JOURNAL OF MATERIALS SCIENCE 19 (1984) 3079–3089

Calculation of deposition conditions for Si_3N_4 from a SiL_4–NH_3 gas phase (L = H, Cl, Br, CH)

J. F. LARTIGUE, M. DUCARROIR, B. ARMAS
Laboratoire des Ultra-Rèfractaires, CNRS, b.p.5, 66120 Odeillo/FontRomeu, France

Deposition conditions yielding silicon nitride are calculated for a set of initial gaseous systems, by complex thermodynamic equilibria computations. The influence of temperature, total pressure and reactant gas ratios on the composition and yield of the condensed phase are shown for SiH_4/NH_3, $SiCl_4/NH_3$, $SiBr_4/NH_3$, $Si(CH_3)_4/NH_3$ and $SiH_4/CH_4/NH_3$ systems. The interest of such calculations is to give an efficient approach for experimental studies of vapour-deposition systems.

1. Introduction and previous work

Silicon nitride is a potentially attractive ceramic material for high-temperature mechanical uses, due to its refractory properties, chemical stability, strength and resistance to creep.

It is now well known that mechanical properties are closely related to the way Si_3N_4-based ceramics are prepared. Hot-pressed silicon nitride (HPSN) has higher strength than reaction-bonded silicon nitride (RBSN) [1]. Authors believe that chemical vapour deposition, which enables fully dense materials with controlled microstructures to be formed (CVD Si_3N_4), will lead to a further improvement in properties [2, 3].

The purpose of this thermodynamic study is to provide accurate information concerning the possibilities of Si_3N_4 deposition from different vectors with the objective of determining the most favourable conditions for the reaction, and thereby define the domain within which a matrix of experiments may be conducted.

Investigations into this topic have been limited. Mellottee and Cochet [4] thoroughly studied the SiH_4/NH_3 gas system. They demonstrated the influence of temperature, ratio of reactant gases and dilution (H_2, N_2, Ar) on the deposition process. Fischer [5] made an overall study of the formation of Si_3N_4 from a mixture of tetramethylsilane (TMS) and ammonia. He gives the Gibbs free energy of Reaction 1 as a function of temperature below 1500 K:

$$3\ Si(CH_3)_{4g} + 4\ NH_{3g} \rightarrow Si_3N_{4s} + 12\ CH_{4g} \quad (1)$$

$$\Delta G^0_{500\,K} = -2300\,kJ \qquad \Delta G^0_{1500\,K} = -2500\,kJ$$

This possible means of decay for $Si(CH_3)_4$ is compared to other reactions with Si, C, CH_4, H_2, SiC as products. Reaction 1 is thermodynamically favoured. The data used in our work lead to higher values of the free enthalpy for the above reaction:

$$(\Delta G^0_{500\,K} = 1370\,kJ; \quad \Delta G^0_{1500\,K} = -1800\,kJ)$$

A thermodynamic approach for the formation of silicon nitride by nitridation of SiO_2–C mixtures with N_2 or NH_3, with Fe as a catalyst, mentions the Si–N–H system. However, no results are given [6]. In addition, Spear and Wang [7] give the CVD phase diagram in the Si–Cl–N–H system with SiH_2Cl_2 and NH_3 as reactants. At low pressures (40 Pa), Si_3N_4 is deposited when there is a lack of silicon in the gas phase. A two-phase deposit (Si_3N_4 + Si) occurs where the SiH_2Cl_2/NH_3 ratio is higher than 1.5 at temperatures ranging from 573 to 1073 K. The calculated yield of condensed phase is 100% at 1073 K.

2. Experimental systems

A method of minimization of the free enthalpy is used to calculate the equilibrium compositions for the following systems:

Si–N–H (reagents SiH_4–NH_3)

Si–Br–N–H (reagents $SiBr_4$–NH_3)

Si–Cl–N–H (reagents $SiCl_4$–NH_3)

TABLE I Species used for calculations

System			
Si–N–H	Si–C–N–H	Si–Cl–N–H	Si–Br–N–H
Si_s	Si–N–H system	Si–N–H system	Si–N–H system
Si_g	plus	plus	plus
$Si_{1,g}$	C_s	Cl_g	Br_g
$Si_{2,g}$	SiC_s	$Cl_{2,g}$	$Br_{2,g}$
$N_{2,g}$	CH_{3g}	$SiCl_g$	$SiBr_{2,g}$
$H_{1,g}$	CH_{4g}	$SiCl_{2,g}$	$SiBr_{4,g}$
$H_{2,g}$	C_2H_{2g}	$SiCl_{3,g}$	BrN_g
SiN_g	C_2H_{4g}	$SiCl_{4,g}$	HBr_g
Si_2N_g	HCN_g	HCl_g	
$Si_3N_{4,s}$	$Si(CH_3)_4$	$SiH_2Cl_{2,g}$	
SiH_g	$HSi(CH_3)_3$	$SiHCl_{3,g}$	
$SiH_{4,g}$	$H_2Si(CH_3)_2$		
$NH_{2,g}$			
$NH_{3,g}$			
$N_2H_{2,g}$			

Si–C–N–H (reagents $Si(CH_3)_4$–NH_3 and SiH_4–CH_4–NH_3)

Thermodynamic data for the first three systems are taken from a bank of critically evaluated and updated data available on transpac and euronet networks (Thermodata, B.P. 66, 38402 – St Martin d'Hères, France). Two condensed phases are taken into account: Si and Si_3N_4, with a unitary activity. The existence of equivalent compounds in the gas phase is also considered as possible. Table I summarizes the species considered in each system. Steele [8] recently measured the enthalpy of formation of TMS (Si–C–N–H system) ΔH_f^0 (TMS_g) = $-(233.2 \pm 3.2)\,kJ\,mol^{-1}$. Benson's value is notably different: $-110\,kJ\,mol^{-1}$ [9] but the entropy $S(T)$, necessary for calculations, is given. From both values anyway, TMS is not stable enough between 800 and 1800 K to appear in the equilibrium composition. The choice of its thermodynamic data has no influence on the results. Data for methylsilanes are those mentioned by Benson, Table II [9]. The calculations use the possible equilibrium phases of the Si–C–N ternary systems Si, C, Si_3N_4, SiC. There is no evidence of the existence of compounds such as Si_2C_2N or Si_3C_3N [10]. In addition to this, there is no solubility in the condensed phase, as shown by Kieffer *et al.* [11] in their study of two isothermal sections (1900 and 2000 K). Because no other data are available, it will be stated that the equilibria existing at 1900 K remain unchanged between 800 and 1800 K. It is likely that this supposition will be correct because the three binary systems remain unchanged in that range of temperature.

3. Results and discussion

The calculation of complex equilibria makes a prevision possible for deposition phase diagrams as well as the composition of the equilibrium gas phase and yields, as a function of usual experimental parameters (P, T, initial composition). The evolution of the four systems mentioned above with temperature and the atomic ratio N/Si for two values of the total pressure is calculated. The two values of P (atmospheric pressure and some 10^2 Pa) are chosen to match the two main CVD techniques. N/Si is used because it is easily related to the initial composition of an SiL_4–NH_3 gas phase and to the stoichiometry of silicon nitride (N/Si = 4/3); it is one of the possible independent parameters to define the thermodynamic system with respect to its variance.

According to the formation of Van Zeggeren

TABLE II Thermodynamic data for methylsilanes

Species	(k cal)	(cal K^{-1})	C_p(T) (cal K^{-1})			
			300	500	800	1000
$Si(CH_3)_4$	−26	85.8	33.5	46.5	60.5	67.3
$HSi(CH_3)_3$	−21	79.0	28.4	39.2	50.5	55.9
$H_2Si(CH_3)_2$	−17	71.7	22.0	30.7	39.8	44.0

and Storey [12] the number of degrees of freedom of a chemical system with M elements and including S condensed species plus one complex gas phase is: $F = M - S + 1$.

The thermodynamic variables to be specified are two (usually T and P) plus $n = F - 2$ independent ratios of elemental abundances. For a gas phase equilibrium ($S = 0$) the maximum variance is obtained: 4 for the Si–N–H system and 5 for Si–C–N–H, Si–Cl–N–H, Si–Br–N–H. Variance is an important notion which, under certain conditions, enables the determination of deposition phase limits with only one equilibrium calculation at each temperature.

3.1. Si–N–H system

This system was studied previously [4] and is used for comparison purposes. Silane, being metastable, readily dissociates to yield a condensed phase: Si and/or Si_3N_4. The equilibrium gas phase is simple: mainly N_2 and H_2, and silicon vapour remains below $10^{-4}\%$ (Table III). Two phase limits are obtained: $Si/Si + Si_3N_4$ and $Si + Si_3N_4/Si_3N_4$ (Figs. 1 and 2). They are accurately known from a few calculations inside the two-phase domain where the variance is 2. T and P being specified the composition of the gas phase is determined: it is independent of N/Si. Then, at each temperature, the phase limits are deduced from atom balance equations.

The results are in perfect agreement with those of Mellotee and Cochet [4]: the $Si_3N_4 + Si/Si_3N_4$ phase limit is the same for similar conditions; the transformation yield of SiH_4 into Si_3N_4 is 100% in the one-phase domain and the influence of total pressure is compatible with that of dilution. The existence of deposited silicon with $N/Si < 5$ was proved experimentally by Mollimard *et al.* [13] at 1300 K, atmospheric pressure, with H_2 as a diluent.

The conclusion is that high pressures, low temperatures and excess of the nitrogen vector ($N/Si > 4/3$) are the best conditions to obtain pure Si_3N_4.

TABLE III Equilibrium compositions

	$1SiH_4 + 1NH_3$	$1SiH_4 + 2/3NH_3$
P	1 torr	760 torr
T	1450 K	1400 K
$H_{2,g}$	3.500 mol	3.000 mol
$N_{2,g}$	0.044 mol	0.000 mol
Si	0.316 mol	0.500 mol
Si_3N_4	0.228 mol	0.167 mol

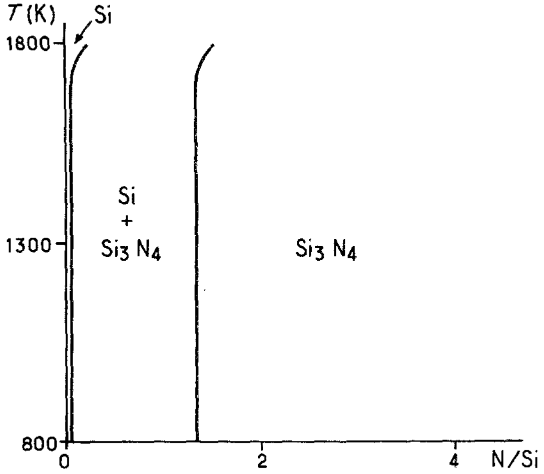

Figure 1 Si–N–H system; $P = 1.01 \times 10^5$ Pa; $H/Si = 4 + 3N/Si$. Deposition phase diagram.

3.2. Si–C–N–H system

There are four possible condensed phases: Si–C–SiC–Si_3N_4. The study is limited to 800 to 1800 K, N/Si between 0.2 and 10, pressures of 506 and 1.01×10^5 Pa with an initial gas phase containing TMS and ammonia. Within such limits, three solid phases can co-deposit, and no silicon appears (Figs. 3 and 4). The silicon vector $Si(CH_3)_4$ is totally dissociated the way SiH_4 is, and the yield of silicon nitride in the Si_3N_4 and $Si_3N_4 + C$ domains is 100%. When three condensed phases coexist (in agreement with the Si–C–N phase diagram) the variance is 2. The limits of the three-phase domain are determined in the way explained for Si–N–H, with only one calculation at each temperature.

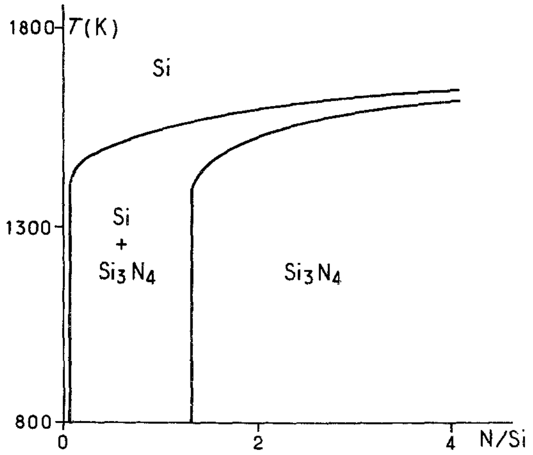

Figure 2 Si–N–H system; $P = 131$ Pa; $H/Si = 4 + 3$ N/Si. Deposition phase diagram.

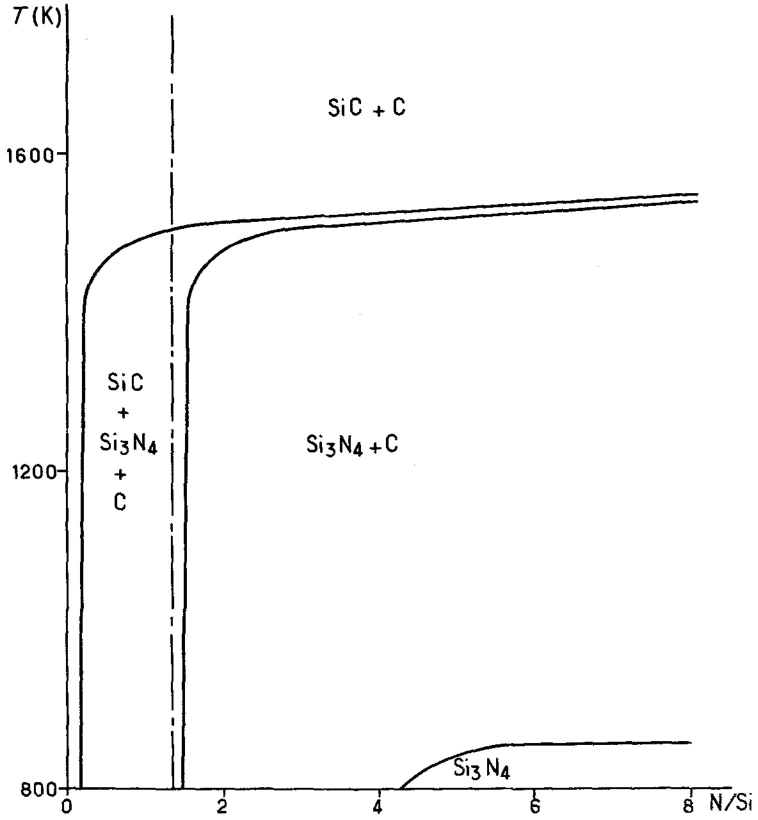

Figure 3 Si–C–N–H system; $P = 1.01 \times 10^5$ Pa; C/Si = 4; H/Si = 12 + 3 N/Si. Deposition phase diagram.

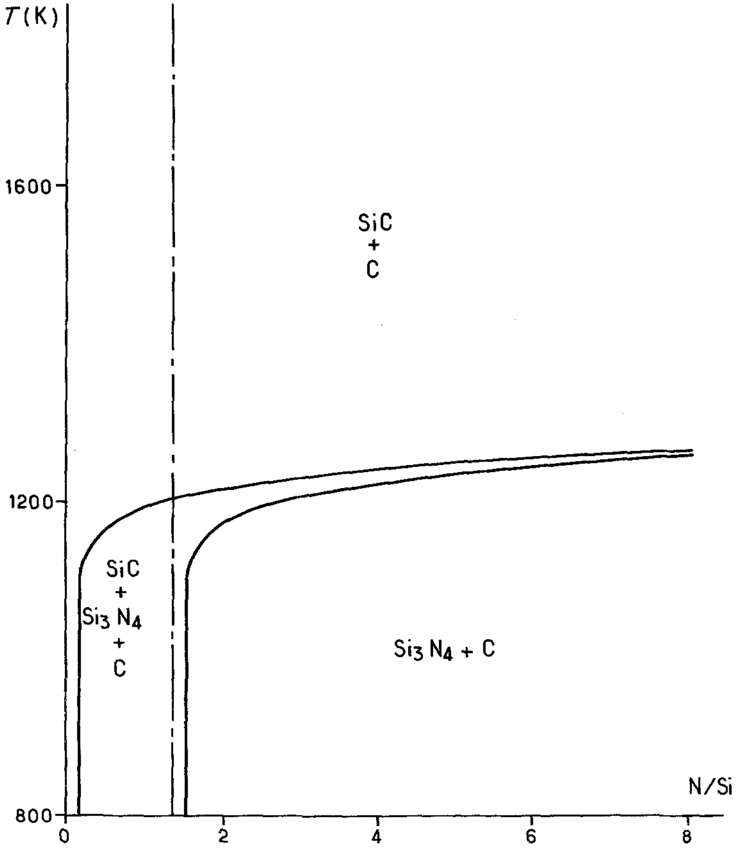

Figure 4 Si–C–N–H system; $P = 506$ Pa; C/Si = 4; H/Si = 12 + 3 N/Si. Deposition phase diagram.

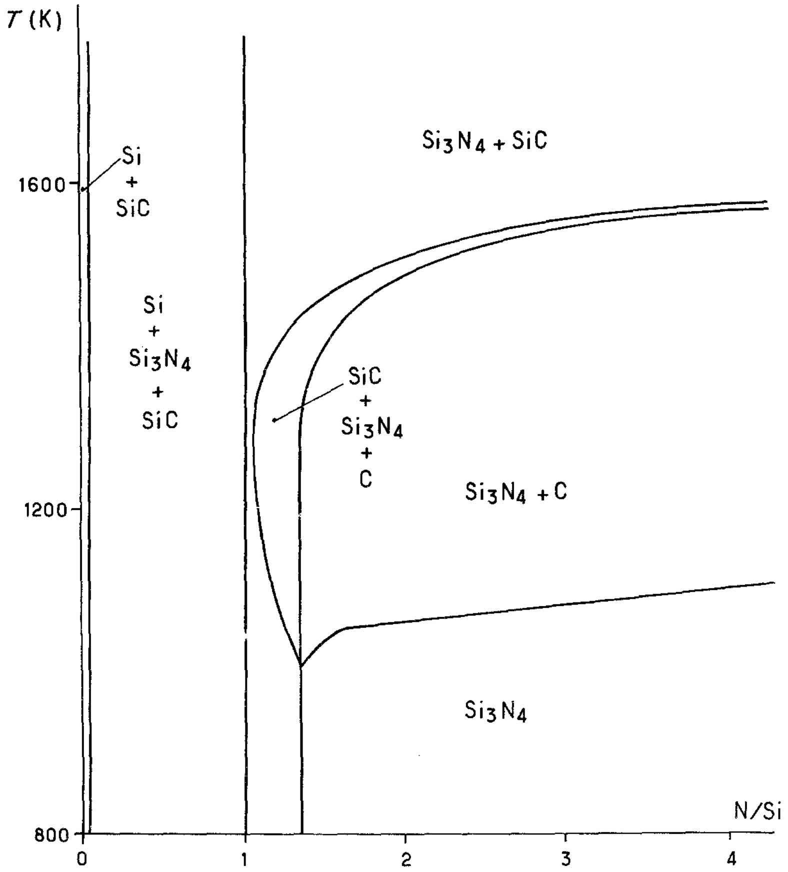

Figure 5 Si–C–N–H system; $P = 1.01 \times 10^5$ Pa; C/Si = 1/4; H/Si = 5 + 3 N/Si. Deposition phase diagram.

Silicon carbide tends to appear at high temperatures, except when the initial gas phase is deficient in ammonia. Carbide is found even at 800 K with $N/Si < 0.1$.

The pure Si_3N_4 domain exists only at atmospheric pressure, low temperature and $N/Si > 4.2$. Under such conditions, carbon is trapped in the gas mainly as methane, which becomes unstable at higher temperatures.

With $N/Si > 1.33$, a slight increase of temperature (30 K) results in the deposition of SiC instead of Si_3N_4. The evolution in the conditions of the complex equilibrium is described from mass balances by the simple reaction:

$$1/3\ Si_3N_4 + C \rightarrow SiC + 2/3\ N_2, \qquad (2)$$

showing that the main phenomenon involved is the relative stability of Si_3N_4 and SiC.

The widths of the three-phase domain in the Si–C–N–H system, and the two-phase domain in the Si–N–H system have roughly constant values, independent of temperature and equal to 4/3 on the N/Si axis. This is a consequence of the almost total absence of silicon-bearing molecules in the gas phase, except at high temperatures where they reach 0.1 mol %.

Because of the few gaseous species at the equilibrium, Si–C–N–H is a "clean" system and Si_3N_4 is thermodynamically favoured by high pressure, low temperature and excess ammonia. Kinetic problems will arise under such conditions.

It is evident that an initial gas phase $Si(CH_3)_4/NH_3$ cannot result in an Si_3N_4 + SiC deposit, or a wide Si_3N_4 domain. C/Si = 4, a consequence of the choice of reagents, makes it unavoidable to deposit C when SiC and Si_3N_4 are present together. An initially low carbon gas phase will therefore make carbon disappear. Calculations are undertaken to prove this, with the following initial gas phase at $P = 1.01 \times 10^5$ Pa:

$$SiH_4 + 1/4\ CH_4 + nCH_3$$

$$C/Si = 1/4;\ H/Si = 5 + 3n;\ N/Si = n$$

All the available carbon at high temperature is in the form of silicon carbide. The Si_3N_4 domain is wider and the high temperature deposits have an Si_3N_4 + SiC composition (Fig. 5).

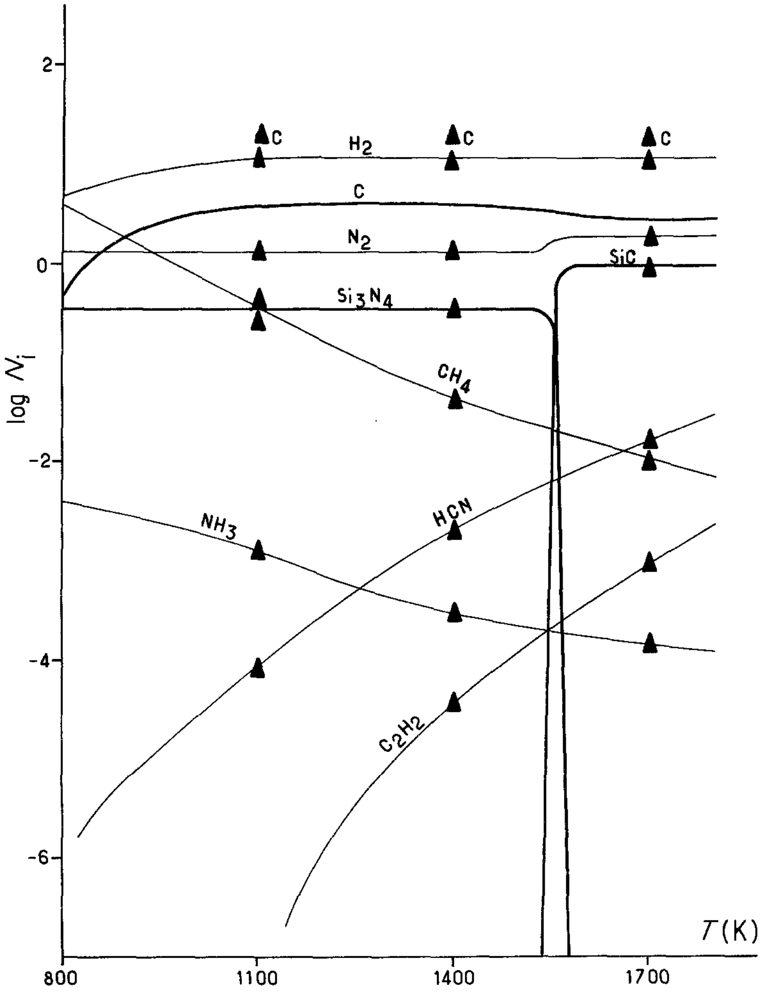

Figure 6 Equilibrium composition from $Si(CH_3)_4 + 4NH_3$; (▲ from $Si(CH_3)_4 + 4NH_3 + 10C$); $P = 1.01 \times 10^5$ Pa; (N_i = mol).

This phase diagram is easy to explain when split into three sections:

1. $N/Si < 1$. All the carbon and nitrogen are used to make SiC and Si_3N_4. Because of the lack of nitrogen, some silicon remains free;

2. $1 < N/Si < 1.5$. Transition: free silicon becomes Si_3N_4, and SiC is replaced by the stable carbon-containing phase at the temperature under consideration and an excess of nitrogen;

3. $N/Si > 1.5$. Carbon is in different forms, CH_4 (pure Si_3N_4 domain) then C and eventually SiC. The remaining silicon is in the form of the nitride Si_3N_4.

The limits between two-phase and three-phase domains are deduced from a minimum number of calculations with the above-mentioned techniques, checked by additional calculations.

As experimental deposits are often prepared on graphite substrates (cheap, electrical conductive, easy to machine and to remove by burning) it is necessary to know the changes induced by carbon in the equilibria. Given the simple composition of the gas phase (Fig. 6) adding carbon to the initial composition ought to have little influence even on hydrocarbons. Calculations after adding 10 carbon atoms show no change (black triangles in Fig. 6).

3.3. Si–Br–N–H system

Unlike the first two systems, the silicon vector is never totally dissociated. At temperatures higher than 1250 K, $SiBr_2$ becomes increasingly stable and traps silicon into the gas phase, stopping Si_3N_4 deposition (Fig. 7). This evolution of the equilibrium composition, between 1300 and 1600 K is shown by Reaction 3 at low pressure:

$$Si_3N_{4,s} + 6HBr_g \rightarrow 2.5SiBr_{2,g} + 0.5Si_s + 2N_{2,g} + Br_g + 3H_{2,g}. \qquad (3)$$

In such a system, the yield, ρ, of silicon nitride

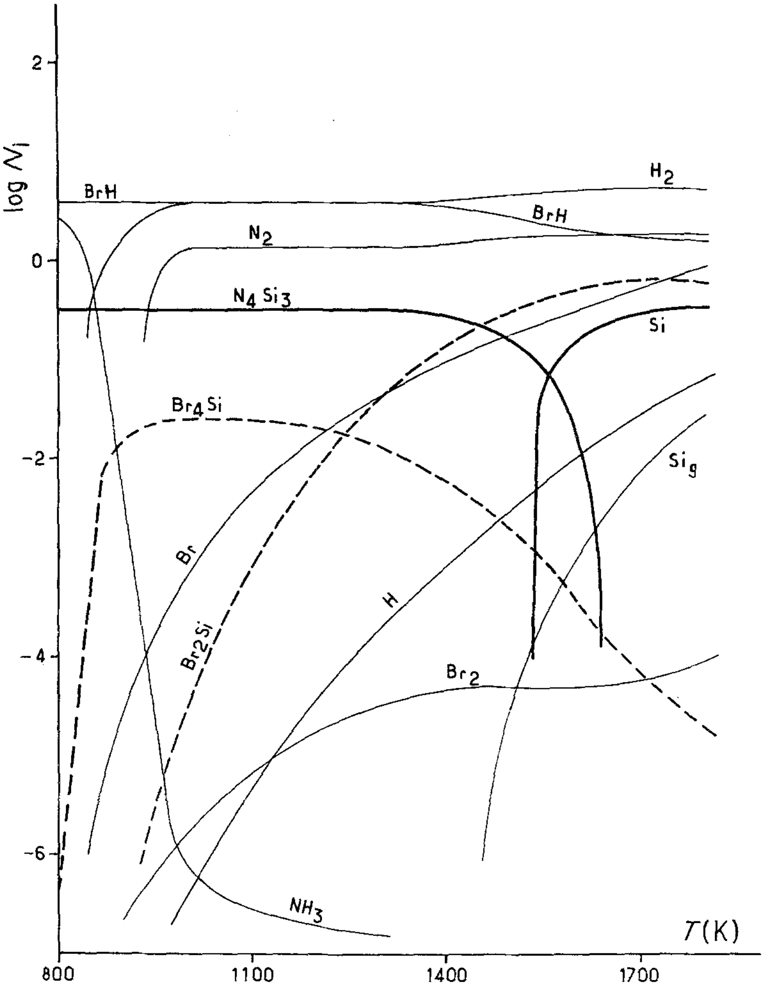

Figure 7 Equilibrium composition from $SiBr_4 + 4\ NH_3$; $P =$ 131 Pa; (N_i = mol).

becomes interesting. ρ is the ratio of the calculated equilibrium quantity of nitride to the maximum possible quantity (without thermodynamic limitations). With an initial composition $1 SiBr_4$ and $x NH_3$, it is given as a function of x by:

$$x \leqslant 4/3 \quad \rho = 100 \left[\frac{4\,(Si_3N_4)_{eq}}{x}\right] \%$$

the maximum quantity of Si_3N_4 is $x/4$ (limited by NH_3);

$$x \geqslant 4/3 \quad \rho = 100 \left[\frac{3\,(Si_3N_4)_{eq}}{1}\right] \%$$

the maximum quantity of Si_3N_4 is 1/3 (limited by $SiBr_4$). Constant yield curves are added to the deposition phase diagram.

Fig. 8 shows that Si_3N_4 is the only possible condensed phase at atmospheric pressure. At low pressures, either Si or Si_3N_4 is obtained. At high temperature and low N/Si values, a domain of homogeneous gas phase equilibrium appears (Fig. 9). At the Si_3N_4/no deposit or Si_3N_4 + Si/Si limits, $SiBr_2$ becomes the major silicon-bearing molecule in the equilibrium gas phase. This is an undesirable situation for silicon nitride deposition. $SiBr_2$ is associated with deposited silicon if a limiting value for N/Si is reached. This value increases with temperature (Si/no deposit limit).

At fixed temperature and pressure, the Si_3N_4 yield is minimal at N/Si = 4/3, stoichiometry of the nitride. Around this value, the yield increases with excess of a reagent. The single points on the dotted lines are a consequence of the change of the definition of ρ. Vertical parts of the constant yield curves, especially at atmospheric pressure, shown an independence from temperature that tends to disappear at low pressure. However, high-yield curves are little shifted by a change in pressure.

To sum up, conditions are found where the

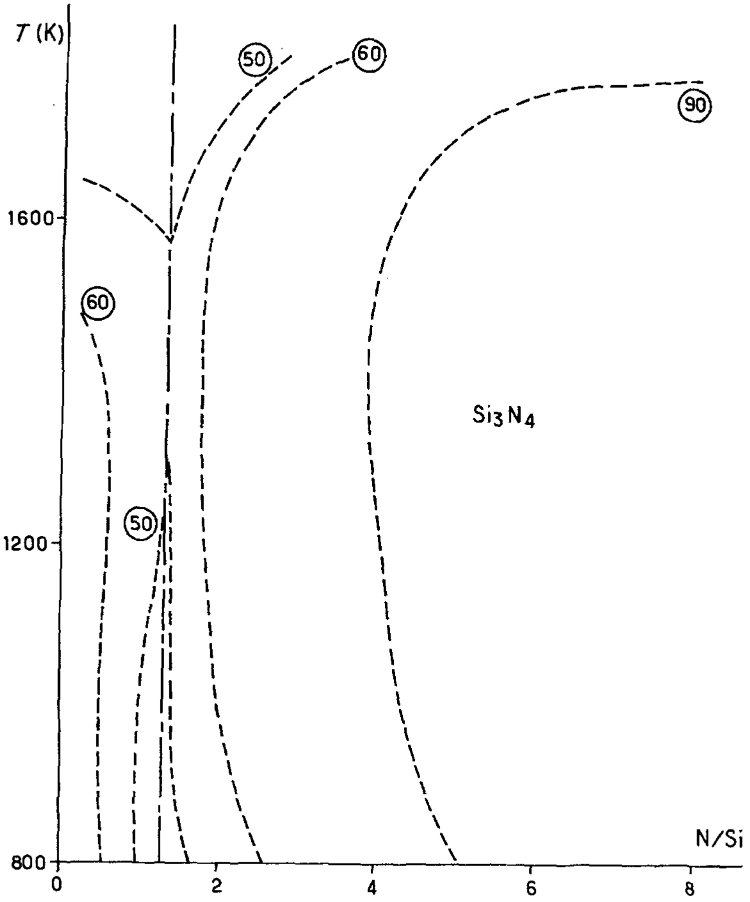

Figure 8 Si–Br–N–H system; $P = 1.01 \times 10^5$ Pa; Br/Si = 4; H/Si = 3N/Si. Deposition phase diagram and constant yield curves.

deposition of Si_3N_4 is not sensitive to the experimental parameters: atmospheric pressure, N/Si > 4 (excess ammonia), between 1000 and 1600 K.

3.4. Si–Cl–N–H system

A wide range of temperature and initial composition is obtained to deposit Si_3N_4. Homogeneous gas-phase equilibria appear at high temperature (Figs. 10 and 11). The change in total pressure from 1.01×10^5 Pa to 131 Pa, results in a shift of the limit between Si_3N_4 and homogeneous gas phase equilibrium areas: 400 K towards low temperatures.

The reason for the lack of condensed phase is the same for both halide systems. Silicon chlorides, $SiCl_2$ and $SiCl_3$, appear at lower temperatures than the homologous bromides and in quantities increased by low pressures (Fig. 12).

The constant yield curves are roughly the same as those calculated for the Si–Br–N–H system, but there are no vertical sections. Yields are strongly dependent on total pressure, and initial composition $NH_3/SiCl_4$. High yields are obtained with higher N/Si values than are necessary with the bromide system, because of the stability of the initial halide.

A high yield will be obtained with a minimal quantity of ammonia at low pressures, and depositing parameters will be easier to maintain where the constant yield curves have a weak curvature (weakly dependent on temperature). To be coherent with experimental conditions, calculations are made with carbon added to the initial composition. The results are shown by the black triangles in Fig. 12. Below 1100 K, no important changes of the equilibrium composition are seen. At high temperatures, Si_3N_4 disappears and is replaced by SiC; $SiCl_4$, $SiCl_3$, $SiCl_2$, SiCl have lower concentrations. The deposition phase diagram is strongly altered.

4. Conclusions

The results obtained for the four deposition systems are a preliminary step towards guiding

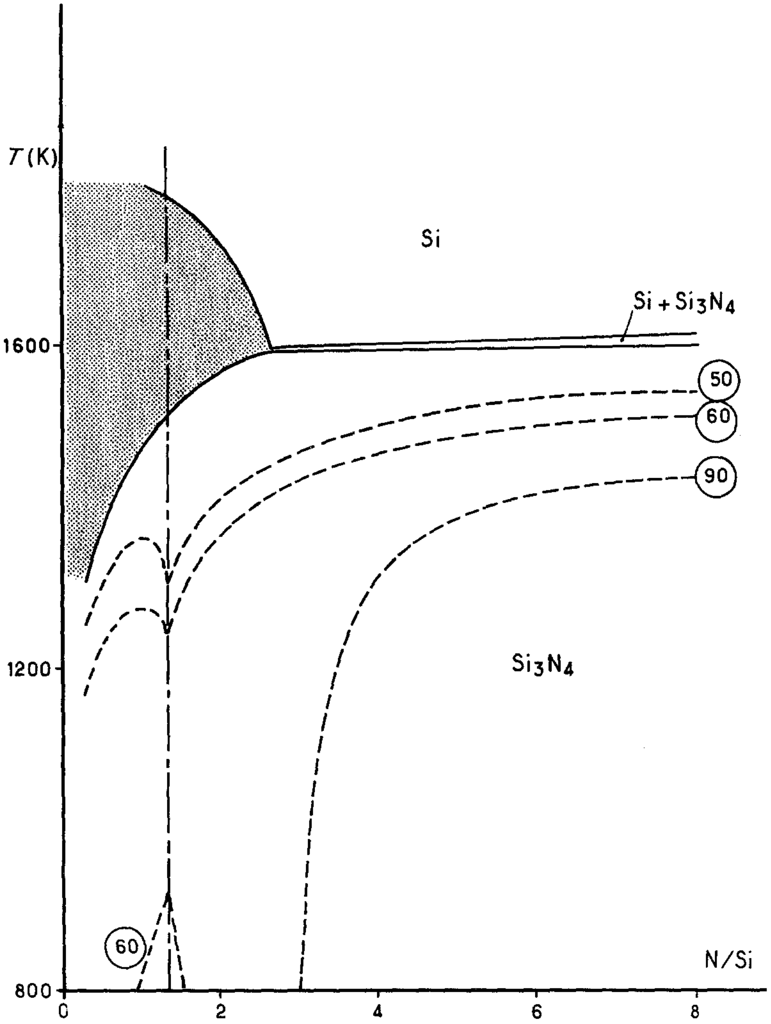

Figure 9 Si–Br–N–H system; $P = 131$ Pa; Br/Si = 4; H/Si = 3N/Si. Deposition phase diagram and constant yield curves (shaded area = homogeneous gas phase equilibrium).

experimental study. The nature and yield of deposits can be predicted at given temperatures, pressures and compositions.

As a rule, the nitrogen vector must be in excess to obtain high yields for the conversion of the silicon vector into silicon nitride. In any case, pure nitride is obtained at low temperatures (800 K) and its deposition domain is reduced at low total pressures.

SiH_4/NH_3 and $Si(CH_3)_4/NH_3$ systems are "clean" ones, with simple compositions of the gas phase. In the former, the conversion is total even at low temperature and immediately above N/Si = 4/3. The latter does not easily yield Si_3N_4 without carbon and the best conditions are $T \sim 800$ K, N/Si > 4, $P = 1.01 \times 10^5$ Pa. It must also be taken into account that the decomposition of methane is kinetically slow and the experimental domain for pure silicon nitride might be much larger than the theoretical one. Additionally, it is worth noting that $Si(CH_3)_4$ is not dangerous to handle, unlike SiH_4 which is auto-flammable and explosive. Such facts added to the theoretical results makes $Si(CH_3)_4$ a system worthy of study.

Halide systems ($SiCl_4$–NH_3, $SiBr_4$–NH_3) give Si_3N_4 deposits with high yields for a wide range of experimental conditions. Yields are strongly dependent on the N/Si ratio of the initial gas phase. An excess of NH_3 is necessary (higher for Si–Cl–N–H than for Si–Br–N–H to obtain the same yield). The equilibrium gas phase is complex and the predominance of silicon subhalides at high temperatures may inhibit deposition.

Acknowledgements

Financial support of the French Ministry of

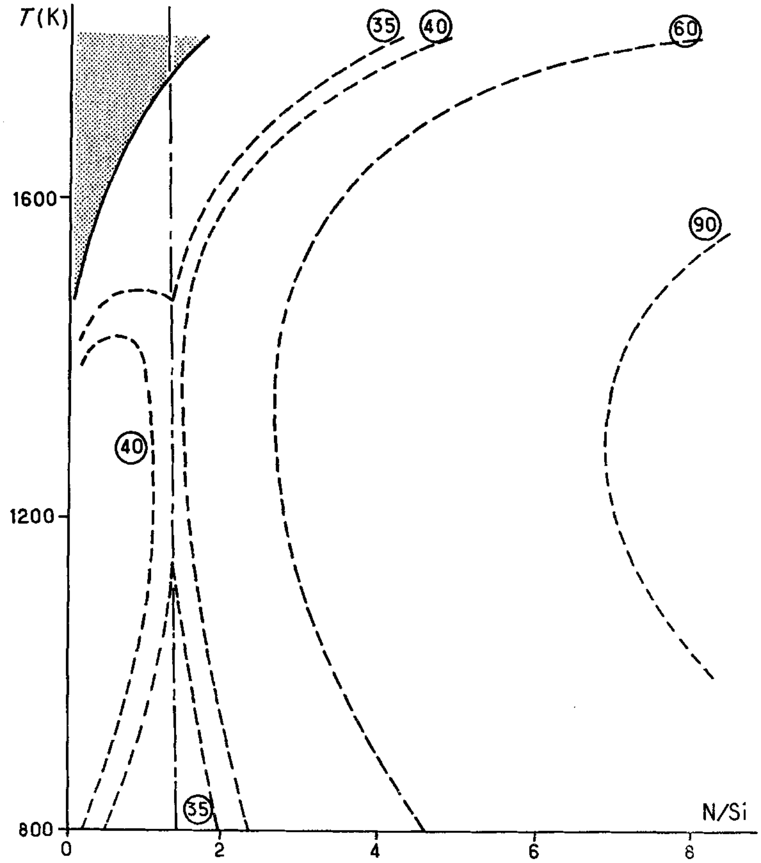

Figure 10 Si–Cl–N–H system; $P = 1.01 \times 10^5$ Pa; Cl/Si = 4; H/Si = 3N/Si. Deposition phase diagram and constant yield curves (shaded area = homogeneous gas phase equilibrium).

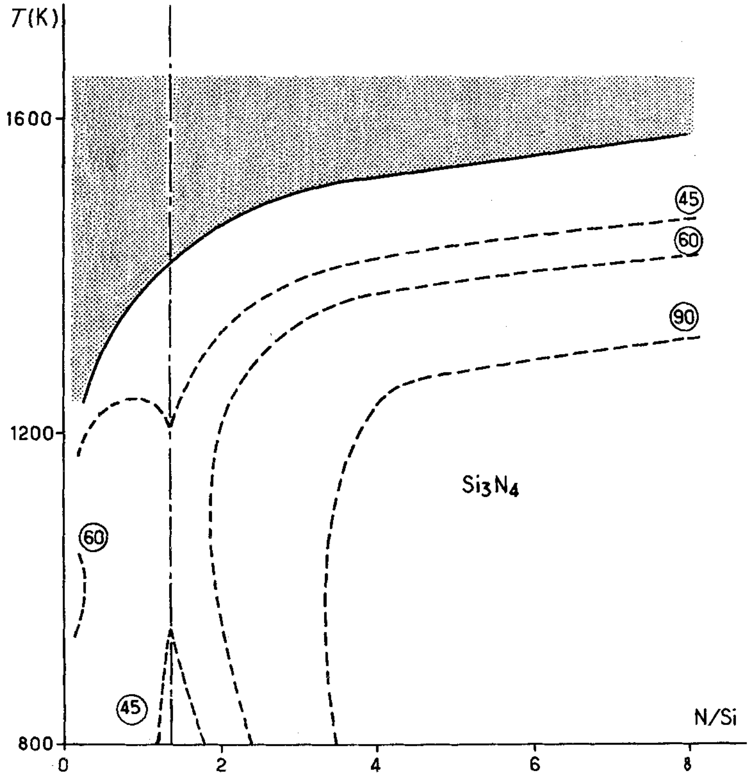

Figure 11 Si–Cl–N–H system; $P = 131$ Pa; Cl/Si = 4; H/Si = 3 N/Si. Deposition phase diagram and constant yield curves (shaded area = homogeneous gas phase equilibrium).

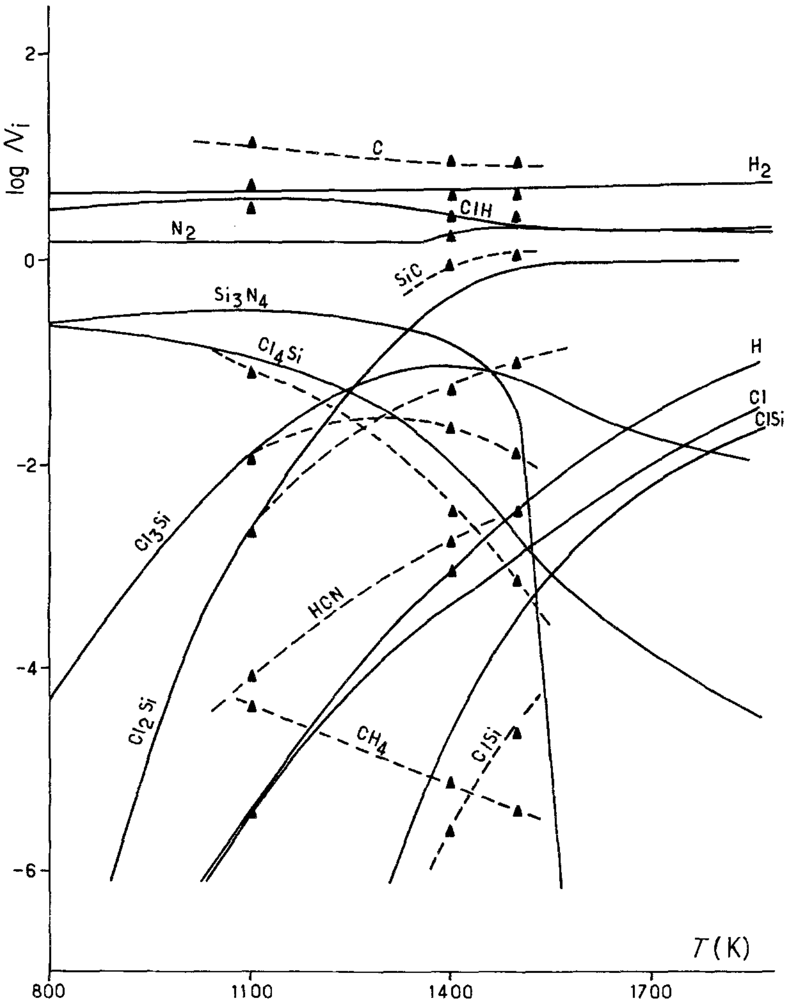

Figure 12 Equilibrium composition from $SiCl_4 + 4NH_3$; (▲ and dotted line from $SiCl_4 + 4NH_3 + 10C$); $P = 131$ Pa; (N_i = mol).

Defence (DRET) (contract no. 82 34 030 00 470 75 01) is gratefully acknowledged. All the computations were made on line using the minimization method previously described by Bernard *et al.* [14].

References

1. G. ORANGE and G. FANTOZZI, Text presented at J.E.N.I.S., University of Rennes (F), May (1962).
2. J. L. CHERMANT, R. MOUSSA and F. OSTERSTOCK, *Rev. Int. Hautes Temp. Réfract, Fr.* **18** (1981) 5.
3. D. J. GODFREY, in Conference Proceedings AGARD, CP – 276 (1980), p. 21-1.
4. H. MELLOTTEE and G. COCHET, *Rev. Int. Hautes Temp. Réfract. Fr.* **13** (1976) 31.
5. H. FISCHER, *Z. Phys. Chemie Lepzig* **252** (1973) 213.
6. S. A. BADRAK, T. S. BARTNITSKAYA, I. M. BARYSHEVSKAYA, T. YA. KOSLAPOVA, P. P. PIKUZA, B. G. TRUSOV and V. P. TUROV, *Poroshk. Metall.* 9 (225) (1981) 66.
7. K. E. SPEAR and M. S. WANG, *Solid State Technol.* (July) (1980) 63.
8. W. U. STEELE, *J. Chem. Thermodynamics* **15** (1983) 595.
9. S. W. BENSON, "Thermochemical Kinetics", 2nd edn. (John Wiley, New York, 1976) p. 298.
10. M. BILLY and F. COLOMBEAU, *Compt. Rend. Acad. Sci.* **264** C, (1967) 392.
11. A. R. KIEFFER, P. ETTMAYER, E. GUGEL and A. SCHMIDT, *Mat. Res. Bull.* 4 (1969) S 153.
12. F. VAN ZEGGEREN and S. H. STOREY, "The Computation of Chemical Equilibria" (Cambridge University Press, 1970) p. 18.
13. D. MOLLIMARD, H. MELLOTTEE and R. DELBOURGO, *Bull. Soc. Fr. Ceram.* **105** (1975) 11.
14. C. BERNARD, Y. DENIEL, A. JACQUOT, P. VAY and M. DUCARROIR, *J. Less Common Metals* **40** (1975) 165.

Received 19 September
and accepted 19 December 1983