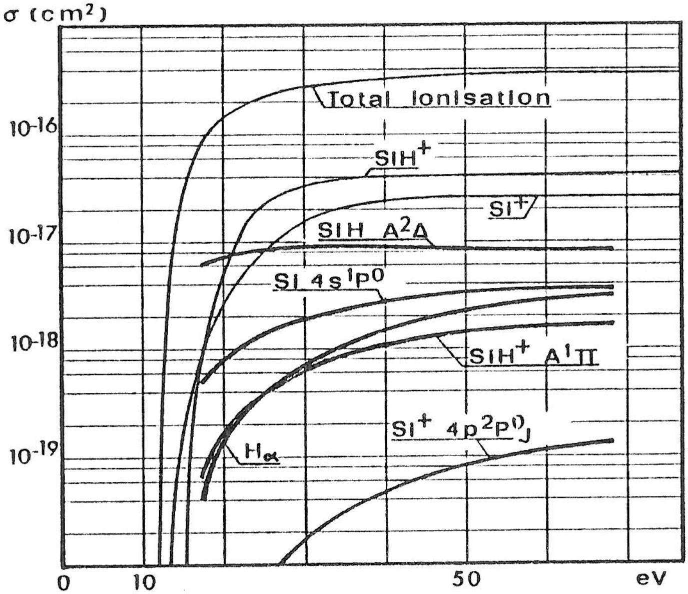

Fig. 3 - Electron impact on silane : measured cross-sections for photo emission from the specified energy levels of SiH, Si, SiH^+, H and Si^+ (thick lines); total and partial ionisation cross-sections from ref. [15] (thin lines).

From the observed emission data, cross-sections for various photoemissive processes were duduced. The system was calibrated with a H_2 plasma and the calibration procedure was checked to give proper values (13) with a CH_4 plasma. The results for SiH_4 are given in fig. 3 and are consistent with data obtained for CH_4 by De Heer (13).

4. CONCLUSIONS

In a dc multipole discharge, spontaneous emission in the visible range is a primary process closely related to ionisation or electron induced silane dissociation. It bears little relationship to secondary processes such as polymerisation or proton exchange, and reveals little about the actual composition of the flow reaching the substrate. The relative amplitudes of the lines are governed by the fast electron distribution function. An illustrative example is given in fig.4 where the relative amplitudes of the Balmer lines and the SiH bands are observed to vary drastically with primary electron energy. It is interesting to observe that the fast electron distribution function may be deduced from such emission spectra .Moreover, the absolute emission rates can be

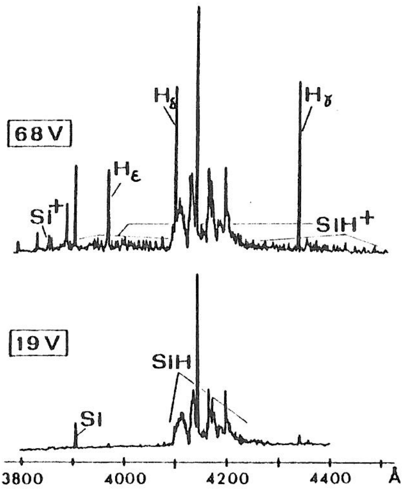

Fig. 4 - Typical emission spectra for 0.5 mTorr, 80mA discharge in silane and for 68 and 19 eV primary electron energy.

related to the ionisation rate and the dissociation rate within the plasma. To reach these goals, further studies are in progres in order to : i) measure the emission cross sections at low energy, ii) analyse the possible quenching effects at high pressures.

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