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THE ROLE OF CHAIN REACTIONS IN THE PLASMA DEPOSITION OF HYDROGENATED AMORPHOUS SILICON. A COMPARISON OF RATES.

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ABSTRACT:

Silane consumption rates in plasmas by primary and secondary processes are compared. The computations show that, under most conditions used for the plasma deposition of hydrogenated amorphous silicon, species arising from chemical chain reactions are more important in silicon transport than fragments directly formed on electron impact. The effect of assumptions required in calculating the latter rate are explored and the consequences of the model are examined.

1. INTRODUCTION

Efforts to understand the mechanism of glow discharge deposition of hydrogenated amorphous silicon (a-Si:H) have relied on diagnostic techniques [1-5] to observe the numerous species present in the SiH_4 plasma. Many of these species have been shown individually sufficient to produce a hydrogenated silicon solid. Nevertheless, the mechanism of the plasma deposition of a-Si:H remains the subject of controversy.[6].

It is the purpose of this paper to demonstrate that insight on the deposition mechanism of hydrogenated amorphous silicon (a-Si:H) can be gained by inspecting the consumption rates of SiH_4 by various species in the plasma. We base our considerations on typical plasma conditions used in our a-Si:H deposition system (15.2 cm dia parallel plates, 2.0 cm separation, radial flow, $T_s=275$ °C; SiH_4 flow rate 10.0 sccm at 150 mtorr; 13.6 MHz RF resulting in a DC equivalent field of 13.4 V cm^{-1} and a power density of 1.5 mw cm^{-3}). The considerations should also hold, however, for other systems as long as the flow rate and absorbed power scale with the surface area exposed to the plasma.

More than 90 % of the silicon removed from SiH_4 in a typical plasma ends up as solid deposit as mass spectrometric analyses of the effluent show that the only volatile products (other than hydrogen) are small quantities of disilane and trisilane. The high yield of solid allows one to approximate the deposition rate (in units of atoms of silicon per second) with the removal rate of SiH_4:

$$\frac{d[a-Si:H]}{dt} \cong -\frac{d[SiH_4]}{dt} \qquad (1)$$

The right-hand side of equation (1) is, of course, the sum of the rates of parallel reactions between silane and various reactive species in the plasma. We propose to examine the significance of various routes for the deposition of a-Si:H by focusing our attention on comparing the more easily established consumption rates of SiH_4 by the various species.

2. SILANE CONSUMPTION RATE IN CHAIN REACTIONS

Chemical chain reactions of the type (2) are thermodynamically allowed as the replacement of two Si–H bonds with H–H and Si–Si bonds is thermoneutral or exothermic.[7]

$$A_j + SiH_4 \rightarrow A_{j+1} + H_2 \qquad \text{(Reaction 2)}$$

Here the subscript j denotes the number of silicon atoms in the chain carriers A. We use ionic reaction rates and neglect possible contributions from gas phase free radicals and from surface-bound chain carriers, thereby providing only a lower limit for the total silane removal rate in chain reactions. This is done mostly because of the contrasting availability of data for ionic versus radical reactions.

Exothermic ion molecule reactions are well known[8] to have large and energy independent reaction rate constants which are only weakly dependent on the exact composition of the ion. For reactions between silane and its fragment ions experiments show rate constants of several times 10^{-10} cm^3 sec^{-1} per molecule whether for thermalized ions[9] or $SiH_x{}^+$ ions of a few eV kinetic energy.[10]

Mass spectrometry of ions effusing from silane plasmas has measured high abundances of ions containing more than one silicon atoms.[2,3,11] The distribution of the ion abundances as a function of pressure led to a mechanism[2] which required that (i) Reactions 3 and 4 are the most rapid reactions of ions in the silane plasma, (ii) that their rates are not strongly dependent on the number of silicon atoms per ion, *j*, and (iii) that the ratio of the eliminative addition to charge or hydride ion transfer rates, k_3/k_4, is about 1/2.

$$Si_jH_k^+ + SiH_4 \rightarrow Si_{j+1}H_{k+2m}^+ + (2-m)H_2 \qquad \text{(Reaction 3)}$$

$$Si_jH_k^+ + SiH_4 \rightarrow Si_jH_{k+4-x}\bullet + SiH_x^+ \qquad \text{(Reaction 4)}$$

It follows that the rate constant of the most rapid exothermic reaction of any silicon containing ion with SiH_4 must be about the same magnitude as the measured rate constants of $SiH_x{}^+$ ions. This allows us to write the rate of silane removal by ions, instead of a sum of individual rates, as the product of an average rate constant, k_{IM}, with the number density of silane molecules, *N*, and with the number density of all ions regardless of their composition.

$$\text{rate}_{IM} = k_{IM}\, n_e\, N \qquad (5)$$

Because of the requirement of charge neutrality in the bulk of the plasma, we have replaced in equation (5) the number density of the ions with the equal density of electrons, n_e. For the numerical value of the rate constant we take the average of rate constants of $SiH_x{}^+$ ions adding SiH_4 available from the literature,[9,10] $k_{IM} = 3\times10^{-10}$ cm^3 sec^{-1}.

Note that silane consumed in the ionic reactions includes silicon transported to the wall (or substrate) by neutral silicon containing products of Reaction 4. Thus it allows for a-Si:H deposition at the cathode in DC discharges albeit at a reduced rate.

3. RATE OF ELECTRON IMPACT FRAGMENTATION

$$e^- + SiH_4 \rightarrow SiH_m + e^- + (H_2, H, H^-, e^-) \qquad \text{(Reaction 6)}$$

The set of fragmentation reactions (6) are primary sources of reactive fragments in the plasma, and they are important as they influence the steady state concentration of chain carriers. They need not, however, contribute a significant fraction of the silicon that is deposited as solid.

The consumption rate of SiH_4 by the above reactions can be written as equation (7) with the rate constant given[12] by (8).

$$\mathrm{rate}_{\mathrm{frag}} = k_{\mathrm{frag}}\, n_e\, N \tag{7}$$

$$k_{\mathrm{frag}} = \int_0^{\infty} \left(\frac{2\,\varepsilon}{m}\right)^{1/2} \sigma_{\mathrm{frag}}(\varepsilon)\, f(\varepsilon)\, d\varepsilon. \tag{8}$$

Here ε and m are the kinetic energy and mass of the electron, $f(\varepsilon)$ is the normalized electron energy distribution function, and σ_{frag} is the fragmentation cross section. Each of the above processes will contribute to the fragmentation cross section when the electron energy is above the endothermicity of the reaction.

In order to evaluate the rate constants, several approximations and assumptions need to be made:

(a) Distribution function. The best approximate explicit form suitable for typical plasmas in SiH_4 is the Druyvesteyn distribution function, $f_D(\varepsilon) = c_D \varepsilon^{1/2} \exp\left[-0.548(\varepsilon/\bar{\varepsilon})^2\right]$, where $\bar{\varepsilon}$ is the mean energy and c_D is a normalization constant. This is equivalent[12,13] to an approximation that assumes that the collision cross section, σ_t, is independent of energy and that in each collision electrons lose a constant fraction, λ, of their energy. In silane in the 0.1 to 0.5 eV range only a small variation (0.2 to 0.4) in λ has been found. In order to facilitate comparisons to earlier literature, we have carried out the computations in duplicate using both the mathematically more easily handled Maxwellian, as well as a Druyvesteyn distribution.

(b) Mean electron energy. Precise experimental values are not available for $\bar{\varepsilon}$ in RF silane plasmas under deposition conditions. Within the same approximation and with the same assumptions as needed for the validity of the Druyvesteyn distribution, theory predicts[13] an inverse dependence of the mean electron energy on pressure. Furthermore, assumption of reasonable values for parameters lead to theoretical estimate, for typical plasma conditions, of $\bar{\varepsilon} = 1.46$ eV. A reasonable range extrapolated from measurements under different conditions[14,15] appears to be 0.7 to 4 eV. We have chosen to treat $\bar{\varepsilon}$ as a parameter and have computed the fragmentation rates for a large series of mean electron energies.

(c) Fragmentation cross section. The cross sections for dissociation of SiH_4 into neutral fragments is assumed to vary with electron energy in a manner similar to CH_4 and CF_4[16] as illustrated in Fig. 1. The best estimates for the constants defining are shown in Table I and were arrived at as follows. In regime I, that is above the energy threshhold, E_I, corresponding to the endothermicity of the reaction, the cross section is assumed to be constant and equal to the sum of the cross sections observed[17] for dissociative attachement reactions resulting in SiH_x^- fragments. In regime II, that is above a threshhold corresponding to the onset of optical

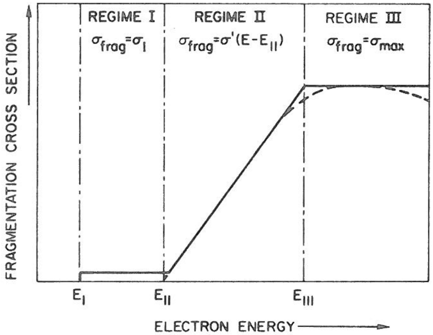

Fig. 1. Schematic energy dependence of fragmentation cross sections. Solid line: as assumed in the model; dashed line: typical experimental.

absorption to the first electronic excited state, we assume a linear dependence of the cross section on $\bar{\varepsilon}$ with a slope obtained by extrapolating to below 20 eV recent measurements of Perrin et al.[18] The Regime III (saturation) cross section is from Ref. 18. Note that assuming[19] that cross sections for all excitations for silane scale with methane with a factor of 6, as has been suggested for low energy excitations,[20] result in $\sigma'=1.46\times10^{-16}$ cm^2/eV, and $\sigma_{max}=24.6\times10^{-16}$ cm^2.

4. RESULTS AND DISCUSSION

Comparing equations (5) and (7) we note that as long as we wish to obtain only ratios of silane consumption rates by chain and electron impact reactions, we need not specify either silane or the electron number densities.

Results for computations with the best set of assumptions, namely the Druyvesteyn distribution with cross sections specified for SiH_4 in Table I, are shown by the solid line in Fig. 2. We observe that the electron impact fragmentation rate constant stays below the ionic chain rate constant (dash-dot line at constant 3×10^{-10} cm^3 sec^{-1}) until the mean electron energy exceeds 3.1 eV. Assumption of the less likely Maxwellian distribution (dashed line) predicts, for all values of the mean energy, higher but not drastically different fragmentation rate constants. With the Druyvesteyn distribution, at $\bar{\varepsilon}$ = 1.46 eV, which is the mean energy previously estimated for the "typical" silane plasma, the silane consumption by ions is seen to be about 30 times the electron impact fragmentation rate.

The change in curvature in the middle of Fig. 2 arises from the fact that at low $\bar{\varepsilon}$ contributions to k_{frag} from Regime I of the cross section predominate whereas at higher $\bar{\varepsilon}$ contributions from Regime II take over. We have also investigated how variations in the assumed parameters defining σ_{frag} in the three regimes influence the computed results.

Relatively minor effects on the conclusions are shown by substantial changes in the Regime I cross section (Fig. 3)

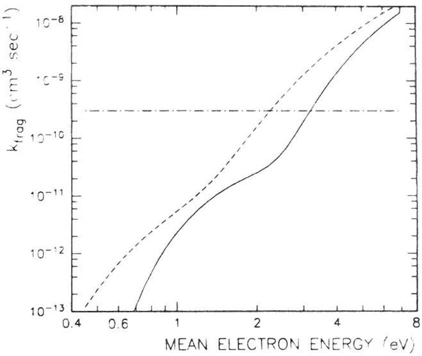

Fig. 2. Fragmentation rate constant of silane computed for a range of mean electron energies. Solid line: with best assumptions; dashed line: Maxwellian distribution. Also shown is (dash-dot line) the silane consumption rate constant in ion molecule reactions.

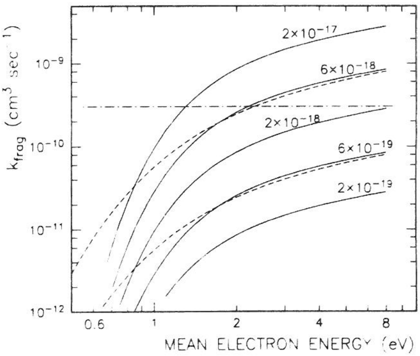

Fig. 3. Effect of the variation of the regime I cross section on the fragmentation rate constant, with $\sigma'=\sigma_{max}=0$. Solid line: Druyvesteyn, dashed line: Maxwellian distribution.

and by the Regime II threshhold (Fig 4A). Possible errors in the Regime III cross section have no significant effect. The mean electron energy at which k_{frag} reaches the value of k_{IM} is, however, rather sensitively affected by uncertainties in the Regime II σ' (Fig. 4B). This leads to the conclusion that precise experimental determination of the slope of the fragmentation cross section with energy in the linear regime should have high priority.

For the typical silane plasma with any reasonable set of assumptions the rate of silane consumption in ionic chain reactions exceeds the rate of SiH_4 removal by electron impact fragmentation. As we have shown, the ratio of these rates is a very sensitive function of the mean electron energy. Since $\bar{\varepsilon}$ depends on the pressure, it should be possible to find plasma conditions where one or the other mechanism predominates.

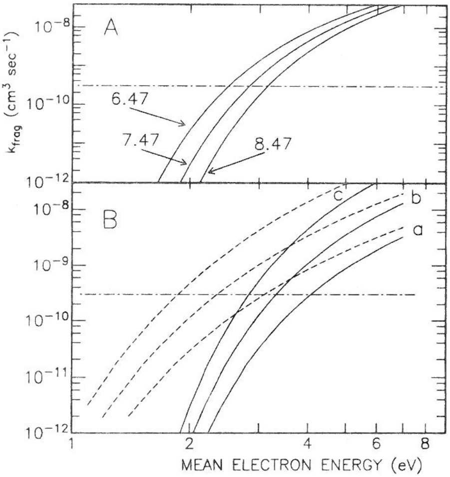

Fig. 4. Effect of the regime II parameters on the fragmentation rate constant. A. Variation of threshhold, with $\sigma_I=0$, $\sigma'=1.65\times10^{-16}$ cm^2/eV, and $\sigma_{max}=2.46\times10^{-15}$ cm^2. B. Variation of slope with $\sigma_I=0$, $E_{II}=7.47$ eV, $\sigma_{max}=2.46\times10^{-15}$; solid line: Druyvesteyn, dashed line: Maxwellian distribution. For the pairs of curves marked *a*: $\sigma'=1\times10^{-17}$, for *b*: $\sigma'=4\times10^{-17}$, and for *c*: $\sigma'=1.65\times10^{-16}$ cm^2/eV.

The high ionic chain vs electron impact silane consumption ratio implies only that species transporting the majority of silicon to the growing a-Si:H film are formed in ionic chain reactions, *not* that they are charged. This is because within the set of exothermic ion molecule reactions, on average the charge or hydride ion transfer reaction (4) has twice the rate of the addition elimination reaction (3).

There are two consequences of the model for plasma conditions where silane consumption is dominated by ion molecule reactions which are, at least in principle, experimentally verifiable. First, the size distribution of hydrogen-deficient neutrals must closely follow the size distribution of ions which is known.[2,3,11] Secondly, within the regime where the consumption of silane by ion molecule reactions is predominant, the a-Si:H deposition rate depends only on the ion (=electron) concentration and not on the mean electron energy. Consequently it predicts that in this regime a proportionality must exist between deposition rate and ion concentration even as the plasma conditions, such as pressure, that change the mean electron energy are varied.

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Table I

Constants defining the fragmentation cross section of tetrahedral molecules. Data for methane and carbon tetrafluoride are from Ref. 16, and for silane are the best estimate.

	E_I (eV)	σ_I (cm^2)	E_{II} (eV)	σ' (cm^2/eV)	σ_{max} (cm^2)	$E_{III}=E_{II}+\sigma_{max}/\sigma'$ (eV)
CH_4	3.66	$<1.0\times10^{-17}$	10.0	0.275×10^{-16}	4.1×10^{-16}	24.9
CF_4	1.83	$<2\times10^{-18}$	13.8	0.122×10^{-16}	5.55×10^{-16}	59.3
SiH_4	2.20	6×10^{-19}	7.47	0.47×10^{-16}	11×10^{-16}	23.4

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