THE DOMINANT REACTION CHANNELS OF PLASMA - INDUCED
SILANE DECOMPOSITION AND OF a-Si AND nc-Si DEPOSITION

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ABSTRACT
Chemical relaxation mass spectrometry and thermogravimetric measurements were used to study the kinetics of plasma-induced silane decomposition and of deposition of amorphous and nanocrystalline silicon, a-Si and nc-Si, respectively. The dominant mechanism of the gas phase silane decomposition is the electron impact induced fragmentation,
\[ \text{SiH}_4 \rightarrow \text{SiH}_2 + \text{H}_2 \] The hydrogen abstraction, \( \text{SiH}_4 + \text{H} \rightarrow \text{SiH}_3 + \text{H}_2 \) might be significant only under conditions of silicon etching. Ion impact induced decomposition on the surface of the growing film is the dominant mechanism of nc-Si deposition.

1. INTRODUCTION
The worldwide interest in the basic studies and applications of a-Si and nc-Si (the latter is sometimes called "microcrystalline") stimulated a number of studies into the kinetics and mechanism of silane decomposition. Turban et al [1-3] suggested that the silane fragmentation, \( \text{SiH}_4 \rightarrow \text{SiH}_2 + \text{H}_2 \) should be the dominant reaction channel also under plasma conditions as it is during thermal decomposition. More recently, Weakliem et al [4,5] claimed to have shown that the hydrogen abstraction, \( \text{SiH}_4 + \text{H} \rightarrow \text{SiH}_3 + \text{H}_2 \) is the dominant reaction path. We shall show that this conclusion is incorrect and that the original suggestion of Turban et al was justified.

Weakliem et al used NO as a "radical scavenger". From the observation that the formation of solid a-Si:H was suppressed by an admixture of NO to the silane discharge, they concluded that this is due to the scavenging of \( \text{SiH}_3 \) radicals by NO. However, a simple thermodynamic calculation shows that, in a mixture of gaseous silanes and any of the nitrogen oxides, the chemical equilibrium is far on the side of solid SiO\(_2\) (or SiO\(_2\)N\(_2\)). Indeed, silicon dioxide and -oxinitride films were deposited from a mixture of SiH\(_4\) and nitric oxide already many years ago [6]. (Weakliem et al also observed formation of such films during their experiment [5].) Furthermore, Weakliem et al used NO in the active discharge where it likely underwent excitation and dissociation (NO is thermodynamically unstable with \( \Delta F^0 \) (300K) = 20.7 kcal/mole). Thus, the suggested scavenging effect, \( \text{SiH}_3 + \text{NO} \rightarrow \text{SiH}_2\text{NO} \), cannot be considered as a proof of the mechanism by such an experiment.

In the present paper we shall report on results obtained by chemical relaxation mass spectrometry which allows one to follow the kinetics of the reaction directly on the real time scale. In addition it will be shown
that the deposition of nc-Si under conditions close to Partial Chemical Equilibrium, PCE, where the best quality films are obtained [7,8], is controlled by ion-impact-induced decomposition of silane on the surface of the growing film.

2. EXPERIMENTAL

The chemical relaxation mass spectrometric method was described in our previous papers where also details on the apparatus and results, to which we shall refer here, are given [9,10]. In the present paper we used, in addition, mixtures of silane and hydrogen as starting gas in order to compare the results obtained with pure silane, and with hydrogen and solid silicon.

The kinetics of film deposition was studied in an apparatus described in ref. [8] where also some preliminary results can be found. In both cases, a D.C. discharge was used.

3. RESULTS AND DISCUSSION

Figure 1 shows a typical relaxation response of silane and molecular hydrogen to a small, sudden change of the discharge current. It is seen that SiH₄ and H₂ show exactly the opposite response with the same relaxation time. This conclusion is valid for the whole range of SiH₄ concentration from pure silane to Partial Chemical Equilibrium which corresponds, under the discharge conditions of Fig. 1, to [SiH₄]₀ ≈ 0.3 vol% in H₂ [9]. Moreover, we have verified that this conclusion remained valid also if either mixtures of silane and hydrogen were admitted into the discharge ([SiH₄] > [SiH₄]₀ ≈ 0.3 vol%) or if hydrogen was allowed to react with solid silicon in the discharge tube ([SiH₂] < [SiH₄]₀ ≈ 0.3 vol%). Thus, during the first step of the plasma-induced decomposition of silane, H₂ is formed directly.

Only two reaction paths can be consistent with this result:

Electron impact fragmentation, eq. (1)

$$\text{SiH}_4 \xrightarrow{\text{e}^-} \text{SiH}_2 + \text{H}_2$$  

and hydrogen abstraction

$$\text{SiH}_4 + \text{H} \xrightarrow{} \text{SiH}_3 + \text{H}_2$$  

(2)

In order to decide which of these two possible mechanisms is dominant we consider the dependence of the reaction rate (which is in this case proportional to the inverse relaxation time, $1/\tau$) on the concentration of atomic hydrogen. This is independent of [H] in the first and directly proportional to [H] in the second case, eqs. (1) and (2), respectively.

Figure 2 shows the dependence of $1/\tau$ on the $t_\text{res}/t_\text{char}$ ratio for the case where pure silane was admitted into the discharge tube. It is seen that for $t_\text{res}/t_\text{char} \rightarrow 0$ the reaction rate does not approach zero as it should if hydrogen abstraction, eq. (2), were the dominant mechanism. Thus, electron impact induced fragmentation, eq. (2), is the dominant mechanism of silane decomposition under conditions far away from PCE where a-Si is deposited.

We are presently interested in further details of this reaction channel: Is a direct electronic excitation (via which states) or vibrational excitation and v-v pumping dominant? Both may operate at the observed time scale.

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The increase of $1/\tau$ with increasing $t_{res}/\tau_{char}$ might be partially due to reaction (2), but increasing (vibrational?) excitation of silane with its decreasing concentration (see Fig. 3 in ref. [11]) seems to be a more likely reason. Also this question requires further studies.

A similar conclusion applies also to conditions during silicon etching (i.e., when pure hydrogen is admitted into discharge tube covered with solid silicon, see Fig. 3 in ref. [11]), when $[\text{SiH}_4] < [\text{SiH}_4]_{\text{equil}}$.

We have shown earlier [12,8] that, under conditions close to PCE and at floating substrate potential, the deposition rate of nc-Si is directly proportional to the flux of low energy ions ($E < 10 \text{eV}$) towards the surface. More recently we have found that this proportionality remains valid also for deposition under negative bias $V_b \sim 0$ to $-300 \text{V}$. The data are summarized in Fig. 3. The proportionality factor of $0.5$ to $0.7$ is relatively high and it suggests that ion-impact-induced fragmentation of silane on the surface is the dominant reaction channel. (Here, we are discussing only the first step in a complex mechanism.)

Similar measurements were done also at other temperatures between 150 and 450°C. A very weak temperature dependence of the proportionality factor with an activation energy of about 0.7 to 1.5 kcal/mole was found. This finding lends a further support to the above suggested mechanism, in particular if the value of activation energy is compared with that found for thermal decomposition of silane at silicon surface of 16 to 18 kcal/mole [13].

At a more negative bias, $V_b < -300 \text{V}$, the proportionality factor decreases due predominantly to increasing sputtering of the deposited silicon. Indeed it was found that for $V_b < -100 \text{V}$ ion-impact-induced radiation damage is produced in the deposit [8]. More details will be published in a paper to follow.

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**REFERENCES**

SiH₄ admitted, far from PCE, p=0.7 Torr, T=200°C, $t_{res}=0.2\text{ s, } \tau_{char}=0.15\text{ s}$

Fig. 1: A typical relaxation response of silane and molecular hydrogen.
\[ \frac{1}{\tau} = \frac{A(K_H)}{B(K_H)} - C_{SiH_4} \]

\[ \text{SiH}_4 \xrightarrow{e^-} \text{SiH}_2 + \text{H}_2 \]

**Fig. 2:** Dependence of the inverse relaxation time, which is proportional to the reaction rate, of the first step of silane decomposition on the ratio of the residence time to characteristic time.

**Fig. 3:** Dependence of the deposition rate of nc-Si on the ion flux towards the surface. ● - floating potential \( V_b \) - negative potential \( V_b \sim -10 \) to \(-300\) V. 
\( T_{\text{substrate}} = 260^\circ\text{C}. \)