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Critical nucleation concentration for monosilane as function of temperature observed in a free space reactor

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Abstract

Today's most frequently used production path for polysilicon and solar grade silicon (SG-Si) is based on thermal decomposition of trichlorosilane (SiHCl_3) in a Siemens-type reactor. Due to the batch-wise mode of its operation and its requirement for heating and cooling, the Siemens technology is an energy demanding procedure. As an alternative to this process, SG-Si can be produced through the thermal decomposition of monosilane (SiH_4), for example in a fluidized bed reactor or a centrifugal chemical vapour deposition reactor. In order to avoid production of fine particulates and related clogging, this process requires knowledge of the nucleation properties of silane. In this work, the critical concentration for particle nucleation from SiH_4 , diluted in H_2 has been determined for temperatures in the range 400 - 700 °C. For this purpose, we used a free space reactor and an optical particle detector of own design for in-situ monitoring of the reactor exhaust. In a plot of logarithmic critical nucleation concentration against inverse temperature, an almost linear relation was found for temperatures below approximately 500 °C and above approximately 600 °C. Between 500 and 600 °C, a less temperature dependent behavior is observed. Apparent activation energies are estimated to be 32 kcal/mol for temperatures below 500 °C, 8 kcal/mol for temperatures between 500 and 600 °C and 23 kcal/mol for temperatures above 600 °C. The first and last of these values agree well with existing literature. The low temperature dependence in the range 500 °C to 600 °C, however represents a deviation from earlier studies. Investigations of reactor exhaust by GC-MS (gas chromatography - mass spectrometry), allowing detection of the concentrations of higher order silanes (disilane (Si_2H_6), trisilane (Si_3H_8), etc) as function of reactor temperature, suggest that the low temperature dependence of the nucleation concentration for some conditions is related to an increase of the concentration of Si_2H_6 and Si_3H_8 at the same temperature range.

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1. Introduction

Up to 40 % of the energy needed for the production of a solar panel based on multicrystalline silicon cells is consumed during the preparation and purification of the silicon feedstock [1]. Therefore, finding ways of reducing the energy consumption in these processes can greatly contribute to the minimization of the cost for solar panels, as well as reducing their carbon footprint and energy payback time. Production of silicon from SiH₄ through the use of a Fluidized Bed Reactor (FBR) or a Centrifugal Chemical Vapor Deposition Reactor (CCVDR) is a less energy consuming alternative to the traditional production path based on Siemens technology (e.g.[2], [3]). In these reactors, SiH₄ gas decomposes thermally to form solid silicon. For the production of Solar Grade silicon (SG-Si), heterogeneous decomposition (deposition of solid silicon on an existing silicon surface) is desired. Homogeneous decomposition (formation of free standing particles from the gas phase), on the other hand, may cause challenges related to reactor clogging in addition to dramatically reduced production yield.

As a result of the industrial importance for the semiconductor industry, as well as the solar cell industry in later years, several studies of thermal decomposition and nucleation of SiH₄ have been conducted. In 1971, Eversteijn [4] observed gas-phase decomposition of SiH₄ diluted in hydrogen (H₂) in a horizontal epitaxial reactor at atmospheric pressure. The author suggested that the decomposition takes place if and only if the SiH₄ concentration in this layer exceeds a critical value, which was found to be highly temperature dependent. Values for the critical concentration for silicon particle nucleation from monosilane (SiH₄) diluted in H₂ in the temperature range 780-1136 °C were determined. When the critical SiH₄ concentration was plotted logarithmically against inverse temperature, a linear relationship was found (see Fig. 3.(b)). From this relationship, a value of 38 kcal/mol for the activation energy of the gas-phase decomposition of SiH₄ in H₂ was estimated.

In 1988 Qian et al. [5] conducted a similar study, in which the critical nucleation concentration for SiH₄ in a low pressure chemical vapor deposition (CVD) reactor was investigated. These authors kept the concentration fixed (100% undiluted SiH₄) and for each temperature varied the pressure gradually, until nucleation was observed. This procedure differs from that of Eversteijn, in which the pressure was kept constant and the concentration of SiH₄ was increased gradually. Qian et al. investigated temperatures in the range 700-750 °C. The corresponding critical SiH₄ pressures were found in the range 1.5-1.87 mbar. Based on their experiments Qian et al. found a linear relationship between the logarithm of the critical nucleation pressure, and the inverse temperature. The activation energy of the decomposition reaction was estimated to be approximately 8 kcal/mol.

Six years later, Sloodman and Parent [6] extended the knowledge on homogeneous gas-phase nucleation of SiH₄ by finding the critical nucleation concentration for SiH₄ diluted in various gases (argon, helium, nitrogen and hydrogen) at temperatures between 550 and 720 °C. For all gases they found that the logarithm of the critical nucleation concentration was proportional to the inverse of the corresponding temperature (see Fig. 3.(b)). For the H₂ diluted SiH₄, they estimated the activation energy to be 26 kcal/mol. A large difference was found between the critical nucleation concentration for SiH₄ diluted in H₂ and SiH₄ diluted in inert gasses. They explained the difference in nucleation onset by displacement of the equilibrium reaction



which is assumed to be the first step of the thermal decomposition of SiH₄. In this reaction, the third body M can be the carrier gas, the reactor wall or even SiH₄ itself [6]. This third species brings excess energy into the system, causing the reaction to take place. M itself, however, does not change during the reaction; M and M' differ only in energy content, not identity. A high H₂ concentration will alter the equilibrium of reaction (1) by favoring its backwards rate relative to the forwards reaction rate. The concentration of SiH₂ will decrease accordingly. Since a high concentration of SiH₂ leads to faster nucleation speed, because it promotes the formation of Si-Si bonds, reducing the SiH₂ concentration will cause a retardation of the nucleation process. The argumentation of H₂ retarding the nucleation process was used also by Qian et al. [5] in order to explain the difference between their results,

observed in undiluted SiH₄ and Eversteijn's results [4] observed for H₂ diluted SiH₄. Sootman and Parent [6] further summarized and compared different available studies on SiH₄ decomposition. In their comparison, they include studies both at atmospheric pressure and at lower pressures. The nucleation data is, however, compared according to the observed critical *concentration* of SiH₄, not according to its pressure.

In 2003 Nijhawan et al. [7] investigated thermal decomposition of SiH₄ at low pressures (~ 0.13 mbar) in a parallel-plate showerhead-type reactor with undiluted SiH₄. Their results are similar to those obtained by Qian et al. [5] at similar pressures, and give an estimated activation energy of 12.6 kcal/mol. Nijhawan et al. further compared the nucleation data from so far presented studies, similarly to what Sootman and Parent did some years earlier. However, they present the nucleation data in terms of critical SiH₄ partial pressure, rather than in terms of a critical concentration. This approach seems to give somewhat better agreement between the studies than the comparison of Sootman and Parent [6] which is based on SiH₄ concentration only. None of the above mentioned studies seem to take the influence of both pressure and concentration into account separately.

1.1. Kinetic considerations

Table 1 summarizes the values that various authors have estimated for the activation energy of the SiH₄ decomposition reaction. The details about the results from the current study will be given later in this article.

Table 1. Key parameters from earlier conducted studies on nucleation of SiH₄ in H₂.

Author, Year	Estimated apparent activation energy (kcal/mol)	Temperature range	Pressure
Eversteijn [4]	38	780 - 1136 °C	Atm. pressure
Murthy et al. [8]	24	900 - 1100 °C	Atm. pressure
Qian et al. [5]	8	700 - 750 °C	1.5-1.87 mbar
Sootman and Parent [6]	26	550 - 720 °C	Atm. pressure
Nijhawan et al. [7]	12.6	635 - 850 °C	~ 0.13 mBar
This study	32	400 - 500 °C	Atm. pressure
This study	8	500 - 600 °C	Atm. pressure
This study	23	600 - 700 °C	Atm. pressure

It should be noted that the values shown in Table 1 probably should be regarded as *apparent activation energies* rather than as true activation energies. Whereas a true activation energy can be found only for an elementary reaction (i.e. an individual step in a reaction mechanism), these values are estimated based on “the nucleation reaction” which includes a large number of elementary reactions. The apparent activation energy will then give an indication of the activation energy of the elementary reaction which is limiting for the overall reaction at the present reaction conditions. If the reaction (1) always is the rate limiting step in the overall nucleation reaction, the apparent activation energy of the nucleation reaction might be a good estimation for the activation energy of this reaction.

The reaction rate r of an elementary reaction can be described as

$$r = k [B]^b [C]^c \quad (2)$$

where k is the rate constant of the elementary reaction, and $[B]^b$ and $[C]^c$ are the concentration of the reactants, raised to the power of the stoichiometric coefficient of the species in the elementary reaction. The rate constant k is given by Arrhenius equation:

$$k = Ae^{-E_a/RT} \quad (3)$$

with E_a being the activation energy of the reaction, T the absolute temperature, R the ideal gas constant and A a pre-exponential factor related to the frequency of molecule collision. By taking the natural logarithm of equation (3), it is

easily seen that the activation energy E_a can be found from the slope of an Arrhenius plot (a plot of the natural logarithm of k against inverse temperature) multiplied by $-R$.

If it is desired to relate the activation energy of a reaction to the concentration of one of the reacting species (as was done for the reaction under consideration e.g. by Eversteijn [4], Murthy et al. [8], Sloodman and Parent [6] and also in this work) equation (3) must be substituted into equation (2), yielding:

$$r = Ae^{-E_a/RT} [B]^b [C]^c \quad (4)$$

As soon as this substitution is introduced, the value E_a in the resulting equation will not be a general value for the activation energy of a reaction anymore; it will depend on the chosen reaction through which the concentrations [B] and [C] and the corresponding coefficients b and c are defined. The value obtained for E_a will then be the *apparent activation energy* for the reaction under consideration. This apparent activation energy can be found experimentally by solving equation (4) for the logarithm of the concentration of species B, which yields

$$\ln([B]) = \frac{-\frac{E_a}{RT} + \ln\left(\frac{A [C]^c}{r}\right)}{-b} \quad (5)$$

and plotting this logarithm against inverse temperature. The resulting plot is *pseudo-Arrhenius plot*, from which the apparent activation energy can be found as the slope, multiplied by the gas constant R and the stoichiometric coefficient b .

If it is desired to deduce the reaction rate coefficient k from the pseudo-Arrhenius plot it is necessary to take the concentration of the third body (M) into account. This point, which can be seen from equation (2), was also emphasized by Petersen and Crofton [9] in 2003. These authors suggests that the discrepancy between the reported values for the rates of reaction (1) has occurred because previous authors have failed to take the concentration of other gases (represented by M in reaction (1)) into account. They then show that dividing the apparent reaction rates in these studies by that study's value for [M], results in very good agreement between the experiments.

1.2. Motivation

Despite Petersen and Crofton's clarification, regarding the influence of third body M on the reaction rate of SiH_4 decomposition [9], further contributions are needed for a deeper understanding of the dependence of this process on temperature, pressure, SiH_4 concentration and dilute gas. To this end, we have determined the critical nucleation concentration for SiH_4 diluted in H_2 in the temperature range from 400 to 700 °C, thereby extending the temperature range which already is investigated in literature to considerably lower values. Moreover, in order to provide a deeper understanding of the chemical path leading to nucleation, we have monitored the concentrations of SiH_4 , disilane (Si_2H_6) and trisilane (Si_3H_8), in the reactor exhaust as function of reactor temperature. These species are believed to be intermediate steps on the chemical pathway from SiH_4 to solid silicon particles.

2. Experimental

Our nucleation experiments were carried out in the FSR outlined in Fig.1.(a). The reactor has a diameter of 156 mm and a length of 100 cm and is divided into four heating zones, each with a length of 25 cm. The temperatures are kept by heaters outside the reactor tube, and can be set to different values in each of the heating zones. Two sets of internal temperature probes are positioned in the reactor core, one at inner wall, and one in the reactor center, to accurately measure the temperature in situ in the four different heating zones. In this experiment zone number three, hereafter called the reaction zone, was the warmest temperature zone. The decomposition reaction is thus assumed to take place mainly in this zone. Mass flow controllers are used to monitor and control the flow rate and composition of reaction gas (SiH_4 and H_2 , premixed before entering) into the reactor. At the gas flow used for this experiment, the residence time for the gas in the reaction zone is approximately 3 - 4 s, depending on temperature.

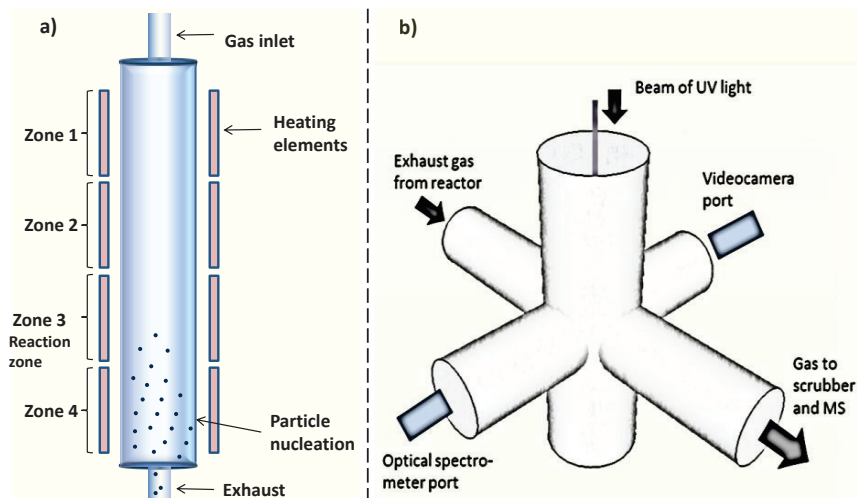


Fig. 1. (a) Illustration of the free space reactor used for nucleation experiments; (b) Illustration of the exhaust monitor used for detection of the critical nucleation concentration.

In order to detect the critical nucleation concentration for various temperatures, the temperature in the reaction zone was in this experiment increased step-wise, from approximately 400 to 700 °C. For chosen temperatures, the concentration of SiH_4 in the pre-mixed incoming reaction gas was slowly increased until particles were observed in the exhaust, as an indication that nucleation had taken place. The optical monitoring setup used for this purpose is described in the following section. After nucleation was observed at one temperature, the SiH_4 concentration was returned to zero, before the reactor was heated to the next temperature step, and the process was repeated. The temperature in the reaction zone, as well as the SiH_4 inlet concentration is shown in Fig. 3.(a). The reactor was kept at atmospheric pressure throughout the experiment.

A second reactor, similar to the one described above, was used in the experiments related to the chemical composition of the exhaust gas. In this experiment, the SiH_4 concentration was kept constant at 10%, whereas the reactor temperature was varied stepwise from 500 to 650 °C. The pressure was kept constant at approximately 1 atm. At each temperature step, the gas composition was analysed with a gas chromatograph and mass spectrometer (GCMS) setup, described below.

2.1. Optical monitoring

For the detection of particles in the exhaust (i.e. detection of the critical concentration for nucleation), an optical monitoring setup of our own design (Fig.1.(b)) was used. This instrument has been especially designed for the monitoring needs for SiH_4 decomposition reactors, and includes a light source (100 W mercury short arc), two CCD cameras and an optical spectrometer (Ocean Optics Maya 2000). During an experiment, the light source illuminates the reactor exhaust, whereas the cameras and the spectrometer are used to monitor light scattered on particles in the exhaust flow. The amount of light scattering from the exhaust will depend on whether or not the exhaust contains particles, i.e. whether or not nucleation has taken place in the reactor. The imaging capabilities of the exhaust monitoring setup also contribute to understanding the flow pattern (e.g. laminar flow or turbulent flow) present in the reactor.

2.2. Chemical monitoring

The chemical composition of the gases exiting the reactor was determined with a Gas Chromatography Mass Spectrometer (GCMS) specially designed for detection of silanes (see Fig. 2). We provide only a brief description of this instrument here; details will appear in a future publication.

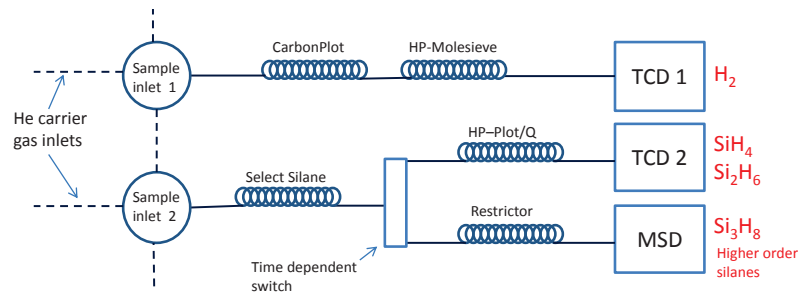


Fig. 2. Schematic sketch of the GCMS. The species that are detected in each of the detectors, are indicated in red.

Exhaust gasses are injected into the GC in two parallel streams, both of which use He as carrier gas. The first stream is dedicated to H_2 detection and uses CarbonPlot (Agilent) and HP-Molsieve (Agilent) columns to separate gases before detection in a Thermal Conductivity Detector (TCD). The second stream is dedicated to detection of silanes and uses a Select Silanes GC column (Agilent) to separate gases before entering the MS. SiH_4 and Si_2H_6 are shunted from the MS, further separated in a column of the type HP-Plot/Q and detected in a second TCD.

3. Results & Discussion

3.1. Nucleation

The determined onset of nucleation as a function of the temperature in the reaction zone of the FSR and the SiH_4 inlet concentration is shown in Fig. 3.(a). All data is shown as a function of time. The arrows indicate the time at which particles in the exhaust for each set of increasing temperature and SiH_4 inlet concentration were first observed. This is taken as the critical concentration for that temperature. The black bars following each arrow show the time range over which particles in the exhaust were observed. When the SiH_4 concentration was turned down to zero after each temperature step, signs of nucleation observed in the exhaust monitor quickly disappeared. This is seen in Fig. 3.(a) by the termination of the black bars at the time the SiH_4 concentration is turned down.

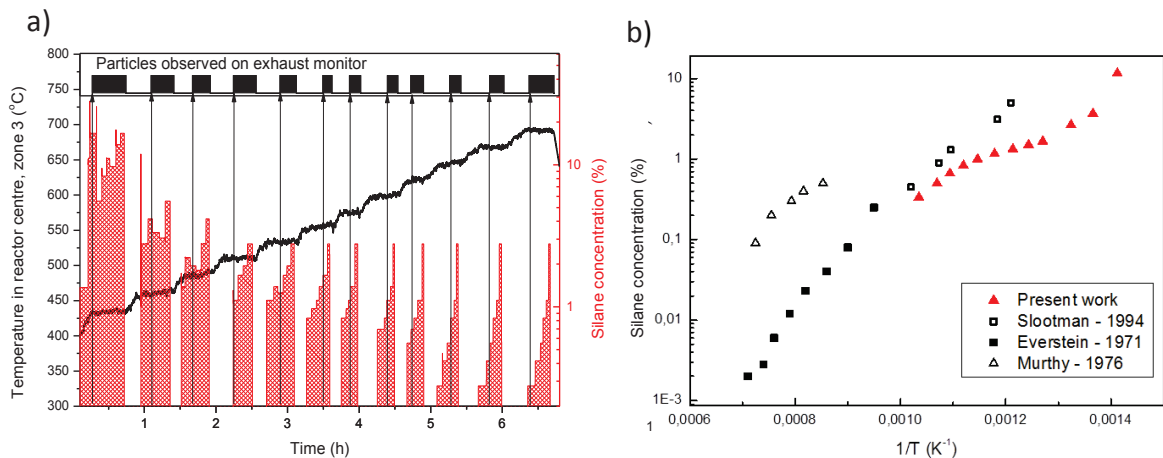


Fig. 3.(a) Reactor center temperature in the reaction zone (black) and SiH_4 inlet concentration (red) at different times during the experiment. The upper part of the figure indicates the time intervals in which particles were observed in the exhaust monitor. The beginning of each nucleation event, indicated with an arrow, corresponds to the set of conditions (temperature and SiH_4 concentration) for which silicon particles starts to form. The arrows thus relate temperatures to corresponding critical SiH_4 concentration; (b) Comparison of critical nucleation concentration and temperature observed in this work with data previously reported in literature. Adapted from [6].

Fig. 3.(b) shows critical nucleation concentration values from the same experiment plotted semi-logarithmically against inverse temperature. Results from the studies listed in Table 1 (only those that have investigated critical nucleation concentration rather than critical nucleation pressure) are also shown. For the highest and lowest parts of the temperature range in our study (below approximately 500 °C and above approximately 600°C) an almost linear relation is observed, whereas in the intermediate temperature range a region with a less steep nucleation curve is seen. Based on each temperature interval of the curve, (400 – 500 °C, 500 – 600 °C and 600 – 700 °C) apparent activation energies are estimated. This estimation is done in accordance with equation (5), with the SiH₄ concentration inserted for [B] and the coefficient b chosen to unity. Linear regression of the natural logarithm of the SiH₄ concentration values is used. The obtained apparent activation energies are 23 kcal/mol for temperatures above 600 °C, 8 kcal/mol for temperatures between 500 and 600 °C and 32 kcal/mol for temperatures below 500 °C. The apparent activation energies for the highest and lowest temperature range correspond well to values from other studies listed in Table 1. However, the result for the intermediate temperature region (500 - 600 °C) represents a significant deviation from the results of the other studies shown in Fig.3.(b) and suggests that the nucleation process under investigation might be governed by different limiting reactions under different temperature regimes. This hypothesis is further elaborated on in the following section.

Among the studies listed in Table 1, that of Slootman and Parent [6] is the only one whose temperature interval overlaps with the temperature interval that we have investigated. We have therefore critically looked for differences between these two studies that may cause the differing results. Pressure, residence time and reactor length are, to a good approximation, the same in the present work as reported by Slootman and Parent. Therefore, we do not believe that differences in these parameters contribute significantly to the observed deviations. The large difference in reactor diameter (8 mm vs. 156 mm) may, on the other hand, influence the result. Both in our reactor and in the reactor used by Slootman and Parent the reaction gas is heated by conduction from the reactor wall. A large diameter, combined with high gas flow is therefore likely to cause larger spatial temperature variations throughout the reactor. In order to reduce the uncertainty related to this temperature gradient, our temperature measurements were done in the middle of the reaction zone, centrally in the reactor. An eventual systematic error in the temperature measurements would cause a left-right shift in the nucleation curve shown in Fig.3.(b). The slope of the curve, however, is not likely to be altered.

3.2. Chemical analysis

Fig. 4. shows normalized concentrations of SiH₄, Si₂H₆ and Si₃H₈, as measured with GCMS, in the reactor exhaust as function of reactor temperature. The normalization is done for each of the species by dividing the species concentration at each measurement by the maximum concentration of that species. Without normalization, the concentrations of Si₂H₆ and Si₃H₈ are approximately two and three orders of magnitude smaller than the SiH₄ concentration, respectively. At 500 °C ($1/T \approx 0.0013 \text{ K}^{-1}$) the concentrations of Si₂H₆ and Si₃H₈ are low, indicating that little SiH₄ has decomposed to form higher order silanes. However, at 550 °C the concentrations of Si₂H₆ and Si₃H₈ have increased, a signature of thermal decomposition. The subsequent decrease in the concentrations of Si₂H₆ and Si₃H₈ suggests that further reactions have taken place, in which these species have contributed to the formation of longer silane chains or to particle nucleation. These results corresponds well to observations by Slootman and Parent [6].

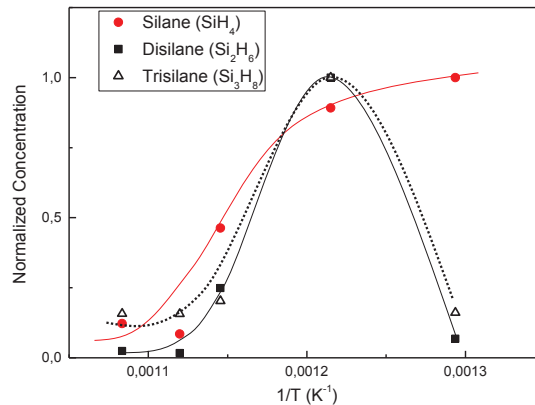


Fig. 4. Normalized concentrations of silane, disilane and trisilane in FSR exhaust, as function of reactor temperature. The normalization is done for each species separately, by dividing the species concentration at each measurement by the maximum concentration of that species in the measurement series. The lines are guides to the eye.

One should notice that the peak concentration of Si_2H_6 and Si_3H_8 displayed in Fig. 4. occurs at approximately the same temperature as the flat part of the nucleation curve in Fig. 3.(b). This fact leads us to hypothesize that the flat part in the nucleation concentration curve (Fig. 3.(b)) has a relation to the increased concentration of higher order silanes in that temperature range. One possible explanation to the observed nucleation behavior is thus the following: As temperature increases from room temperature to approximately 500 °C, a steadily decreasing concentration of SiH_4 is necessary for the creation of nuclei, because the present silane molecules have increasing amount of internal energy. We may assume that the splitting of SiH_4 to SiH_2 and H_2 (reaction (1)) is the limiting step for the entire nucleation reaction in this temperature region, meaning that the rate of this reaction will determine the combination of temperature and concentration at which nucleation occurs. For some combination of temperature, silane concentration and pressure, one of the elementary reactions that transform Si_2H_6 and Si_3H_8 to other species becomes rate-limiting. This rate seems to be less temperature dependent; meaning that even if the temperature is further increased nucleation will not take place at decreasing SiH_4 concentrations. Instead Si_2H_6 and Si_3H_8 may “pile up” in the reactor, causing the high concentrations of these species at intermediate temperatures (500 - 600 °C) seen in Fig. 4., as well as the flat part of the curve in Fig. 3.(b).

The change in apparent activation energy for a multistep reaction from a high apparent activation energy at low temperatures to a lower apparent activation at higher temperatures can be an indication of a shift of rate control to a different step within one reaction pathway [10]. One may realize this by imagining Arrhenius plots (natural logarithm of k plotted against inverse absolute temperature) of the elementary steps in a two-step reaction. If the stoichiometry and concentration of reactants are the same for two elementary reactions, the reaction with the lower k (i.e. the lower line in the plot) will always be the one limiting the overall reaction speed. If the reaction step that is limiting at low temperature has a high activation energy, the extrapolation of the Arrhenius line of this reaction step into the neighboring, warmer temperature region will be above the Arrhenius line of the lower activation energy reaction which limits at higher temperatures. Thus, in the high temperature region, the reaction step which is limiting at lower temperatures, will not affect the overall reaction rate. This explained situation matches the transition between the lowest temperature region (400 - 500 °C) and the intermediate temperature region (500 - 600 °C) observed in our study.

Between the intermediate and the high temperature region, however, the apparent activation energy changes from a lower to a higher value as temperature increases. Based on the same explanation as in the above paragraph, one may realize that such a change in apparent activation energy should be impossible within the frame of one reaction mechanism. Considering the complexity of the reaction under consideration, it is not unlikely that the reaction mechanism through which the reaction mainly proceeds changes from one pathway in one temperature region, to another, parallel pathway in another region. Such a change will result in high apparent activation energy in the higher temperature region and a lower apparent activation energy in the lower temperature region [10]. This combination of activation energies corresponds to the transition between the intermediate and the high temperature region in our investigation, and we therefore hypothesize that the observed change in apparent activation energy

between the high temperature and the intermediate temperature region is caused by a shift of the rate control to another parallel pathway.

In pseudo-Arrhenius plot of a multistep reaction, not only activation energies of reaction steps but also the concentrations of all involved species, as well as their stoichiometric coefficients may influence the resulting curve shape (cf. equation (5)). Therefore, one should be cautious when drawing conclusions based on apparent activation energies based from such a plot only. An alternative explanation to the segmented curve shown in Fig. 3.(b), is that the process is activated (i.e. follows Arrhenius behavior) at low temperature while at high temperature it is limited by equilibrium concentrations and mass transport, rather than by the activation energy of a certain reaction step. The origin of the observed behavior will be subject for further investigations.

4. Conclusions

We have determined the critical concentration for particle nucleation from SiH_4 gas diluted in H_2 for varying temperatures. For temperatures below 500 °C and above 600 °C we observed a linear relation between inverse temperature and corresponding critical nucleation concentration plotted semi-logarithmically, corresponding well to literature. For intermediate temperatures, the reaction showed a much weaker temperature dependence. The apparent activation energy for the nucleation reaction was estimated to 23 kcal/mol for temperatures above 600 °C, 8 kcal/mol for temperatures between 500 and 600 °C and 32 kcal/mol for temperatures below 500 °C. The weak temperature dependence between 500 °C and 600 °C represents a deviation from the behavior described in literature (see Fig. 3.(b)) and suggests that the nucleation process under investigation is subject to different limiting reaction steps in the different temperature regimes. This hypothesis is supported by GC-MS investigations showing enhanced concentrations of Si_2H_6 and Si_3H_8 in the same temperature range as the flat part of the nucleation curve, indicating a bottleneck for the further evolution of these species into even higher order silanes.

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