

PROCESS ANALYSIS AND MODELING OF THIN SILICON FILM DEPOSITION BY HOT-WIRE CHEMICAL VAPOR DEPOSITION

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ABSTRACT: A quantitative model of the Hot-wire Chemical Vapor Deposition of thin silicon films from pure silane is described and its results compared with experimental data. The model incorporates both the reactor design and reaction kinetics. Predicted results of the silane conversion and growth rate as a function of the residence time, pressure and wire temperature are in reasonable agreement with experimental data. Although insensitive to film structure, model results indicate a dependence of the film crystalline fraction on the ratio of the atomic hydrogen flux and the total silane radical flux.

Keywords: Modelling - 1: CVD Based Deposition - 2: Si-Films - 3

1. INTRODUCTION

The need to reduce manufacturing costs of c-Si wafer-based photovoltaic modules has attracted significant interest in thin film silicon technologies. By combining large area monolithic integration on low cost substrates and improved manufacturability, thin film silicon can become a lower cost alternative to c-Si. In theory, thin Si solar cells have also the potential to exceed the efficiency of thick Si solar cells due to reduced volume recombination, provided that successful light trapping and surface passivation can be achieved [1,2]. Therefore, by retaining properties of c-Si, thin film silicon can lead to cost reductions without sacrificing the performance and stability of the resulting photovoltaic modules.

Hot-wire Chemical Vapor Deposition (HWCVD) is a technique that has the potential to meet all of these requirements. Yet, after a decade of research, HWCVD remains largely undeveloped. Several research groups have demonstrated its use to deposit thin film polycrystalline silicon [3-7]. However, the deposition parameter space has been only sparingly covered, and because of the dependence of these results on the varying reactor configurations, experimental observations are difficult to compare and reproduce. Even if a more comprehensive body of empirical knowledge existed at the laboratory scale, it would not constitute the required basis for developing large-area manufacturing technology. A science and engineering framework that explains and predicts various laboratory results as well as translates a process from the laboratory to the manufacturing stage is therefore necessary. Building such framework requires quantitative modelling of the relationship between reactor geometry and processing parameters, on one hand, and the gas phase reaction chemistry and film growth on the other.

In this paper, a quantitative reactor-reaction model of a HWCVD process is presented. Model predictions of the reactant conversion and growth rate are compared with experiments as a function of the residence time, total pressure and wire temperature. Although, the model is insensitive to film structure, inferences are drawn relating the film crystalline fraction to the predicted gas phase

2. EXPERIMENTAL

Thin silicon films were deposited from pure silane onto 1 in² 7059 corning glass and single-crystal (100) silicon substrates. The depositions were carried out in a multi-wire HWCVD reactor which allows uniform deposition over a 6x6 in² area. The wire material was high purity Ta and its temperature was monitored with a dual-wavelength pyrometer focused onto the wire through a viewport. The depositions were performed at wire temperatures between 1550 to 1850 °C and reactor pressures between 25 to 700 mTorr. The silane flow rate varied from 5 to 60 sccm and was monitored by a mass flow controller. Independent heating of the substrates allowed the substrate temperature to be varied from 280 to 480 °C. The silane utilization, or conversion was calculated from the known inlet silane pressure and the outlet silane pressure measured by a mass spectrometer. The film growth rate was obtained both by measuring the film thickness and the weight gain on the substrates. The silicon film crystalline fraction was determined from Raman spectroscopy [8].

3. MODEL DESCRIPTION

3.1 Reactor Model

A schematic diagram of the reactor system is shown in Figure 1. For simplification purposes, the reaction zone in which the model is applicable was reduced to the volume bound between substrate holder and the filament holder (see Fig. 2). The wire is wound into five parallel strands, standing 1.6 in. from the holder and 1 in. from each other. Nine substrate samples on which the growth rate is measured are arranged into a 3x3 matrix, 1.4 in. from the wire strands. The area covered by both the substrate and wire holder is 6x6 in². The transport and conservation of gas phase species is modeled by one-dimensional diffusion coupled with reactions at the wire and in the gas phase. The boundary conditions are given by the incoming and outgoing fluxes of silane, measured by a mass flow controller and the mass spectrometer, respectively. A zero

starts in vacuum. Two fitting parameters are used to represent the cross-sectional area for diffusion and the total deposition area in the reactor zone, respectively. In order to assess the model predictions of spatial variations in the process, three different substrate positions along the direction of flow were selected. These positions, defined as inlet, center and exit, represent the three rows in the substrate matrix perpendicular to the flow direction.

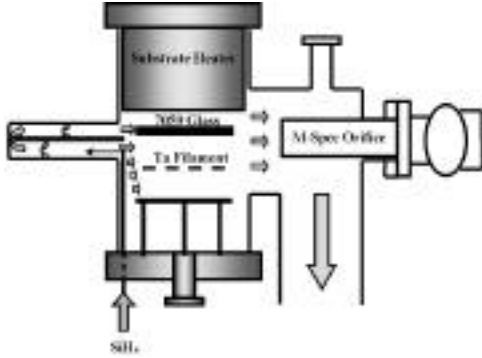


Figure 1: Reactor schematic.

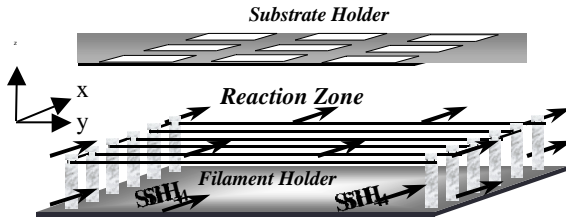


Figure 2: Modeled reaction zone.

3.2 Reaction Model

The reactions leading to Si film deposition from SiH_4 can be divided into three sets (see Table I): wire, gas phase and substrate kinetics. The wire is the initiator of the reaction chemistry and leads to the formation of only $\text{Si}_{(g)}$ and $\text{H}_{(g)}$ radicals. The remainder of the silane radicals are formed in the gas phase by hydrogen abstraction. Radical-silane reactions also form higher silanes (Si_2H_6) which lead to polymeric film formation. All radicals are assumed to lead to deposition on the substrate, and a solid-state reaction (rearrangement), although not part of the model, is included to qualitatively explain the influence of atomic hydrogen on the film crystalline fraction. The kinetic expression and rate constants for silane decomposition at the wire were obtained from a fit of experimental data. However, all other rate expressions and constants were obtained from the literature.

3.3 Model Assumptions

- All radicals are assumed to have short lifetimes (pseudo steady-state approximation). Thus, their net rate of generation is zero.
- The filament array is assumed to be a continuous plane of equivalent surface area.
- The gas phase temperature is assumed to have constant value of 150 °C for all conditions.

Table I: Reactions in the deposition of Si films from SiH_4 .

Silane cracking (wire):	$\text{SiH}_{4(g)}$	$\text{Si}_{(g)} + 2\text{H}_{2(g)}$
Hydrogen cracking (wire):	$\text{H}_{2(g)}$	$2\text{H}_{(g)}$
H abstraction (gas phase):	$\text{SiH}_{4(g)} + \text{H}_{(g)}$	$\text{SiH}_{3(g)} + \text{H}_{2(g)}$
Disproportionation (gas phase):	$2\text{SiH}_{3(g)}$	$\text{SiH}_{2(g)} + \text{SiH}_{4(g)}$
Polymerization (gas phase):	$\text{SiH}_{2(g)} + \text{SiH}_{4(g)}$	$\text{Si}_2\text{H}_6(g)$
Film deposition (substrate):	$\text{SiH}_{x(g)} + \text{H}_{(g)}$	$\text{SiH}_{x(ad)} + \text{H}_{(ad)}$
Rearrangement (substrate):	$\text{SiH}_{x(ad)} + \text{H}_{(ad)}$	$\text{Si}_{(s)} + (x+1)/2\text{H}_{2(g)}$

4. EXPERIMENT AND MODEL COMPARISON

4.1 SiH_4 Conversion

Figures 3 and 4 show a comparison of model predictions and experimental measurements of the silane conversion as a function of residence time and total pressure, respectively. Residence time is a reactor parameter which denotes the average time gas phase species spend in the reactor zone. Quantitatively, residence time is proportional to the reactor pressure and inversely proportional to the flow rate. In both cases, the model results are in good agreement with the experimental data. In the model, the effect of residence time is represented by the number of collisions a molecule undergoes while residing in the reaction zone. Therefore, the longer silane molecules remain in the reactor, the higher their probability of colliding with the wire or other radicals. Similarly, as the pressure increases, the rate of impingement of silane onto the wire also increases. At higher pressures, additional pathways become available for silane conversion, as the mean free path decreases and gas phase reactions become more probable. The effect of filament temperature on silane conversion (not shown) follows a similar trend as that observed for the residence time and total pressure. In this case, the probability of conversion increases as the energy transfer between the wire and silane molecules increases. For all conditions considered, conversion in this HWCVD process is at least a factor of two higher than typical conversions obtained in PECVD processes.

4.2 Growth Rate

In Figure 5, model and experimental results are compared for varying residence times at two pressures. In general, the growth rate increases with the process ability to break down silane (i.e., conversion) and the rate of silane supply. Since residence time is inversely proportional to the silane flow rate, the decrease in growth rate with increasing residence time simply represents a decrease in silane supply. Conversely, Figure 3 shows that the silane conversion increases over this range of residence time. Consequently, over the range of conditions considered, the growth rate is independent of conversion and limited by the supply of silane.

At higher pressures, Figure 5 shows that the growth rate decreases along the flow direction. As the pressure increases, the rate of silane radical collisions with the reactor surfaces increases. As a result, the film precursors are depleted faster near the reactor inlet. Furthermore, at lower residence times, depletion effects are exacerbated. This is caused by the increasing flow rate giving rise to a faster growth rate, and thus, a faster depletion rate. In fact,

on growth rate than the silane flow rate, and that the growth rate is controlled by the rate of silane decomposition. In other studies of HWCVD, silane is typically diluted in hydrogen at hydrogen to silane ratios between 50 to 100 [3,9,10]. For these cases, silane depletion effects will be greater at the same growth rates as with pure silane. Since the concentration of silane is lower, higher pressures and silane flow rates will be needed to obtain the same growth rate. As discussed, these are conditions that lead to increased depletion.

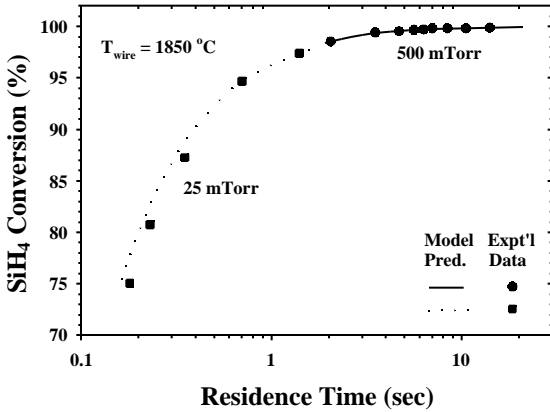


Figure 3: Silane conversion as a function of residence time.

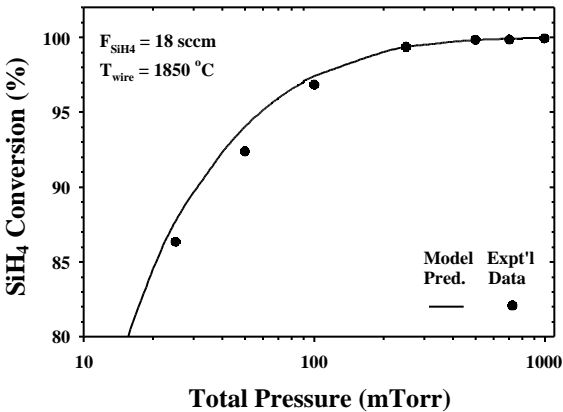


Figure 4: Effect of total pressure on silane conversion.

The effect of filament temperature on the growth rate is shown in Figure 6. The model and experimental data agree within the growth rate measurement error. The increase in growth rate with wire temperature is the result of the increase in conversion. The growth rate increases slightly with wire temperature. This change is parallel to that of conversion which changes only from 96 to 99 % over the temperature range considered. Again, the gradient in film thickness at higher filament temperatures results from silane depletion.

4.3 Radical Concentrations and Crystalline Fraction

Although the scope of the model does not include changes in film structure, a relationship between crystalline fraction and gas phase chemistry can still be elucidated indirectly. Model predictions of the gas phase composition indicate that the concentration of Si₁ is at least an order of

magnitude larger than the those of other silane radicals over all conditions considered. This result rules out the possibility of competing film precursors, leading to either crystalline or amorphous structure. It has also been proposed that the concentration of atomic hydrogen plays a role in determining film structure [11]. In Figures 7a-c, the variation of crystalline fraction (symbols) with residence time, total pressure and wire temperature, respectively, is shown. The effects are presented for substrate positions near the inlet, at center and near the outlet of the reaction zone, with the purpose of illustrating structural variations along the direction of flow. Model predictions of atomic hydrogen flux, which is directly related to the atomic hydrogen concentration, indicate an increase with the pressure and wire temperature. The results of Figure 7b-c show a similar trend for the crystalline fraction with the same variables. However, while the crystalline fraction increases with residence time (Fig. 7a), model results show a constant atomic hydrogen flux. Therefore, changes in the atomic hydrogen flux alone can not explain the observed variation in film structure.

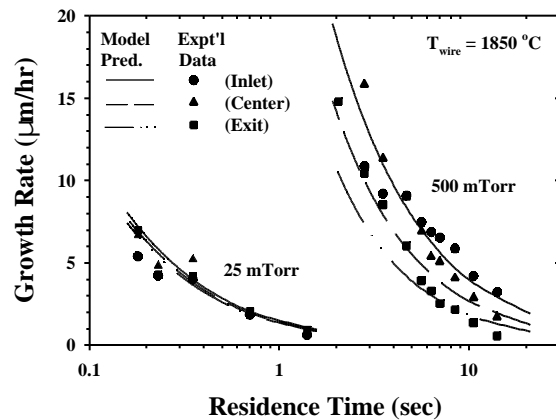


Figure 5: Growth rate variation with residence time and total pressure.

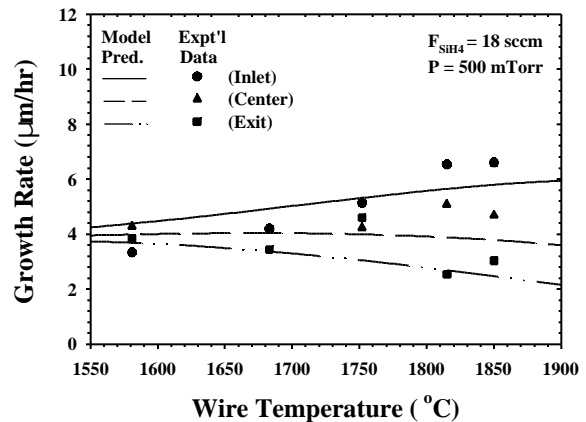


Figure 6: Growth rate as a function of wire temperature.

Because the effect of atomic hydrogen occurs on a growing film, the rate of arrival of new precursor species must also play a role in determining film structure. In Figure 7, the ratio of the atomic hydrogen flux to the total silane radical flux, R_H/R_{dep} , predicted by the model (lines)

It is important to note that since all radicals lead to deposition, the total silane radical flux (R_{dep}) is essentially the deposition rate. Clearly, for all cases the crystalline fraction increases with R_H/R_{dep} . In addition, the model predicts variations in R_H/R_{dep} with substrate position which parallel those observed in crystalline fraction. R_H/R_{dep} increases with total pressure and wire temperature because R_H increases with these variables more rapidly than R_{dep} . In the case of the residence time, while R_H remains constant, R_{dep} decreases with residence time because of a decrease in the silane supply. A similar argument applies to the variation R_H/R_{dep} with substrate position since R_H remains constant and R_{dep} decreases toward the outlet due to silane depletion.

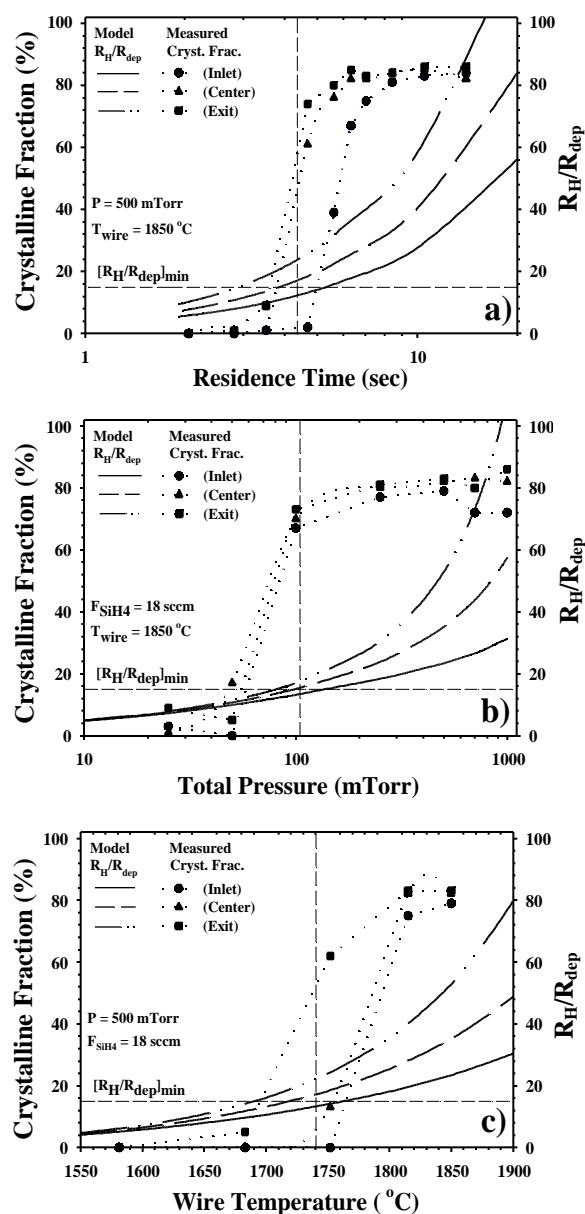


Figure 7: Crystalline fraction and ratio of atomic hydrogen flux to total silane radical flux as a function of: a) residence time; b) total pressure; and c) wire temperature at various positions along the direction of SiH_4 flow.

For all cases in Figure 7, the amorphous-crystalline transition appears to occur at the same value of R_H/R_{dep} ($[R_H/R_{dep}]_{min} = 15$). Above this value, the crystalline fraction increases rapidly and becomes constant at a value above 80%. Since the error in the crystalline fraction measurement is $\pm 20\%$, these films are considered crystalline. The step-like transition to crystallinity suggests that only a critical value of R_H/R_{dep} is needed to obtain crystalline films and that the effect of atomic hydrogen on film structure reaches a saturation level. Consequently, the critical value of R_H/R_{dep} may represent the minimum amount of hydrogen required to passivate a finite number dangling bonds at the film surface. Passivation of surface defects, in turn, allows for the ordered incorporation of subsequent precursor atoms reaching the film.

5. CONCLUSIONS

The presented model predicts within reasonable agreement the effects of residence time, pressure and wire temperature on the silane conversion and growth rate within the range of conditions considered. Optimum and uniform film growth and properties requires careful selection of process variables for a given reactor configuration. Model results suggest that a critical ratio of the atomic hydrogen flux to the total silane radical flux is needed to effect the amorphous-crystalline transition. This points to a saturation of the atomic hydrogen effect on structure which may be explained by the passivation of a finite number of free bonds or defects at the film surface.

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