

QUALITATIVE ANALYSIS OF THE VAPOUR-PHASE EQUILIBRIUM COMPOSITION IN THE SYSTEMS Si-Cl AND Si-Cl-H BY MATRIX-ISOLATION IR SPECTROSCOPY*

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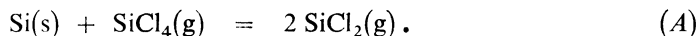
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The vapour phase in the systems Si-Cl and Si-Cl-H in equilibrium with solid silicon has been analyzed qualitatively by matrix-isolation IR spectroscopy. At 1 300 K, the analysis revealed SiCl₄, SiCl₃ and SiCl₂ in the system Si-Cl, and HCl, SiCl₄, SiCl₃, SiCl₂, SiHCl₃ and SiH₂Cl₂ in the system Si-Cl-H. No SiHCl, a compound which according to equilibrium calculations represents one of the dominant components, could be detected.

In the first part of our paper¹ we have reported results of calculations of chemical equilibria in the systems Si-Cl and Si-Cl-H, obtained on the basis of a set of critically assessed and consistently selected input thermodynamic data for individual substances. Comparison of these results with published experimental data for the vapour-phase equilibrium composition in the above systems has shown some discrepancies. These may be due to inaccuracies in the thermodynamic data used in the calculations, as well as to limited capabilities of the experimental methods employed so far to detect highly reactive radicals and compounds stable at high temperatures only.

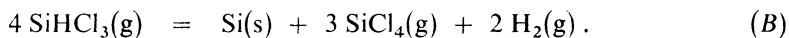
A number of papers have been devoted to the study of equilibrium in the system Si-Cl. Most of the authors²⁻⁸ has determined equilibrium constant for the reaction



Both Ban^{9,11} and Farber and Srivastava^{10,12} used mass spectrometry for direct determination of vapour-phase composition in equilibrium with solid silicon. For the temperature range 1 000–1 300 K and a pressure of 101.3 kPa Ban proved the presence of SiCl₄ and SiCl₂ in the system Si-Cl-inert gas and SiCl₄, SiHCl₃, SiH₂Cl₂, SiCl₂, HCl and H₂ in the case of the system Si-Cl-H. At a pressure of about

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10 kPa, Farber and Srivastava detected SiCl_4 , SiCl_3 , SiCl_2 and Si in the vapour phase of the system Si-Cl (1 590–1 790 K) and SiCl_4 , SiHCl_3 , SiH_2Cl_2 , SiHCl_3 , HCl and H_2 in the vapour phase of the system Si-Cl-H (900–1 500 K), however silicon subchlorides were not detected in the latter case. Wolf and Teichmann⁸ investigated equilibrium for the reaction



As in the case of reaction (A), they have determined the degree of conversion of this reaction from overall pressure change or change in the amount of the solid silicon. Woodruff and Snachez-Martinez¹³ analyzed the vapour phase in equilibrium with solid silicon using gas chromatography (GC). No conclusions can be made as to the presence of individual substances in the vapour from their plots of the equilibrium $(\text{Si}/\text{Cl})_{\text{eq}}$ molar ratio vs the initial $(\text{Cl}/\text{H})_{\text{in}}$ molar ratio and temperature.

A number of experimental studies have been devoted to the vapour-phase composition in the system Si-Cl-H under non-equilibrium conditions commonly used in Si epitaxial layers deposition. The gaseous substances were identified by various analytical methods and, in most cases, HCl, SiCl_4 , SiCl_2 , SiHCl_3 and SiH_2Cl_2 were found to be present in the vapour. The samples of the vapour phase for IR spectroscopy^{14,15}, mass spectrometry^{16–20} and GC (ref.²¹) were usually taken by a capillary outside the reactor. In this case, undesired chemical conversion may have taken place during the time period between sampling and analysis, and the composition of the sample analyzed might differ from that under the high-temperature conditions within the reactor. This has been confirmed by some results obtained by IR spectra^{10,15}. While analysis of the vapour phase “in situ” at a high temperature revealed the presence of HCl, SiCl_4 , SiCl_3 , SiCl_2 , SiHCl_3 and SiH_2Cl_2 , no SiCl_2 and SiCl_3 were detected in cooled samples of the gas withdrawn by a capillary outside the reactor. Fluorescence spectroscopy^{22–26} allows, in principle, vapour-phase analysis to be made “in situ” at a high temperature. However, only one substance was detected by this method in the system Si-Cl-H. An intense fluorescence signal of this substance precludes detection of the other components of the vapour phase. Sedgwick et al.^{22–24} identified this substance as SiCl_2 , whereas Ho and Breiland²⁵ believe that it is SiHCl .

The aim of the paper is a qualitative analysis of the vapour-phase equilibrium composition in the systems Si-Cl and Si-Cl-H using matrix-isolation infrared (MIIR) spectroscopy. The main attention is devoted to the detection of relatively unstable substances which according to equilibrium calculations are present in the vapour phase of the above mentioned systems, but their presence has not been experimentally proved satisfactorily.

EXPERIMENTAL

Apparatus and Chemicals

The apparatus for experimental study of the vapour-phase composition in the systems Si-Cl and Si-Cl-H consisted of three main parts:

a) a part for the preparation of initial vapour phase with a well-defined composition, *b)* a high-temperature reactor, *c)* a low-temperature cryostat.

In designing the apparatus, the main emphasis was placed on close connection between the reaction and the cryostat, a feature essential for detection of relatively unstable substances. In our arrangement, the distance between the reaction space heated to 1 250–1 300 K and the cryostat window cooled to about 21 K was about 15 cm, and the time it took to transfer a vapour-phase sample from the reactor to the cryostat was estimated to be less than 0.1 s.

Argon (N 470 sort, Technoplyn Prague) dried over anhydrous P_4O_{10} was used as the matrix gas. Dry argon was passed through a diffusion saturator²⁷, where it was saturated with $SiCl_4$ (semiconductor purity, Institute of Glass and Ceramic Materials of the Czechoslovak Academy of Sciences) to a concentration of about 0.1 mol %. So prepared mixture was either fed directly to the reactor or mixed with hydrogen (25 sort, Technoplyn Prague) in a proportion of about one part of H_2 to ten parts of the $Ar + SiCl_4$ mixture. The hydrogen was withdrawn directly from the outlet of the cryostat, in which it served as a cooling medium. Previous cooling to about 21 K had freed it completely from any residual impurities. The overall vapour-phase flow rate was between 2 and 4 litre/hour, and all experiments were carried out at atmospheric pressure.

The reactor was made of quartz and its outer wall was heated by a resistance heater. A layer of crushed single crystal silicon (semiconductor purity, ČKD Prague) of 1–2 mm grain size was placed in the constant temperature zone. The reaction temperature was measured by a Pt-Pt, Rh thermocouple inserted in a quartz test tube whose tip extended to the centre of the layer. The accuracy of temperature measurement was $\pm 1^\circ C$, and the variation of the temperature in the reactor was within a maximum of $\pm 5^\circ C$. Since the reactor had been designed so as to minimize the free space, there was virtually no effect of thermal diffusion²⁸. The reactor was connected to the cryostat through a short length of quartz capillary tubing joined to a glass valve with a Teflon cone. The joint was cemented to a dural flanged radiator with a resin. This design made it possible to reduce substantially the distance between the reactor and cryostat.

A two-stage cryostat of the Joule-Thomson type was employed, with hydrogen as the cooling medium²⁹, which permitted a minimum temperature of 21 K to be attained. The temperature of the KBr window at which an argon matrix was deposited, was measured by Cu-Constantan thermocouple. The cryostat was evacuated by an AV 63 pumping apparatus (Laboratorní přístroje Prague). The operating vacuum, measured by a Penning vacuumeter (VEB Labor-technik Ilmenau) was about 0.1 Pa at room temperature and about 10^{-3} Pa on cooling to about 21 K. The cryostat was placed in the cell space of a Specord IR 75 spectrometer (C. Zeiss, Jena), permitting spectra to be taken immediately after depositing the matrix.

Spectral Data of Substances in the System Si-Cl-H

The fundamental frequencies for the various substances present in the vapour phase of the system Si-Cl-H are available in the literature³⁰⁻³². When the substances are isolated in a matrix, however, their vibration bands are shifted compared with their positions in the spectrum of the vapour phase, and therefore matrix spectral data are needed for correct identification of the substances present. Unfortunately, such data have only been reported for some compounds

in the system Si-Cl-H, and in many cases they cover just a limited interval of the IR spectral range. The published vibration bands for substances isolated in an Ar matrix are in Table I.

RESULTS AND DISCUSSION

The System Si-Cl

Introductory measurements on the system Si-Cl-Ar were made at room temperature within the reactor. The aim was to test the suitability of the apparatus and to verify the purity of the starting substances (SiCl_4 and argon). Figure 1 shows part of the spectrum for SiCl_4 in an Ar matrix in the $700-400\text{ cm}^{-1}$ range. The bands at 616 and 642 cm^{-1} agree with literature³³. Each band exhibits a fine structure, corresponding to isotopomers of SiCl_4 . In the $4000-400\text{ cm}^{-1}$ range the spectrum also showed weak bands due to CO_2 (2340 and 663 cm^{-1}) (ref.⁴²) and H_2O (3728 and 1598 cm^{-1}) (ref.⁴³). These bands appeared with various intensities in practically all spectra obtained.

The actual study of the equilibrium vapour-phase composition of the system Si-Cl-Ar was made over the temperature range $1260-1320\text{ K}$. Figure 2 shows the spectrum in the $700-400\text{ cm}^{-1}$ region for the vapour phase in equilibrium with solid Si after isolation in an Ar matrix. Compared with the spectrum at room temperature within the reactor, new bands appear at 589 , 518 , 512 and 472 cm^{-1} . On the basis of the knowledge of the initial vapour-phase composition and the data

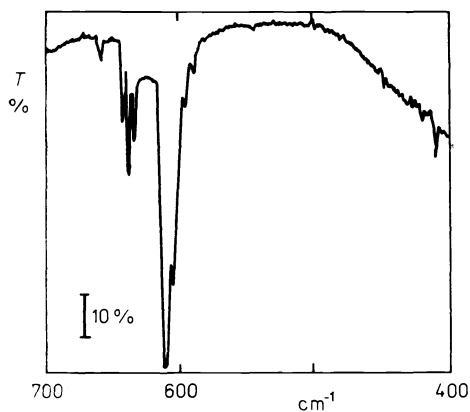


FIG. 1

IR spectrum of the vapour phase of the system Si-Cl in an Ar matrix; reactor temperature, 293 K ; initial composition, $0.1\text{ vol. \% SiCl}_4$ and 99.9 vol. \% Ar

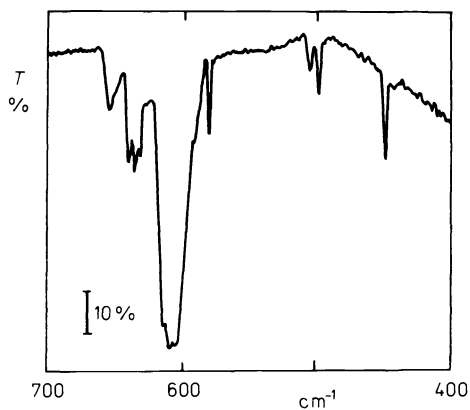


FIG. 2

IR spectrum of the vapour phase of the system Si-Cl in an Ar matrix; reactor temperature, 1300 K ; initial composition, $0.1\text{ vol. \% SiCl}_4$ and 99.9 vol. \% Ar

listed in Table I, these bands can be assigned to SiCl_3 (589 and 472 cm^{-1}) and SiCl_2 (518 and 512 cm^{-1}). It should be noted that the wavenumbers found by us are in most cases shifted to higher values. No band was observed in the vicinity of 535 cm^{-1} , a wavenumber corresponding to the fundamental frequency of SiCl in the vapour phase³¹. Changing the temperature in the reactor over the above mentioned range or varying the vapour-phase flow rate through the reactor between 1 and 5 litre/hour produced no changes in the spectra obtained.

Thus we identified SiCl_4 , SiCl_3 and SiCl_2 in the vapour phase of the system Si-Cl-Ar in equilibrium with solid silicon at about 1 300 K. Using mass spectrometry under similar conditions, Ban⁹ only found SiCl_4 and SiCl_2 . His failure to detect SiCl_3 may have been due to a relatively long period between sample withdrawal and analysis.

TABLE I
IR spectral data of matrix-isolated species of the system Si-Cl-H

Compound	Fundamental frequencies, cm^{-1}	Note	Ref.
SiCl_4	$\tilde{\nu}_3 = 616.5$ $\tilde{\nu}_1 + \tilde{\nu}_4 = 643.0$	<i>a, b</i>	33
SiCl_3	$\tilde{\nu}_1 = 470\text{ m}$ $\tilde{\nu}_3 = 582\text{ vs}$	<i>a</i>	34
	$\tilde{\nu}_1 = 470$ $\tilde{\nu}_3 = 584$	<i>b</i>	35
SiCl_2	$\tilde{\nu}_1 = 512.7\text{ s}$ $\tilde{\nu}_3 = 502.0\text{ vs}$	<i>a</i>	36
	$\tilde{\nu}_1 = 512.5$ $\tilde{\nu}_3 = 501.4$	<i>a, b</i>	37
	$\tilde{\nu}_1 = 512.5$ $\tilde{\nu}_3 = 502$	<i>b</i>	35
SiHCl_3	493 m, 597 vs, 802 vs 825 vs	<i>a</i>	34
SiH_2Cl_2	527 w, 584 m-s, 877 m 948 m, 2 210 w	<i>a</i>	36
SiH_3Cl	663 w, 945 w, 2 198 w	<i>a</i>	36
SiH_4	$\tilde{\nu}_3 = 2 176.7$ $\tilde{\nu}_4 = 905.1$	<i>b</i>	38
SiH_2	$\tilde{\nu}_1 = 1 964.4$ $\tilde{\nu}_2 = 994.8$	<i>b</i>	39
	$\tilde{\nu}_3 = 1 973.3$ $2\tilde{\nu}_2 = 1 992.8$		
SiHCl	$\tilde{\nu}_2 = 808$ $\tilde{\nu}_3 = 522$	<i>b</i>	40
HCl	a broad band in the range $2 900 - 2 840\text{ cm}^{-1}$ with a prominent rotational structure	—	41

^a Only the most intense bands of the fine structure, associated with the most frequently occurring isotopomers, are included. ^b Relative intensities have not been reported.

Comparison with calculated values^{1,44} has shown that the analysis revealed all substances whose mole fractions in the vapour phase are greater than 10^{-6} . No signs were found of the presence of SiCl and Si₂Cl₆, whose calculated vapour-phase mole fractions are below that level.

The System Si-Cl-H

The spectra obtained at room temperature within the reactor for the system Si-Cl-H-Ar showed practically no differences from those for the system Si-Cl-Ar. Further measurements were carried out mostly at 1 300 K. The spectral bands observed and their assignments are summarized in Table II. Figure 3 shows the spectrum in the range 3 000–400 cm⁻¹. As for the system Si-Cl-Ar, no SiCl was detected. Nor was SiHCl found in the analyzed sample, but the situation in this case is somewhat complicated. The vibration bands $\tilde{\nu}_2 = 808$ cm⁻¹ and $\tilde{\nu}_3 = 522$ cm⁻¹ of SiHCl isolated in an argon matrix⁴⁰ are in close vicinity of intense bands at 805 cm⁻¹ (SiHCl₃) and 518 cm⁻¹ (SiCl₂), and there may be some overlap. The only indication for the absence of SiHCl is the fact that no band appeared around 2 000 cm⁻¹, a wavenumber for the Si-H stretching vibration in the gas-phase SiHCl molecule³¹. As for the system Si-Cl-Ar, no changes in the vapour-phase composition due to temperature changes within the reactor over the range 1 240–1 320 K could be detected.

The qualitative analysis of the vapour phase of the system Si-Cl-H-Ar in equilibrium with solid Si at about 1 300 K and atmospheric pressure revealed the presence

TABLE II

Wavenumbers (cm⁻¹) of IR bands observed in the spectrum of the vapour phase of the system Si-Cl-H in equilibrium with solid silicon at 1 300 K after isolation in a low-temperature argon matrix

Wavenumber	Assignment	Wavenumber	Assignment
3 728	H ₂ O	764	?
2 879	HCl	663	CO ₂
2 844	HCl	642	SiCl ₄
2 834	HCl	616	SiCl ₄
2 340	CO ₂	600	SiHCl ₃
2 250	SiHCl ₃	589	SiCl ₃
1 598	H ₂ O	527	SiH ₂ Cl ₂
948	SiH ₂ Cl ₂	518	SiCl ₂
876	SiH ₂ Cl ₂	512	SiCl ₂
829	SiHCl ₃	493	SiHCl ₃
805	SiHCl ₃	472	SiCl ₃

of HCl, SiCl₄, SiCl₃, SiCl₂, SiHCl₃ and SiH₂Cl₂. Direct comparison with experiments of other investigators is difficult to make, since all other measurements were carried out without an inert gas. Moreover as equilibrium calculations indicated, the presence of an inert gas significantly affects the equilibrium vapour-phase composition. It is, however, interesting to compare our results with those of Nischizawa et al.^{14,15}. In the system Si-Cl-H under non-equilibrium conditions at 1 423 K, these workers identified the same compounds as found by us, but failed to detect SiCl₃ in samples of the vapour taken from the reactor and cooled to a lower temperature. This attests to a relatively low stability of SiCl₃ and also shows the adequacy of the method and experimental arrangement used by us to detect these unstable substances.

Comparison with calculated values^{1,44} has shown that the analysis revealed all substances whose calculated mole fractions in the vapour phase are greater than 10⁻⁶. No SiCl, Si₂Cl₆, SiH₄, SiH₃, SiH₂, SiH and SiH₃Cl, whose calculated mole fractions are below that level, could be detected.

CONCLUSIONS

The results of qualitative analysis of the vapour phase in the systems Si-Cl and Si-Cl-H in equilibrium with solid Si have shown that MIRR spectroscopy is capable of detecting the presence of SiCl₄, SiCl₃ and SiCl₂ in the system Si-Cl and of HCl, SiCl₄, SiCl₃, SiCl₂, SiHCl₃ and SiH₂Cl₂ in the system Si-Cl-H. According to equilibrium calculations, SiCl₃ should be present in the vapour phase in a relatively high

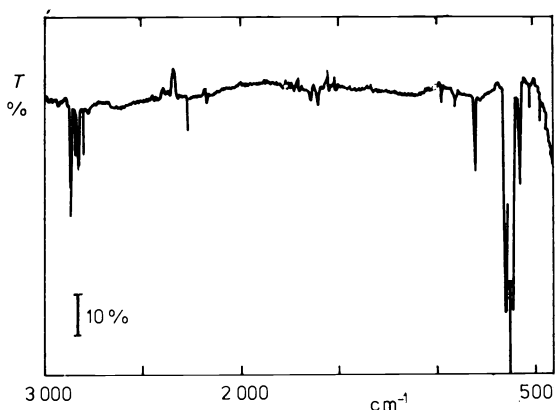


FIG. 3

IR spectrum of the vapour phase of the system Si-Cl-H in an Ar matrix; reactor temperature, 1 300 K; initial composition, 0.1 vol. % SiCl₄, 9.1 vol. % H₂ and 90.8 vol. % Ar

concentration (comparable with that of SiCl_2 or SiH_2Cl_2), but previous studies under equilibrium conditions failed to detect it. This is probably due to the fact that SiCl_3 is stable only at high temperatures and may undergo a rapid conversion before sample analysis can be performed. There remains the question of presence of SiHCl . According to equilibrium calculations, this species is one of the dominant components of the vapour phase at temperatures around 1 300 K and particularly at reduced pressure or at high inert gas concentrations. However, we were not able to detect it.

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