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Thermochemistry of silicon carbide growth by chemical transport reactions

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Chemical Vapour Transport is a well known process widely used for the growth of monocrystals. This paper is a thermodynamic overview of different heterogeneous chemical systems, promising for the growth of silicon carbide by means of chemical transport reactions. The systems are Si-C-Y where Y is oxygen or a chalcogen (S, Se) and Si-C-H-X where X is an halogen (Cl, Br, I). We studied in a first step the gas phase composition obtained from SiC etching with the transporting agent as a function of temperature. In a second step, we report the conditions for the formation of silicon carbide from such a vapour at a different temperature. Finally we discuss optimal conditions of temperatures and thermal gradients required for SiC transport with each systems.

1. Introduction

Silicon carbide, produced by the reaction of silica sand and coke in an electric furnace - Acheson process- is the second most widely used synthetic material in abrasives, refractories and ceramics. Its wide gap semiconductor properties are very interesting in the realisation of high power and high frequency devices functioning under extreme conditions of temperature. Performances of such devices are limited by the crystalline quality of the SiC wafers. In spite of all recent progresses in SiC growth, for both bulk crystals and thin films, much remain to be done, especially in the defects elimination (micropipes, stacking faults, antiphase boundaries...) and in increasing the growth rates. Apart from the other processes used, we performed thermodynamical calculations related to a new way to grow monocrystalline silicon carbide: the Chemical Vapour Transport (C.V.T.). In the CVT process, a source material is etched by a gaseous transporting agent to form volatile species at a temperature T_1. At an other location of the system, these species react at a temperature T_2 for the crystal growth. Gaseous species migrate within the thermal gradient from the source zone to the deposit zone. To our knowledge, this old process, largely used for some materials such as Si, GaAs or ZnSe has never been applied for carbides because of difficulties involved in carbon transport. If we refer to the II–VI semiconductor bulk growth, better crystalline quality with similar growth rate are expected at lower temperatures with CVT than with Physical Vapour Transport [1, 2]. Furthermore, lowering the temperature should avoid the defects formation such as micropipes and macro-defects, attributed to the high temperatures involved in the sublimation process ($1900 < T < 2300$°C).

In this paper, we report an overview of the thermochemistry of different chemical systems, applied to the growth of silicon carbide by CVT. We studied the SiC etching and deposition steps with different transporting agents as a function of temperature. The aim of this work is to clarify the potential of different chemical systems for the chemical vapour transport of silicon carbide.

2. Calculation details

We studied in a closed system the heterogeneous solid/gas equilibria in various systems with the assumption that source and deposit zones are two separated volumes and that equilibrium conditions are reached between the gas and the solid phases at the reaction surface. Kinetic limitations and mass and heat transports were not taken into account. The thermodynamic

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calculations are based on the total Gibbs free energy minimisation from the GEMINI1 computer program and a coherent set of data from Thermodata (Saint-Martin d'Heres, France). A constant total volume of 100 litres allows to use higher quantities of compounds in order to increase the precision of the results.

The three main parameters involved in this work are temperatures of the source (Ts) and the deposit (Td), and the initial amount of transporting agent, from which the total pressure is determined. We overviewed the temperature range from 800 K to 2200 K. Below 800 K, the rate of SiC etching is too low [3]. Above 2200 K, SiC sublimates and chemical transport loses its interest compared to physical transport. So we will mainly focus on temperatures inferior to 2000 K. The initial amounts of SiC and transporting agent were each fixed to one mole. This corresponds to a total pressure around one atmosphere at high temperature (1600 K). As the SiC and the transporting agent amounts were kept to one mole, all the yields calculated (etching or deposition) relative to these values can be considered as amounts in mole. So, all these yields are directly comparable one to each others. It permits to evaluate the etching and transporting capabilities of the different transporting agents.

For all the chemical systems reported here, we studied in a first step the gas phase content resulting from SiC etching with the transporting agent, versus temperature. For this, we noted the equilibrium partial pressures of the different gaseous species obtained after calculations at Ts. In a second step, we examined the solid phase formed at Td (in the deposition zone) from the gas phase composition calculated previously. In practice, we used the partial pressures obtained at Ts to perform a second calculation at Td. We have represented the results in diagrams where the source temperature is the X-axis and the substrate temperature is the Y-axis. In these figures, the domains of solid phases appearance after calculations are noted as a function of Td and Ts. We will take as a rule that the thermal gradient is defined as Td − Ts. So, the top left part of the graphs reports a positive gradient (Td > Ts) and the lower part reports a negative gradient (Td < Ts). The equation line $y = x$ is the inversion line of the thermal gradient sign. On this line, there is no chemical transport as Ts = Td.

The set of species taken into account in this paper are regrouped in Table I. In several cases, the molar heat capacity C_p of underlined species is not defined through a sufficient temperature range. So, we have predicted this data up to 2500 K from the general formula used in this program:

$$C_p(T) = a + bT + cT^2 + dT^{-2} \quad (\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}})$$

This prediction is true in so far as all Cp of the gases involved are continuous functions, well defined by this polynomial form. Moreover, activity coefficients of the gases are equal to unity, assuming the vapour to have an ideal behaviour.

3. Results and discussion

3.1. Halogens

Transport of silicon carbide by means of halogens (Cl, Br, I) is expected to take place according to the global reaction (1) which is the most probable.

TABLE I Set of species considered for this thermodynamical simulation. Underlined species correspond to predicted values of heat capacities up to 2500 K. (a) Si-C-H-X chemical system (X = Cl, Br or I). (b) Si-C-Y chemical system (Y = O, S, Se). Several species are not present for all Y, so these compounds appear with their true formula

a)

	SPECIES CONSIDERED
Solids	C_{gr}, SiC, Si
Liquids	Si
Gas	X, X_2, $\underline{SiX}$, $\underline{SiX_2}$, $\underline{SiX_3}$, $\underline{SiX_4}$, CX, CX_2, CX_3, CX_4, C_2X_2, C_2X_4, C_2X_6, SiC, CSi_2, CSi_3, CSi_4, C_2Si, C_2Si_2, C_2Si_3, Si, Si_2, Si_3, Si_4, Si_5, Si_6, H, H_2, SiH, CH_3, CH_4, C_2H, C_2H_2, C_2H_4, C_2H_6, HX, $SiHX_3$, SiH_2X_2, SiH_3X, C_2HX, CH_3X, SiH_3CX_3, SiH_3CX

b)

	SPECIES CONSIDERED
Solids	C_{gr}, SiC, Si, X, $\underline{SiS_2}$, SiO_2
Liquids	Si
Gas	X, CX, $\underline{SiX}$, X_2, $\underline{X_3}$, $\underline{X_4}$, $\underline{X_5}$, $\underline{X_6}$, $\underline{X_7}$, $\underline{X_8}$, $\underline{SiS_2}$, SiO_2, CX_2, SiC, CSi_2, CSi_3, CSi_4, C_2Si, C_2Si_2, C_2Si_3, Si, Si_2, Si_3, Si_4, Si_5, Si_6

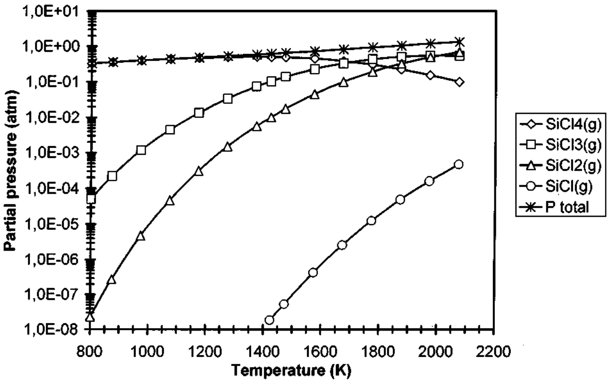

Figure 1 Equilibrium partial pressures of the gaseous species versus temperature for the Si-C-Cl chemical system. $n_{(Cl2)} = n_{(SiC)} = 1$ mol, $V = 100$ l.

$$SiC_{(s)} + 4X_{2(g)} = SiX_{4(g)} + CX_{4(g)} \quad X = Cl, Br, I \quad (1)$$

However, it may be a highly inefficient process. Indeed, as the chemical potentials of halogen in equilibrium with both silicon and carbon are rather different, negligible CX_4 pressures are encountered in equilibrium with SiC under any circumstances.

For example, Fig. 1 reports the equilibrium partial pressures of the gaseous species in the Si-C-Cl chemical system. Whereas silicon leads to silicon chlorides, no carbon species is obtained. In fact, the reaction (2) where free carbon remains in solid state could be more representative.

$$SiC_{(s)} + 2Cl_{2(g)} = SiCl_{4(g)} + C_{(s)} \quad (2)$$

Extraction of metals from carbides by halogens (Cl_2, Br_2, I_2) or their compounds (CCl_4, $CHCl_3$ ...) can lead to the formation of free carbon [4–6]. For SiC, it has been reported that the silicon is preferentially attacked and a carbon-rich layer builds up in the reaction with chlorine containing-gases [3]. In the presence of silicon, the formation of carbon chlorides from direct reaction between chlorine and SiC is disadvantaged. Such species could be observed if silicon was entirely consumed, that is to say in the case of an excess of chlorine. This situation is obviously far from that required for the chemical vapour transport as it involves too high a total pressure in a closed system. Furthermore, the probability of CCl_4 formation decreases with increasing temperature [3]. We can notice however several interesting trends for the silicon behaviour. At low temperatures ($T < 1670$ K), $SiCl_4$ widely prevails, according to the reaction (2) which is very favourable. At high temperatures ($T > 1950$ K), $SiCl_2$ is the most important specie. Schäfer *et al.* and Antipin *et al.* [7, 8] showed the significant role of the dismutation reaction (3) in the transport of silicon.

$$Si_{(s)} + SiCl_{4(g)} = 2SiCl_{2(g)} \qquad (3)$$

For a SiC source, this reaction is observed at higher temperatures because silicon in carbide form is more stable than elemental silicon. Between these two domains of temperatures for which $SiCl_4$ or $SiCl_2$ prevail (1670 K $< T <$ 1950 K), $SiCl_3$ dominates. So, the Cl/Si ratio on the chloride compounds decreases with increasing temperature.

For the other halogens, i.e. bromine and iodine, these general trends are similar. However, whatever the temperature, SiX_3 partial pressure is always small and only SiX_4 and SiX_2 prevail, the former at low temperatures and the latter at higher temperatures. The main difference with chlorine is the limit between these two domains: around 2100 K for bromine and 1600 K for iodine. So $SiBr_4$ dominates on a larger range of temperatures than the other silicon tetrahalides. This point is very interesting as SiX_4 is expected to transport silicon from SiC whereas elemental silicon is usually transported through $SiCl_2$ according to the reaction (3).

3.2. Hydrogen halides

3.2.1. SiC etching

In order to transport SiC, both silicon and carbon must lead to gaseous species with the transport agent. The use of hydrogen halides (HX) could be a good way to reach this goal. For example, we report in Fig. 2, the equilibrium partial pressures of gaseous species obtained from SiC etching with HCl as a function of temperature. The relative evolutions of the silicon chlorides are similar in the two Si-C-Cl and Si-C-H-Cl chemical systems. However, the absolute values of the $SiCl_4$, $SiCl_3$ and $SiCl_2$ partial pressures are slightly smaller with Si-C-H-Cl. Hydrogen leads to the decrease of the silicon halides activity. We can also notice the formation of chlorosilanes like $SiHCl_3$ with pressure large enough to take part in silicon transport. But the most interesting point after the addition of hydrogen concerns the carbon behaviour because hydrocarbon compounds like methane appears. Even if methane partial pressure is not as high as the silicon chlorides ones, it can permit the transport of carbon. The wide divergence between silicon and carbon contents in the gas phase is similar to that found with PVT. Indeed, SiC does not present a congruent sublimation [9]. Its peritectic decomposition leads to solid carbon and a rich silicon vapour. So, no 1 : 1 stoichiometry for silicon and carbon can be obtained in the gas phase.

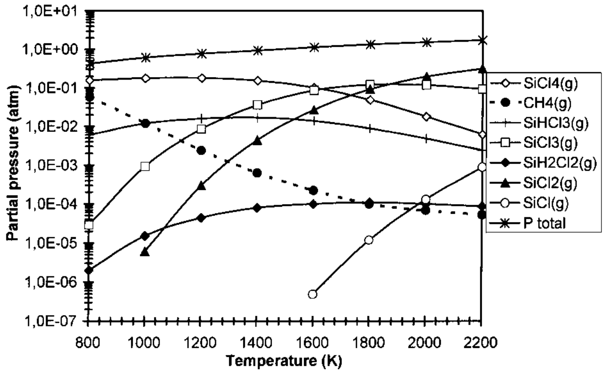

Figure 2 Equilibrium partial pressures of the gaseous species versus temperature for the Si-C-H-Cl chemical system. $n_{(HCl)} = n_{(SiC)} = 1$ mol, $V = 100$ l.

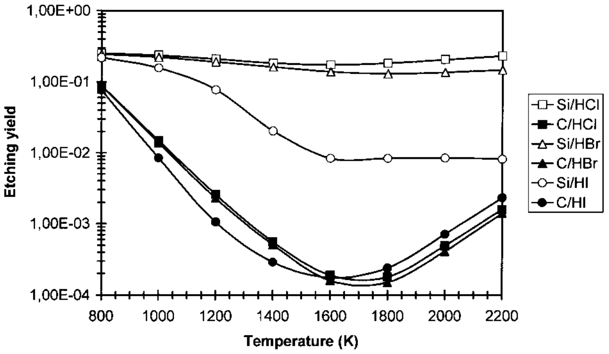

Figure 3 Comparison of the etching yield for both silicon and carbon with the different hydrogen halides. $n_{(HX)} = n_{(SiC)} = 1$ mol, $V = 100$ l.

To compare the three hydrogen halides (HCl, HBr and HI), we report in Fig. 3 the etching yield for both silicon and carbon versus temperature. These yields are calculated from the following ratio: silicon amount in the gas phase over initial silicon amount in SiC form. The same calculation is made for carbon etching yield. First, we can notice that HCl and HBr have a similar behaviour with SiC, unlike HI. For carbon, this yield passes through a minimum around 1700 K for HCl and HBr and 1600 K for HI. The increase observed at higher temperatures is referred to the appearance of other hydrocarbons like C_2H_2. Up to 1600 K, the best carbon yields are obtained with HCl and HBr but above this temperature, HI gives better results. For silicon, it is well known that the corrosive behaviour of the halogen decreases from chlorine to iodine. In our case, this trend is verified. The silicon yield almost doesn't depend on temperature in these conditions for HCl and HBr. However, whereas the Si yield is the same in the three cases at 800 K, it strongly decreases of about one decade between 800 K and 1600 K for HI. Above this temperature, the silicon yield with HI remains constant.

Another way to compare these three hydrogen halides is to report the silicon over carbon ratio r(Si/C)

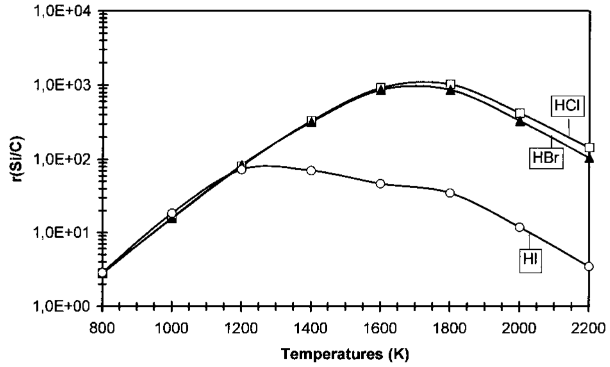

Figure 4 Comparison between Si/C ratios in the gas phase for the different hydrogen halides. $n_{(\mathrm{HX})} = n_{(\mathrm{SiC})} = 1$ mol, $V = 100$ l.

in the gas phase as a function of temperature (Fig. 4). In that case, the difference between each HX concerns the gas phase stoichiometry. Up to 1200 K, the Si/C ratios with the three halides are the same. Above 1200 K, these curves pass through a maximum (1700 K for HCl and HBr) which correspond to the maximum divergence from the stoichiometry 1 : 1 of silicon and carbon in the gas phase. With HI, the maximum is obtained at 1200 K.

In order to reach the best transport effect, we must find conditions for which silicon and carbon contents in the gas phase are maximum with a stoichiometry as close as possible to 1 : 1. Such conditions are observed at low temperatures ($T < 800$ K) or at high temperatures ($T > 1900$ K). They permit the maximum carbon content in vapour phase so as to minimise the Si/C ratio. However, at low temperature, the kinetics are likely to be very slow.

3.2.2. SiC deposition

Now, we will focus on the nature of the solid phases obtained at an other temperature from the various vapour compositions calculated above. Figs 5–7 report the different domains of existence of the solid phases as a function of the thermal gradient for respectively HCl, HBr and HI. Several common trends can be extracted from these three diagrams. Apart from these HX, HF has a particular behaviour as it shows a SiC transport effect in a negative gradient [10].

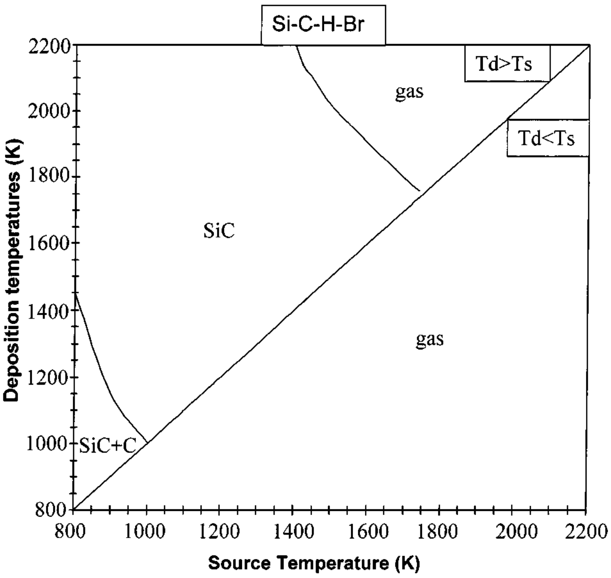

Figure 6 Nature of the solid phase in equilibrium with the gas phase as a function of the thermal gradient in the Si-C-H-Br chemical system. $n_{(\mathrm{HBr})} = n_{(\mathrm{SiC})} = 1$ mol, $V = 100$ l.

With HCl, HBr and HI, the transport is only possible with a positive gradient as shown by the solid phase domains. If Td < Ts, there is no solid phase in equilibrium with the gas phase. This effect was expected as species like methane are less cracked when the temperature decreases and no transport will occur.

With the three hydrogen halides, the chemical vapour transport of SiC is possible from the lower temperature to the hotter temperature. Indeed, the negative sign of the enthalpy change in these systems credits this trends.

3.2.2.1. HCl. Fig. 5 reports the nature of the solid phases obtained in equilibrium with the vapour as a

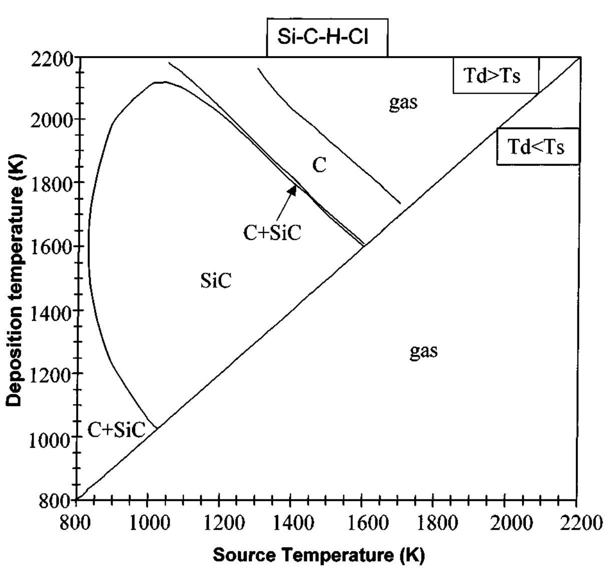

Figure 5 Nature of the solid phase in equilibrium with the gas phase as a function of the thermal gradient in the Si-C-H-Cl chemical system. $n_{(\mathrm{HCl})} = n_{(\mathrm{SiC})} = 1$ mol, $V = 100$ l.

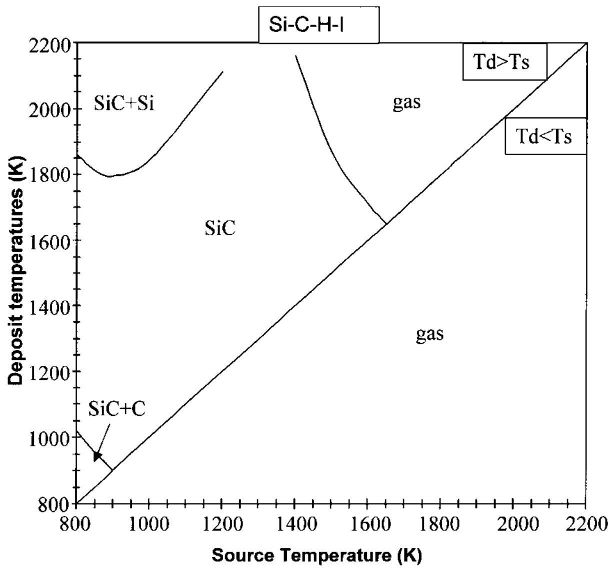

Figure 7 Nature of the deposits in equilibrium with the gas phase as a function of the thermal gradient in the Si-C-H-I chemical system. $n_{(\mathrm{HI})} = n_{(\mathrm{SiC})} = 1$ mol, $V = 100$ l.

function of the temperature gradient in the Si-C-H-Cl system. Solids are only obtained for the increasing part of the Fig. 4. Above the maximum Si/C ratio around 1700 K, it is not possible to form a solid whatever the temperature. SiC alone can be obtained in a wide range of Ts and Td. The SiC area is surrounded by a SiC + C domain. At low source temperature (Ts < 1000 K), carbon yield is high, leading to a small Si/C ratio. Although the 1 : 1 stoichiometry ($r = 1$) in the gas phase is expected for an optimal transport, it seems that in the SiC case, this stoichiometry is not favourable for SiC deposition alone. Above 1600 K in the source zone, it is not possible to form SiC in the deposition zone. We can notice that this limit perfectly concurs with the loss of stability of $SiCl_4$ compared to other halides in Fig. 2. So, when $SiCl_4$ is no longer in majority, i.e. when partial pressures of sub-halides become higher, there is no more silicon in the deposition zone, but only free carbon. This point and the exclusive presence of methane as gaseous carbon compound credits the global reaction (4) for the transport of silicon carbide with hydrogen chloride.

$$SiC_{(s)} + 4HCl_{(g)} = SiCl_{4(g)} + CH_{4(g)} \qquad (4)$$

The species responsible of the SiC transport are then $SiCl_4$ and CH_4. Unlike with the elemental silicon transport, the dismutation reaction of the tetrahalides is not effective for SiC transport.

In order to complete Fig. 5, we report in Fig. 8 the SiC formation yield in the substrate zone as a function of the thermal gradient for different Ts. These curves give an idea of the optimal temperatures for the source and the substrate. First, higher SiC formation yield is obtained by lowering the temperature of the source. It essentially comes from the better carbon yield due to the stability of methane at low temperature. One can remember again that at low temperatures which seems to be thermodynamically suitable in this case, the kinetics of reaction may play an important role. Second, for a fixed Ts, SiC formation yield is quite independent on Td. When Td increases, curves quickly tend to an asymptotic value of SiC yield, which is reached for a thermal difference of about 100 K. However, to avoid the co-formation of carbon with SiC at low source temperature (Ts < 1200 K), a larger thermal gradient is required. Td should be higher than 1250 K to avoid carbon formation when Ts = 900 K. So, it is clear that SiC yield strongly depends on source temperature as the formation of carbonated gaseous compounds (mainly CH_4) is the limiting step.

3.2.2.2. HBr and HI. For these two hydrogen halides, trends are similar to that of HCl. These chemical systems are interesting because SiC alone can form on a larger range of thermal gradient than in Si-C-H-Cl system. Higher process temperatures are possible as no free carbon deposition occurs up to Ts = 1750 K with HBr versus 1600 K with HCl. Concerning the SiC yield, results are similar whatever the hydrogen halide used.

3.3. Oxygen and chalcogens

Chalcogens in elementary form are rarely used for the transport of solid materials. However, the CVT of oxides, sulfides or selenides compounds has already been done with chalcogen as transport agent. For examples, Späh *et al.* [11, 12] have reported epitaxial layers of WSe_2 on $MoSe_2$ and Dalrymple *et al.* [13] have grown the solid solution $Nb_{1-x}Ta_xSe_2$ in Se atmosphere. But to our knowledge, chalcogens have never been employed to transport a chalcogen free material like silicon carbide. So, this approach is new and original. We have studied these chemical systems because carbon is known to form stable species with chalcogens (CS_2) whereas it is not possible to transport carbon through halides compounds.

In this range of temperature, chalcogens are known to form different gaseous polyatomic molecules Y_n(g) with $n = 1$ to 8. However, only two species widely prevail in the conditions studied: Y(g) and Y_2(g).

3.3.1. Sulfur

Fig. 9 presents the partial pressures of the gaseous species obtained in the Si-C-S chemical system versus temperature. Two distinct areas can be isolated depending on the temperature. Below 1520 K, all partial pressures increase in the same way. This is attributed to the presence of a stable silica like solid compound (SiS_2) in equilibrium with the gas phase. Above 1520 K, partial pressures change with a constant total pressure. So from this temperature, no solid sulfur compound is present.

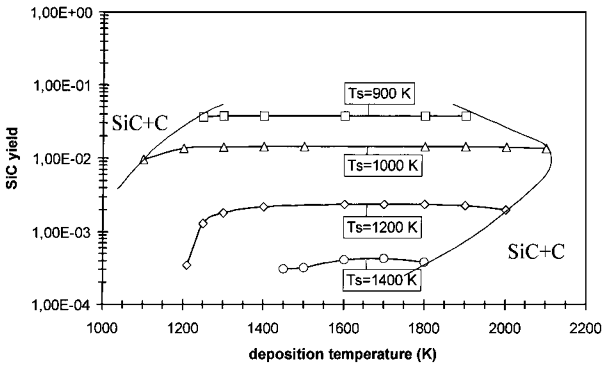

Figure 8 SiC formation yield as a function of the deposition temperature for different fixed source temperatures in the Si-C-H-Cl chemical system. $n_{(HCl)} = n_{(SiC)} = 1$ mol, $V = 100$ l.

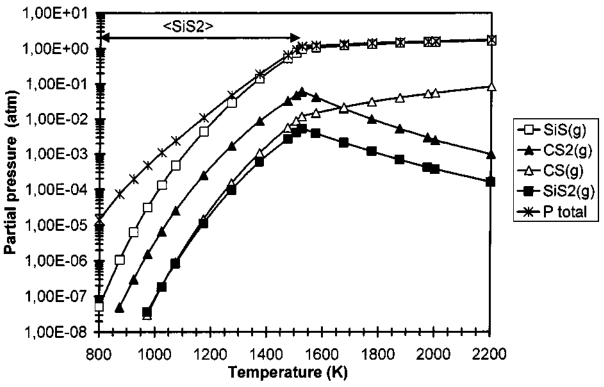

Figure 9 Equilibrium partial pressures of the gaseous species versus temperature for the Si-C-S chemical system. $n_{(S)} = n_{(SiC)} = 1$ mol, $V = 100$ l.

Then, silicon and carbon monosulfides (CS and SiS) concentrations keep on increasing whereas disulfides contents decrease. This is attributed to Boudouard type reactions (5) and (6) which are shifted toward right (formation of monosulfides) with increasing temperature.

$$SiS_{2(g)} + SiC_{(s)} = 2SiS_{(g)} + C_{(s)} \quad (5)$$

$$CS_{2(g)} + C_{(s)} = 2CS_{(g)} \quad (6)$$

The relative evolutions of the partial pressures above 1520 K are characteristic of reactions presenting transport properties. Two global transport reactions prevail depending on temperature. Below 1520 K, direct etching of SiC with sulfur (7) dominates. However, this equilibrium is coupled with the reaction (8). Above 1520 K, the dismutation (9) takes place. Its endothermic nature would permit a transport in a negative thermal gradient (Ts > Td).

$$SiC(s) + 4S(g) = SiS_2(g) + CS_2(g) \quad (7)$$

$$SiS_2(s) = SiS_2(g) \quad (8)$$

$$SiS_2(g) + CS_2(g) + SiC(s) = 2SiS(g) + 2CS(g) \quad (9)$$

As a result, sulfur can lead to both silicon and carbon gaseous species. Even if the Si/C ratio is always superior to one, we show the possibility of SiC formation in Fig. 10 as a function of the source and deposition temperatures. In a negative gradient (Td < Ts), silicon carbide appears in nearly the whole range of temperatures. Only too high ($T > 1900$ K) or too low ($T < 1200$ K) temperatures don't lead to SiC. However, the area for free SiC formation is rather small because of parasitic solid silicon disulfide formation for Ts and Td inferior to 1520 K. One of the basic rules for chemical vapour transport is that all materials produced by the global reaction of transport in the source zone must be volatile. So, it is necessary to use source and deposit temperatures higher than 1520 K in the Si-C-S system so as to reach the SiC/gas equilibrium domain and then to avoid solid SiS_2 formation. In order to select optimal conditions for the transport in such a system, we study the SiC yield versus Td for different constant Ts (Fig. 11). For a fixed Ts, curves first increase strongly with decreasing Td and next reach an asymptotic value of SiC yield. Two important results should be pointed out from this figure. First, the higher the source temperature, the better the SiC yield. Second, for each Ts, the highest SiC yield is always obtained at Td around 1500 K. Thus the optimum thermal gradient only depends on Ts. In other words, to increase Ts means to increase the optimal thermal gradient.

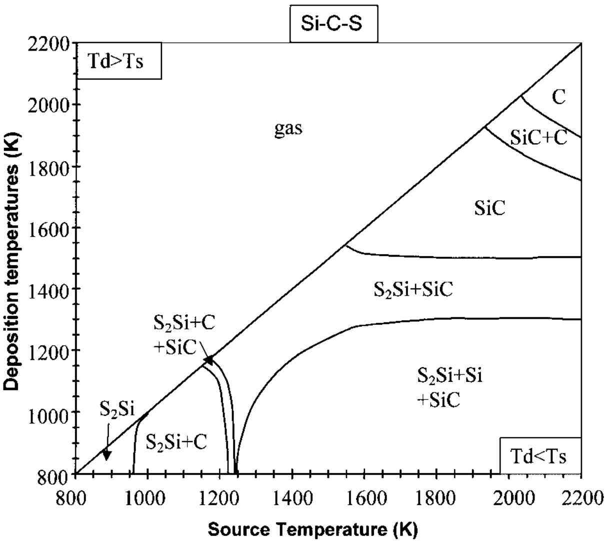

Figure 10 Nature of the solid phase in equilibrium with the gas phase as a function of the thermal gradient in the Si-C-S chemical system. $n_{(S)} = n_{(SiC)} = 1$ mol, $V = 100$ l.

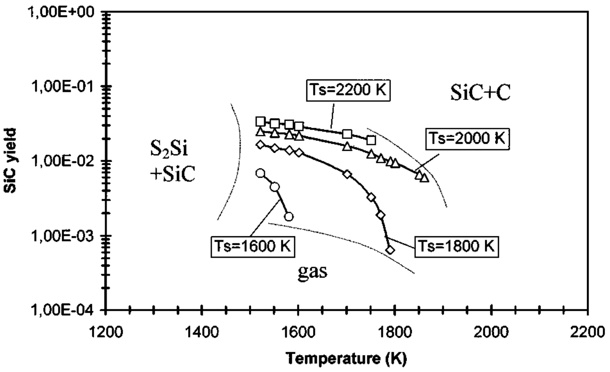

Figure 11 SiC formation yield as a function of the deposition temperature for different fixed source temperatures in the Si-C-S chemical system. $n_{(S)} = n_{(SiC)} = 1$ mol, $V = 100$ l.

3.3.2. Selenium

From Fig. 12, we can see that only three gaseous selenides form in the range of temperature studied: CSe, CSe_2 and SeSi. Below 900 K, Se doesn't react with SiC and there is no gaseous species. From 900 K to 1200 K, silicon and carbon amounts in vapour phase are similar (Si/C ratio = 1) leading to the superimposition of the CSe_2 and SiSe curves. This trend is new as the Si/C ratio in the vapour phase has always been found superior to unity in the other chemical systems. This 1 : 1 stoichiometry, observed at low temperature, could be described by the global reaction (10)

$$SiC_{(s)} + 3Se_{(g)} = CSe_{2(g)} + SeSi_{(g)} \quad (10)$$

To efficiently transport a substance by chemical reactions, the partial pressures of the gaseous species

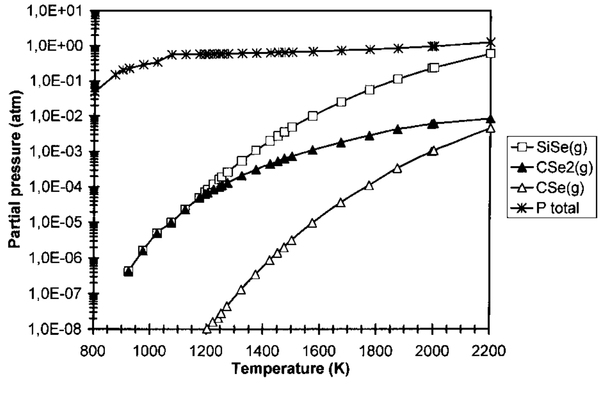

Figure 12 Equilibrium partial pressures of the gaseous species versus temperature for the Si-C-Se chemical system. $n_{(Se)} = n_{(SiC)} = 1$ mol, $V = 100$ l.

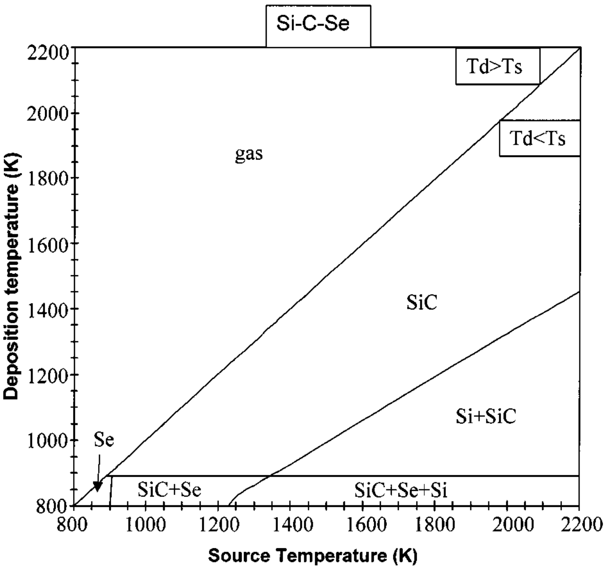

Figure 13 Nature of the solid phase in equilibrium with the gas phase as a function of the thermal gradient in the Si-C-Se chemical system. $n_{(\mathrm{Se})} = n_{(\mathrm{SiC})} = 1$ mol, $V = 100$ l.

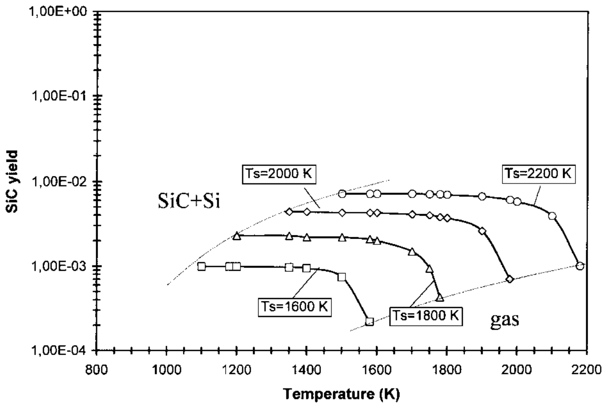

Figure 14 SiC formation yield as a function of the deposit temperature for different fixed source temperatures in the Si-C-Se chemical system. $n_{(\mathrm{Se})} = n_{(\mathrm{SiC})} = 1$ mol, $V = 100$ l.

formed must be sufficient. In this system, the pressures calculated are small at low temperature and higher temperatures are needed to increase the partial pressures. However, in that case, the Si/C ratio shifts toward superior values and the discrepancy toward stoichiometry increases. In Fig. 13, we report the nature of the solid phases obtained from such a gas phase content as a function of the thermal gradient. Two main solid phase domains appear in these conditions. The larger one corresponds to the SiC alone formation area which could permit a wide flexibility in the choice of the thermal gradient. For too high the negative thermal gradient (Td $\ll$ Ts), silicon forms with SiC. For a Td inferior to 900 K, there is systematically formation of solid selenium. As for sulfur, optimal silicon carbide yield is situated at a high Ts and a thermal gradient superior to 200 K (Fig. 14). Above 200 K, SiC yield remains constant.

3.3.3. Oxygen

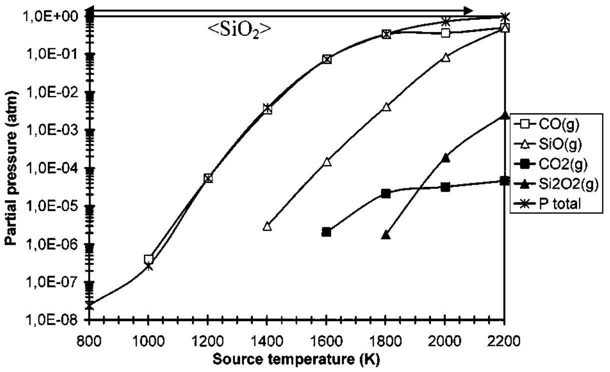

Figure 15 Equilibrium partial pressures of the gaseous species versus temperature for the Si-C-O chemical system. $n_{(\mathrm{O})} = n_{(\mathrm{SiC})} = 1$ mol, $V = 100$ l.

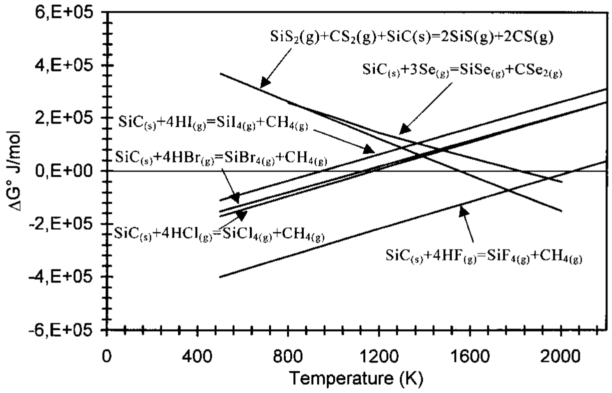

Figure 16 Comparison in an Ellingham diagram of the different global reactions of transport.

Fig. 15 reports the gas phase composition in the Si-C-O system versus temperature. Silicon and carbon gaseous oxides are formed with mono-oxides widely prevailing. High temperatures are required to observe significant partial pressures. However, silica is formed in the source zone up to 2100 K. So, even if SiC transport could be possible for temperatures higher than 2100 K, advantages of such a process will be lost compared to sublimation ones.

3.4. Free gibbs energy diagram

In order to compare the different transporting agents, we have reported in an Ellingham diagram, the standard free enthalpies of the global transport reactions discussed above as a function of temperature for each chemical systems. Good correlation with the simulation performed in this study is found for the optimal temperature of transport and the sign of the thermal gradient. So, we can take these global reactions as a good representation of the SiC transport in each chemical system.

The extrapolation to 0 K gives the standard enthalpy change of the reactions ΔH°. The direction of the transport depends on this value. For hydrogen halides, these values are negative. So according to Vant'Hoff equation [14], the transport will take place from low temperature to high temperature. For chalcogens, transport will take place in the reverse thermal gradient. The slope of this graph gives the entropy variation ΔS° of these same reactions. So the higher the absolute value of entropy, the higher the free enthalpy change for a same temperature difference. Optimal conditions of transport are close to null free enthalpy, i.e. for values of ΔH°

and $T\Delta S^\circ$ of the same order. So, hydrogen halides are transporting agents efficient at low temperatures (from 900 K to 1200 K) where they reach a free enthalpy change near zero. However, in this range of temperatures, kinetics considerations must be taken into account. To avoid kinetic limitations, higher temperatures could be employed but such conditions make the system shift away from optimal equilibrium conditions. Chalcogen will be more efficient at higher temperature: close to 1500 K for sulfur and 1800 K for selenium. We can notice the particular behaviour of HF for which the optimal thermal conditions are closed to 2050 K. Finally, as the transporting agent amounts were kept to one mole all along this paper, one can compare the SiC deposition yield at the optimal equilibrium conditions for each chemical systems. It seems that HX and sulfur show similar yields but Se is three times lower.

4. Conclusion

We have investigated through thermodynamical calculations a new way for the growth of monocrystalline silicon carbide. We have overviewed different heterogeneous solid/gas chemical systems which present chemical transport reactions with SiC. The systems are Si-C-Y where Y is a chalcogen (O, S, Se) and Si-C-H-X where X is an halogen (Cl, Br, I). We studied in a first step the gas phase composition obtained from SiC etching with the transporting agent as a function of temperature. In a second step, we reported the conditions for the deposition of silicon carbide from such a vapour. Thermodynamically, all these chemical systems are able to transport SiC in a thermal gradient. The range of temperature for optimal transport depends on the nature of the transporting agent. Indeed, hydrogen halides (HCl, HBr and HI) can be used at temperature as low as 1000 K in a positive gradient without taking into account kinetic limitations. Sulfur and Selenium are efficient at about 1500 K and 1800 K respectively in a negative gradient. This range of temperature is high but still much lower than the sublimation process. Finally, HF should be used at about 2000 K in a negative gradient but the high reactivity of that compound at high temperature makes it of improper use.

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