SPECTROSCOPIC DETECTION OF PARTICLES FROM SHOCK-WAVE-INDUCED DECOMPOSITION OF SiH_4

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Particle formation from silane pyrolysis was studied in a shock tube Molecular and atomic species (SiH_2, SiH, Si_2, H_2, Si, H) were identified by thermal induced fluorescence at temperatures exceeding 3000 K. At temperatures below 2500 K, silicon cluster formation was detected by optical extinction measurements

1. Introduction

Silane decomposition has received considerable recent attention concerning the production of electronic grade amorphous silicon (α-Si) [1]. In addition, amorphous hydrogenated silicon (α-Si:H) produced by silane decomposition can be used for solar energy conversion in thin film devices. While the majority of α-Si:H is produced by plasma discharges, it was shown recently that homogeneous chemical vapor deposition (HOMOCVD) can also be used for thin film production [2]. Here, the fragment SiH_2 has been proposed to play a dominant role in the deposition mechanism. The authors [2] further suggested their mechanism to be applicable to low-power plasma discharges.

Molecular fragment identification in plasma discharges of SiH_4 [3–5] and SiF_4 [6] has been reported previously. In a most recent study, SiH_2 resulting from phenylsilane photolysis was identified [7].

To our knowledge, a direct identification of fragments and subsequent reaction products resulting from thermal decomposition of silane has not yet been reported. However, from silane pyrolysis experiments [8,9], it was previously assumed that the initial decomposition step is a unimolecular gas reaction ($SiH_4 + M \rightarrow SiH_2 + H_2 + M$). However, in a most recent study [10] it was postulated that silane pyrolysis is initiated entirely by wall reactions involving deposits of α-Si ($SiH_4(\text{wall}) \rightarrow Si(\text{wall}) + (2-\epsilon)H_2 + 2\epsilon H$). The hydrogen atoms are assumed to start a subsequent radical chain process in the gas phase finally leading to rapid silane decomposition. As a consequence of this study [10], a new mechanistic interpretation of silane pyrolysis was reported [11]. The radical chain mechanism [10] was not adopted by the authors [11], because there seems to be experimental evidence that such a process is not effective [9,10]. Instead, gas-phase and wall reactions leading to gradual loss of hydrogen from particles initially produced by SiH_2 insertion into unreacted silane were postulated.

However, neither the chain mechanism [10] nor the revised mechanism [11] describe the present experiments. The observation of early reaction stages must be attributed exclusively to gas reactions leading to silane fragmentation and subsequent silicon cluster formation.

2. Experimental methods

Shock waves were generated in a conventional 12.7 cm diameter single pulse membrane shock tube (length of the high-pressure section 3.6 m; length of the low-pressure test section 5.4 m). The tube was operated with helium (99.999%) as high-pressure section gas and argon (99.999%) as shock wave carrier gas. Silane

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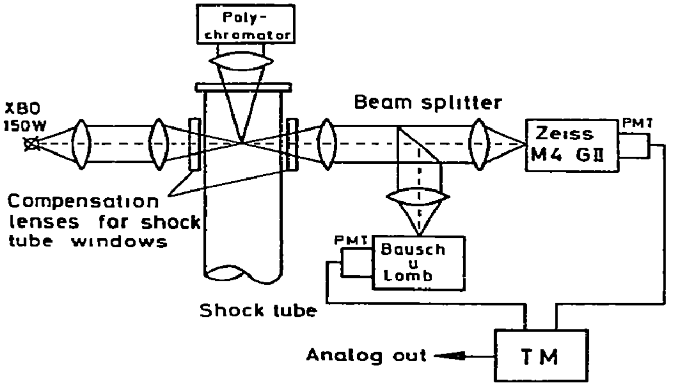


Fig. 1. Schematic experimental arrangement.

premixed in argon (semiconductor purity) was used as test gas. Mylar (Hostaphan, Hoechst) was used as membrane material. Prior to an experiment, the low-pressure section and the supply tubes were evacuated to 10^{-6} Torr. Shock speeds (or Mach numbers) were measured by platinum resistance films (connected to differential amplifiers and TTL norm pulse converters) in the shock tube wall having a response time <1 μs. Shock wave attenuation was also measured and usually was less than 1% per meter. This justifies the application of the hydrodynamic shock tube equations in order to determine the thermodynamic parameters behind the shock waves from the velocity measurements and the gas properties [12].

Fig. 1 shows the schematic experimental arrangement for optical detection of silane fragments and silicon clusters. The prism polychromator (Fuess) detects an integral emission spectrum during the total time behind incident and reflected shock waves (about 2.0 ms). Spectra were recorded on photoplates. Time-resolved measurements were performed simultaneously at two wavelengths selected by monochromators (Zeiss M4 GII and Bausch & Lomb 4850 B) Light signals were detected by two EMI 9659 QB multipliers operated under identical response conditions (1/e response time was 500 ns). Signals were stored in a two-channel 1 MHz transient recorder (Maurer TM 109/2). Two separate time sequence (marker) channels stored the shock wave detector signals for Mach number determination which, in addition, was controlled by digital counters (Kontron 6001).

The high-pressure arc lamp (Osram XBO 150 W4) was used to detect the gas-phase condensation of silicon by optical extinction measurements. All emission experiments were performed without the arc lamp.

3. Results

Fig. 2 shows a microdensitometer recording of an integral emission spectrum in the visible and near UV. Atomic and molecular species identified from photoplate analysis are listed in table 1. H and H_2 emissions only appear at reflected shock temperatures $T_5 >$ 7000 K. The identification of Si_2 is partly based on X–H band transitions not reported in the literature. Therefore, we have calculated the X–H band electronic transitions. Because the calculations reproduced the reported transitions, we used also theoretical lines for Si_2 identification. The respective transitions are identified in table 1 by (th). Calculations were performed on CDC 6600/Cyber 174 computers.

In some emission spectra recorded with a quartz prism polychromator (Fuess), we found some evidence of Si_2 emissions from the near UV band (3489–3785 Å [15]). All other UV emissions are silicon atomic transitions [13]. It was possible to identify all integral emissions observed in various spectra with the species listed in table 1. Therefore we assume that SiH_3 is not significantly involved in the thermal decomposition of silane. However, due to the lack of spectroscopic information, some doubts remain.

The high temperatures behind the reflected shock waves do not exhibit conditions of conventional silane pyrolysis experiments. However, the thermal plasma conditions are more similar to those in low-power plasma discharges than the HOMOCVD experiments [2].

In view of the variety of fragments involved in silane decomposition, it is unlikely that the formation of α-Si:H in low-power plasma discharges can be based exclusively on SiH_2 deposition and its subsequent surface reactions as suggested by the authors of ref. [2].

The lowest temperature for which time-resolved fragment emissions could be observed was about 3000 K. Fig. 3 shows such a recording where the emissions are due to SiH_2 (trace A, 5527 Å [15]) and Si-I (trace B, 2516.13 Å resonance transition [13]). Detector signal a corresponds to incident shock arrival at the observation station. Signal b indicates the reflected

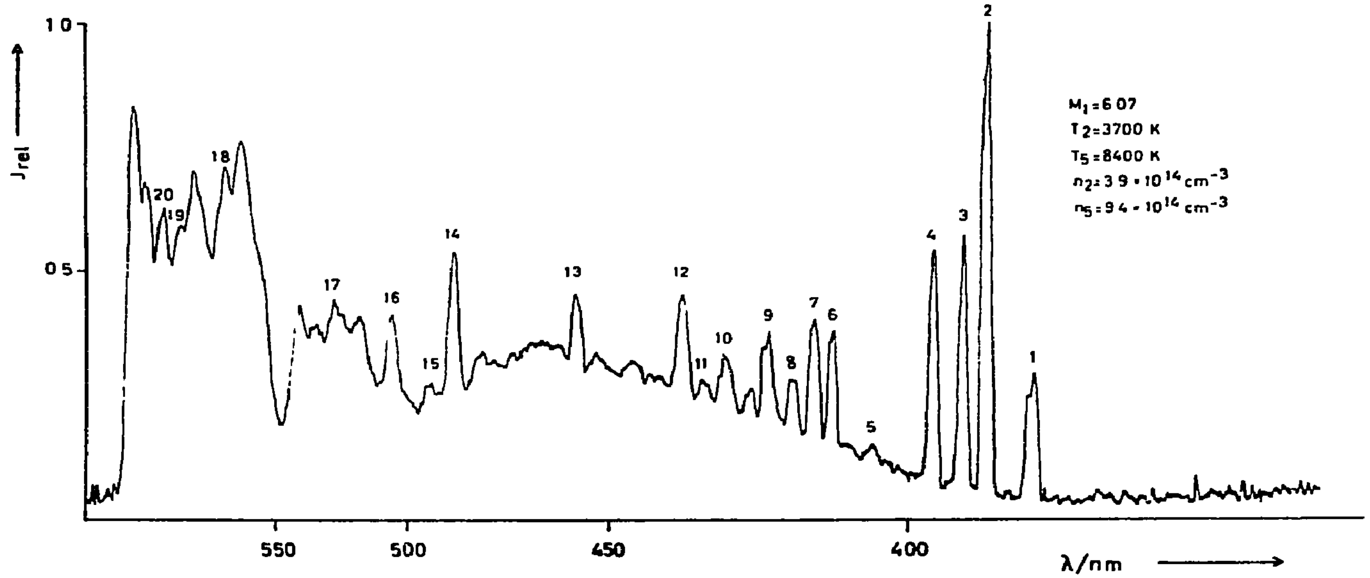
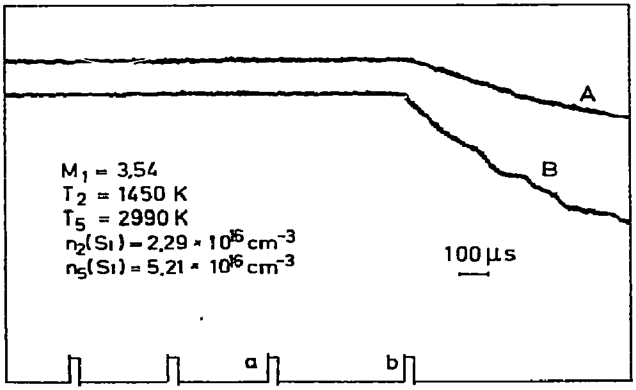


Fig. 2. Integral emission spectrum of particles from silane pyrolysis (glass prism absorption below 4000 Å not considered). The subscript 2 indicates conditions behind the incident shock wave, the subscript 5 indicates the reflected shock conditions M_1 is the incident shock Mach number.

Table 1
Particle identification from representative spectral lines of fig. 2

Line	Particle	Wavelength (Å)	Line	Particle	Wavelength (Å)
1	Si_2	3849[th]	11	Si_2	4283[15]
2	Si	3905[13]	12	H	4340[13]
3	Si_2	3924[th]	13	Si_2	4526[15]
4	H	3970[13]	14	H	4861[13]
5	H_2	4024[14]	15	H_2	4934[15]
6	H	4102[13]	16	SiH_2	5056[15]
7	SiH	4128[15]	17	H_2	5272[15]
8	SiH	4142[15]	18	SiH_2	5797[15]
9	H_2	4205[15]	19	H_2	5994[15]
10	SiH	4259[15]	20	SiH_2	6098[15]

shock arriving at the observation station. The incident shock temperature, T_2 = 1450 K, is too low for a measurable thermal excitation of the fragments. However, silane decomposes rapidly even at incident shock temperatures as low as 1200 K. Concerning a proper gas-dynamic operation of the shock tube, even lower temperatures are subject to increasing uncertainties



◀ Fig. 3. Dual-trace experiment of fragment emission. Trace A: SiH_2 (5527 Å); trace B Si-I resonance transition (2516.13 Å). (a) Incident shock at observation station; (b) reflected shock at observation station.

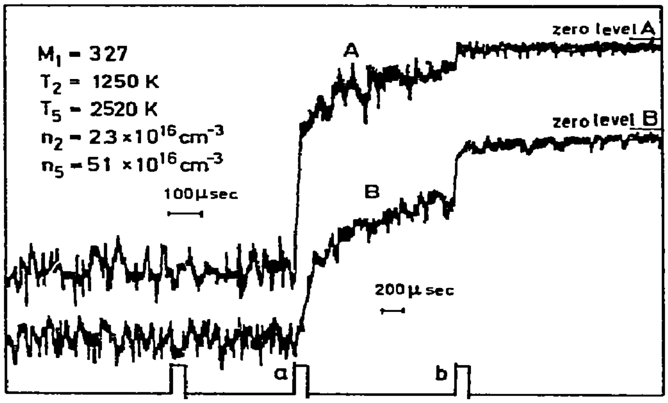


Fig. 4. Dual-trace silicon cluster extinction. (A) 2480 Å; (B) 3660 Å. Clusters form immediately behind the incident shock. Particle density discontinuities at (b) are due to reflected shock compression of the cluster gas.

and such experiments were therefore not performed. However, reaction temperatures of about 1200 K are comparable to those in high-temperature thermal reactors [1] and also to those in the comparative rate shock tube study [9]. In this temperature range, the gas-phase processes in the present study were observed by optical extinction measurements detecting the production of silicon clusters.

Fig. 4 shows a recording, where trace A corresponds to a wavelength of 2480 Å outside the pressure broadened Si-I resonance transition (2516.13 Å). Trace B shows the simultaneously recorded extinction signal at 3660 Å, outside of possible fragment absorption. The difference in relaxation time compared to the real time measurement in the region between the incident and reflected shock wave has been considered. This explains the two different time scales of fig. 4. The optical extinction is due to a gas-phase condensation process. Experiments performed at higher reaction temperatures show that the condensation is related to the silicon phase equilibrium calculated from thermochemical data of ref. [16]. The experiments are not compatible with a different phase equilibrium calculated from thermochemical data of ref. [13]. However, the condensation process cannot be described by the theory of homogeneous nucleation [17,18]. Even at conditions close to the phase equilibrium, condensation takes place irrespective of the basic principles of this theory.

The analysis of various extinction experiments in the accessible wavelength range from 2300 to 8000 Å suggests a λ^{-1} dependence of the extinction signals. This is the wavelength dependence of the absorption cross section of spherical particles in the Rayleigh size region characterized by a complex index of refraction [19]. The formation of silicon clusters in the region behind the incident shock wave requires a considerable production of condensible particles within a reaction time of less than 50 µs for the conditions of the experiment shown in fig. 4.

4. Discussion

The initiation reaction of shock-wave-induced silane decomposition must be a unimolecular, homogeneous gas reaction. Wall interference, as proposed by the authors of ref. [10], leading to a radical chain process can be excluded under low-pressure conditions at temperatures above 1200 K. This follows from the rapid formation of silicon clusters observed in the present study under all conditions, where the thermodynamics of the silicon phase equilibrium allows for a first-order phase transition. Based on previous experience [8,9] and the present fragment identification, the initiation reaction most likely is a molecular hydrogen elimination:

$$SiH_4 + M \rightarrow SiH_2 + H_2 + M . \qquad (1)$$

The emission spectra show that, at temperatures above 3000 K, where thermal excitation of the fragments is sufficient for detection, SiH, Si and Si_2 are the subsequent particles. However, SiH emissions are weak compared to those of SiH_2, Si and Si_2 which suggests the dominant pathway for subsequent particle formation:

$$SiH_2 + M \rightleftharpoons Si + H_2 + M , \qquad (2)$$

$$Si + Si + M \rightleftharpoons Si_2 + M . \qquad (3)$$

At temperatures above 3000 K, higher silicon cluster formation is unimportant, because the thermodynamic conditions correspond to undersaturated stable silicon vapors.

However, fig. 4 shows that silicon cluster formation is important in early reaction stages at temperatures above 1200 K under low-pressure conditions. This, in turn, also excludes the reaction mechanism of ref. [11] in the present experiments. This may, in part, be due to the silane pressure range (above 100 Torr) to which the authors restrict the validity of their mechanism. In the present experiments, silane partial pressures in argon after incident shock compression did not exceed 3 Torr. However, it should be noticed, that the lowest reaction temperature of about 1200 K in the present study (and also the corresponding silane partial pressure) is comparable to the highest reaction temperature in the comparative rate shock tube study (1184 K) [9] having post-shock reaction times of about 300 μs. The authors measured silane loss rates by comparing samples of unshocked and shocked gas. Their (simplified) explanation of silane loss is as follows:

$$SiH_4 + M \rightleftharpoons SiH_2 + H_2 + M\,, \quad (4)$$

$$SiH_4 + SiH_2 \rightleftharpoons Si_2H_6\,, \quad (5)$$

$$Si_2H_6 + M \rightleftharpoons Si_2H_4 + H_2 + M\,, \quad (6)$$

$$Si_2H_4 + M \rightleftharpoons Si_2H_2 + H_2 + M\,. \quad (7)$$

This mechanism does not explain the production of condensible particles (Si or Si_2). Fig. 4 shows a strong cluster absorption signal after a reaction time of 300 μs characteristic of the experiments of ref. [9]. If the mechanism (4)–(7) were to be correct, two last reaction steps in the gas phase would be required:

$$Si_2H_2 + M \rightleftharpoons Si_2 + H_2 + M\,, \quad (8)$$

$$Si_2 + M \rightleftharpoons Si + Si + M\,. \quad (9)$$

In ref. [11], reactions (7) and (8) are assumed to be wall processes. As already mentioned, wall reactions can be excluded in the present experiments. Consequently, the total reaction sequence (4)–(9) finally leading to the production of condensible particles would have to occur as a sequence of homogeneous gas reactions to be applicable to the present experiments. It may be justified to assume, that reactions (1)–(3) and subsequent higher silicon cluster formation are a more adequate description of the gas-phase processes observed in the present study.

It appears, that a conclusive reaction mechanism of silane pyrolysis is not adequately developed at the present time. Such a mechanism cannot neglect the possibility of silicon cluster formation in early reaction stages and the possibility of cluster catalyzed subsequent silane decomposition. Much more detailed experimental information focusing on spectroscopic detection of early reaction stages is required to allow a final conclusion. Further experimental work on the subject is in progress.

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