SPATIAL GENERATION PROFILES OF ACTIVE RADICALS IN PLASMA-ENHANCED CVD OF a-Si:H

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ABSTRACT

Spatially resolved Laser Induced Fluorescence and Optical Emission Spectroscopy were applied in an rf silane discharge, for the simultaneous detection of both ground and excited states of SiH radicals. Axial intensity profiles of these radicals were recorded under various conditions. The experimental observations indicate that the two radicals have different generation paths. LIF profiles are considered to represent the generation profile of all the ground state radicals and they were used as such in kinetic calculations.

INTRODUCTION

The deposition of electronic quality a-Si:H by plasma enhanced CVD has received considerable attention in the last few years, because of the large and continuously growing number of applications of this material.

In this context, considerable attention has been paid to the correlation of macroscopic plasma parameters to the film properties by means of a properly formulated mechanism, because a direct relation between the properties of the deposited film and all the externally set parameters is not possible. An essential part of this effort concerns the identification of the possible growth precursors and the analysis of their role in the elementary gas-phase and surface processes.

Plasma diagnostics have played an important role in providing insight and data for a realistic simulation of these processes. Thus, besides the identification of active species [1], some information about their number density [2] and behaviour [3] is now available. More specifically, spatially resolved optical diagnostics have proven their sensitivity and adaptability in plasma processes, and therefore they are a powerful tool for monitoring the production of reactive intermediates and their response to the variation of macroscopic parameters as well as the discharge geometry [4][5]. The application of laser induced fluorescence (LIF) and optical emission spectroscopy (OES) in silane discharges presents an additional interest because these measurements provide the only in-situ, non-intrusive, spatially sensitive information available. These methods were used, in the work presented here for the detection of ground (SiH) and electronically excited state (SiH*) silylidine radicals. The results obtained were used for the estimation of the energy and space dependence of electron collisional dissociation and dissociative excitation of silane and also for a simplified simulation of gas-phase kinetics.

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EXPERIMENTAL

The experimental arrangement, described in detail elsewhere [3], is composed basically by a diode-type stainless steel reactor with two round parallel electrodes (6 or 10 cm in diameter). The interelectrode distance can be continuously adjusted by moving the grounded electrode. The reactor vessel is equipped with four (5 cm in diameter) quartz windows, perpendicular to each other and to the reactor axis. The gas is fed from the centre of the rf electrode through a porous disk, whereas flow and pressure can be independently controlled. The rf electrode is connected to a 13.56 Mhz generator through an L type impedance matching network. Fluorescence and emission light from the sampled area are collected at right angles with respect to the laser beam, by an f=100 mm quartz lens and arestricted field optical fibre respectively. Axial intensity profiles are obtained by moving the reactor while maintaining constant optical path.

RESULTS AND DISCUSSION

In the present work spatially resolved LIF and OES have been employed for the simultaneous detection of both SiH and SiH* radicals, during the deposition of a-Si:H. These methods were used for recording axial intensity profiles between the two electrodes, in various working conditions. Thus, typical axial concentration profiles of SiH and SiH* are plotted in figure 1. Similar profiles have been recorded for pressures from below 20 mTorr to 400 mTorr (P_{SiH_4} < 100 mTorr) in pure silane and in mixtures with argon, helium and hydrogen.

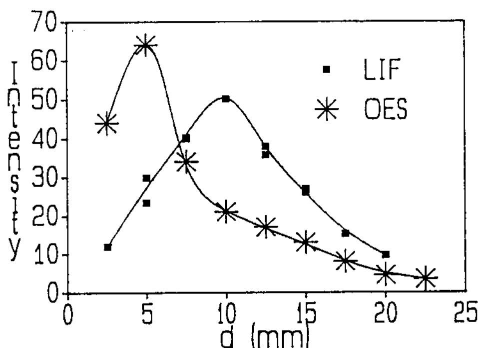
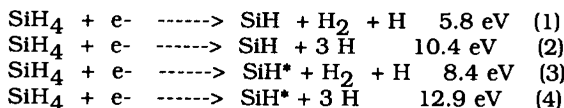


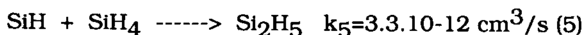
Figure 1 - LIF and OES profiles at 50 mTorr.
I(x) - Intensity (arb.units) as a function of sampled position (x).(x=0, rf) (x=25, ground).

These radicals are produced by one-electron inelastic collisions with silane, as confirmed by the linear dependence of their steady-state concentrations on rf power [6], according to the following reaction scheme (given with the radical formation thresholds).



$$SiH_4 + e^- \text{------>} SiH + H_2 + H \quad 5.8\ eV \quad (1)$$
$$SiH_4 + e^- \text{------>} SiH + 3H \quad 10.4\ eV \quad (2)$$
$$SiH_4 + e^- \text{------>} SiH^* + H_2 + H \quad 8.4\ eV \quad (3)$$
$$SiH_4 + e^- \text{------>} SiH^* + 3H \quad 12.9\ eV \quad (4)$$

After their generation electronically excited SiH* returns to the ground state by emitting a photon, whereas ground state SiH reacts with silane through reaction :



$$SiH + SiH_4 \text{------>} Si_2H_5 \quad k_5=3.3.10\text{-}12\ cm^3/s \quad (5)$$

The rate of this reaction is sufficiently high and dominates over diffusion, in the usual range of pressures. Moreover, since these radicals are highly diluted in silane, despite the large radical concentration differences in space, diffusional transport will take place with equal probability to all directions. This is the case because silane density is almost homogeneous in low depletion conditions. As a result, the intensity at a specific location of the interelectrode space will represent the relative generation rate of these radicals.

Furthermore, there are strong indications that SiH spatial profiles represent the stationary silane fragment generation profiles not only for SiH but also for other low energy radicals as silylene (SiH_2) and silyl (SiH_3). Considering the fact that most of the electron collisional dissociation of silane occurs by high energy 8-12 eV electrons, (considerably higher than the mean electron energy and above the radicals thermodynamic formation threshold [7]) spatial **generation profiles** for SiH_2 and SiH_3 should be very close to that of ground state SiH. However, the total concentration and spatial distribution of each radical is determined by its specific generation, reaction and diffusion rates. Thus their actual **concentration profiles** would be different. Therefore, an accurate estimation of their relative spatial abundance and their availability to surface processes is possible by using LIF profiles as the spatially distributed source of radicals.

On the contrary, the case of electronically excited state SiH^* radicals is not the same. Their spatial profiles present several differences compared to those of ground state SiH. Although they are also generated by one-electron collisions with silane, there is a considerable energetic difference (DE=2.5 eV) in their formation threshold, compared to their ground state counterparts. Accordingly, the experimentally determined appearance threshold of dissociative excitation (>10.5 eV) is much closer energetically to dissociative ionization (>11.9 eV) than to dissociation towards neutral radicals (>8 eV) [8]. This difference, in conjunction with the space variation of the electron energy distribution function (**eedf**) which is caused by the anisotropy of the electron swarm, induces a dissimilar space distribution and behaviour for SiH^*, compared to SiH.

Thus, as one can observe in the previous figure, LIF and OES maxima are located in different regions of the interelectrode gap. Furthermore, the position of the LIF maximum was observed to be insensitive to pressure, flow rate, dilution [3] or interelectrode distance variations [5], whereas the position of the OES curve maximum has been observed to change with pressure.

This phenomenon, observed also in non-reactive gases [9], indicates a close relationship of the SiH^* generation path with the sheath characteristics. Indeed, the sheath thickness decreases as pressure increases while the sheath potential increases as pressure decreases [10]. As a consequence, emission profiles present one maximum located near the sheath boundary, or two maxima located near each one of the sheaths depending on pressure, power density and gas nature. The transition between the two situations occurs at a pressure which is characteristic for each gas and coincides with the transition from the **alpha** to the **gamma** regime as a consequence of the change in the discharge sustaining mechanism [11]. For silane it is observed at partial pressures above 100 mTorr.

Additional evidence for the relation of SiH^* with the sheath is brought by the different trend of the emission intensity compared to LIF. Namely, SiH^* increases with pressure while at the same time SiH decreases. This is due to the fact that the electronic temperature is higher near the sheath compared to the bulk and this difference increases with pressure. In this case secondary electrons penetrate less in the bulk and consequently the generation rate of SiH^* will be higher as the pressure rises (higher collision frequency), whereas the generation rate of SiH will be lower and its depletion rate by collisions with silane (reaction 5) will be higher.

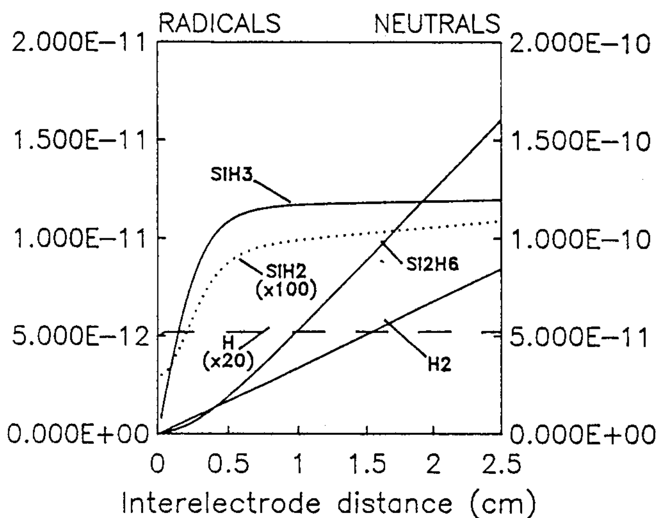
These differences in the behaviour of the two radicals lead to the conclusion that the production of SiH^* depends mainly on the sheath characteristics whereas the production of SiH depends on the power density in the bulk.

Recent experiments concerning the influence of the discharge geometry have brought additional evidence to this assertion [5].

Consequently, the different types of response of these two radicals to energy, space and density variations can lead to important conclusions concerning the variation of the **eedf** and the power dissipated by dissociation and dissociative excitation processes in low pressure silane discharges .

Recently Gallagher [7] and Kuznetsov [12] have used in their calculations emission profiles obtained from nitrogen discharges, as generation profiles of all the radicals. As already explained earlier, these profiles exhibit two maxima located near the electrodes and are probably close to the silane emission profiles in the **gamma** regime. But since the sheath sizes, and consequently the exact location of the maxima, depend on the nature of the gas, this assumption can induce some error in these calculations. The results of this group and the previous discussion suggest that, at least in the **alpha** regime, one should use LIF profiles instead of emission.

The use of the experimentally determined source of radicals in kinetic calculations can lead to a much simpler and accurate solution compared to the models that use simulated space-dependent electron edf. Thus, in the example presented in figure 2 LIF profiles have been used for the calculation of the relative abundance of the main intermediate and neutral products of the dissociation of silane. Mass balance equations for each of these species (neglecting diffusion terms) were integrated in space by approximating the interelectrode space to a plug flow reactor.



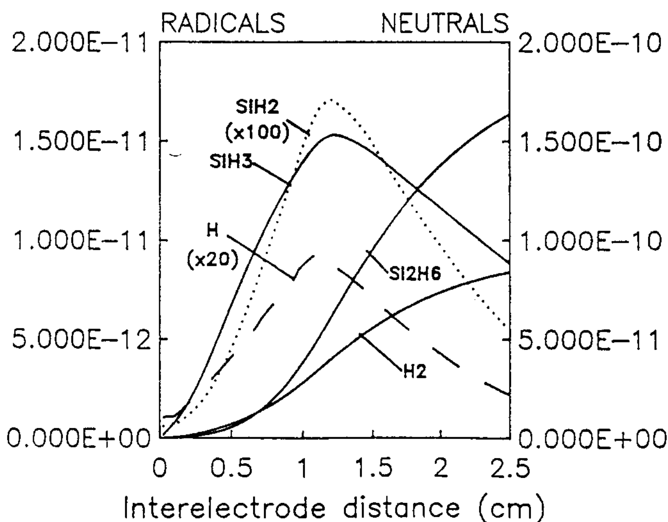


Figure 2 & 3 - Relative abundance of the species for homogeneous radical production and using LIF profiles (from figure 1) respectivelly.

The results obtained in this manner are significantly different than those obtained by using a homogeneously distributed source of radicals in space (figure 3). Two main differences can be observed between these figures. When using LIF profiles, fewer radicals reach the surface and, the SiH_3/SiH_2 flux ratio is two times higher. This is the case because the non-uniform production of radicals increases the importance of the fast second order SiH_3-SiH_3 reactions, in regions of high radical concentration, whereas the production of SiH_2 far from the surface diminishes the probability to reach it before the reaction with silane. If the pressure is increased these effects will be more pronounced although the total concentration of radicals will be higher.

CONCLUSIONS

Ground and excited state SiH radicals have different spatial distribution and different response to the discharge parameters. This is due to the fact that the generation rate of SiH^* is influenced by the characteristics of the sheath, whereas the generation rate of SiH depends mainly on the bulk power density.

It is suggested that LIF profiles can be used as the spatially distributed source of radicals at least in the discharge regime. The use of these profiles, instead of a homogeneous radical production in space, can increase the accuracy of kinetic calculations.

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