Chemical Vapour Deposition of Titanium Diboride Using Boron Tribromide, Titanium Tetrachloride, and Hydrogen

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ABSTRACT: The growth of titanium diboride (TiB_2) by hot-wall atmospheric pressure chemical vapour deposition (CVD) has been studied using titanium tetrachloride ($TiCl_4$), boron tribromide (BBr_3), and hydrogen (H_2). These results and literature data on the growth rate of TiB_2 as a function of B/Ti are used to obtain an expression for the growth rate as a function of the reactant concentrations. Furthermore, an expression for the growth rate as a function of $TiCl_4$, boron trichloride (BCl_3), and H_2 is derived from literature data because of the similarities between these two chemical systems. Thermodynamic equilibrium calculations are performed to evaluate the differences between BCl_3 and BBr_3 as reactants for the synthesis of TiB_2. Based on literature data on the

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growth of TiB_2 by CVD using $TiCl_4$, H_2, and BCl_3, we conclude that the growth rate has a positive order dependence with respect to the H_2 and BCl_3 concentration, and a negative order dependence with respect to the $TiCl_4$ concentration. $BHCl_2$ might be a gas phase species that determines the growth rate. However, there are not enough experimental data available to be conclusive as to whether BCl_3 or $BHCl_2$ is the intermediate gas phase species that determines the growth rate. The experimental results of the growth rate measurements using $TiCl_4$, BBr_3, and H_2 reveal that all growth rate experiments are conducted under steady state conditions, and that the apparent activation energy of the process is 139 kJ/mole. Growth rate measurements as a function of reactor pressure show that the sum of the individual reactant orders has to be equal to 0.75 if a negligible feed rate limitation occurs. The sum of the individual reactant orders is likely to be equal to zero if there is a considerable feed rate limitation. From literature data, it can be concluded that the growth rate has a first order dependence in BBr_3. Furthermore, it is likely that the growth rate has a negative order dependence with respect to a titanium containing gas phase species. This species is probably $TiBr_4$ because gas phase thermodynamic equilibrium calculations suggest that there is an exchange in halide species between $TiCl_4$ and BBr_3 in the gas phase.

KEY WORDS: chemical vapour deposition, titanium diboride, kinetics.

INTRODUCTION

Titanium diboride (TiB_2) can be formed by chemical vapour deposition (CVD). As early as 1931, Von Moers [1] reported the deposition of TiB_2 using gaseous boron tribromide (BBr_3), and titanium tetrachloride ($TiCl_4$) at high temperatures. TiB_2 is attractive because of its good electrical conductivity, corrosion and wear resistance, and high degree of hardness [2–7]. For example, TiB_2 can be used as a coating for electrodes that are used in highly aggressive environments, such as molten aluminium [4]. Conventionally, TiB_2 is formed in an atmospheric pressure CVD apparatus using boron trichloride (BCl_3), $TiCl_4$, and hydrogen (H_2) according to reaction (1) [3–15]:

$$TiCl_4(g) + 2\ BCl_3(g) + 5\ H_2(g) \rightarrow TiB_2(s) + 10\ HCl(g) \qquad (1)$$

TiB_2 can be formed also using diborane (B_2H_6), $TiCl_4$, and H_2 according to reaction (2) [2]:

$$TiCl_4(g) + B_2H_6(g) \rightarrow H_2(g) + TiB_2(s) + 4\ HCl(g) \qquad (2)$$

or it can be formed using BBr_3, $TiCl_4$, and H_2 according to reaction (3) [16–18]:

$$TiCl_4(g) + 2\ BBr_3(g) + 5\ H_2(g) \rightarrow TiB_2(s) + 4\ HCl(g) + 6\ HBr(g) \qquad (3)$$

B_2H_6 is known to have a higher reactivity towards $TiCl_4$ than BCl_3 and BBr_3 [2,17]. However, the toxicity of B_2H_6 is a major disadvantage of this reactant; thus, the use of such a reactant is only justified in limited cases. In principle, the use of BBr_3 is favoured over the use of BCl_3 because of its higher reactivity [17]. However, the chemistry of a combined chloride and bromide system is expected to be more complicated, and BBr_3 has a lower vapour pressure than BCl_3 at room temperature, which complicates the feed of the reactant into the reactor.

To our knowledge, there are no kinetic studies concerning the growth of TiB_2 using the reactant halide precursors. However, there are numerous reports in which the influence of the ratio of two species such as hydrogen over chlorine or boron over titanium on the growth rate is discussed [10–15,17]. The reported experimental standard conditions for the formation of TiB_2 using BCl_3, $TiCl_4$, and H_2 are summarized in Table 1. All data are converted into SI units for comparison.

It should be noted that Pierson and Mullendore [10], and Besmann and Spear [12] have used a cold-wall reactor instead of a hot-wall reactor. The growth rate measurements by Besmann and Spear [12] are performed under experimental conditions where a mass transport limitation in the gas phase determines the growth characteristics. All other reports [13–15] are performed under experimental conditions where a combination of feed rate and surface reaction limitation is likely to be present. The influence of a feed rate limitation on the growth rate has not been discussed by the authors [12–15,17]. Pierson and Mullendore [10] have observed a maximum in the growth rate as a function of H/Cl at a value of ten where the ratio B/Ti was kept constant at two, and the reaction temperature was kept constant at 1173 K. Furthermore, they have reported a maximum in the growth rate as a function of B/Ti between two and four where the ratio H/Cl was kept constant at four, and the reaction temperature was kept constant at 1173 K. Takahashi and

Table 1. Reported experimental standard conditions.

P 10^5 Pa	Inert Carrier Gas	Flow Rate mole/(m^2 s)	*p*(BCl_3) kPa	*p*($TiCl_4$) kPa	H/Cl	Temp. K	Ref.
1	Ar	?	5.2	2.6	4–7	900–950	[10]
0.26	—	0.12	4.05	2.02	2	1400–1800	[12]
1	Ar	0.7	3.5	1.8	10	873–1200	[13]
1	—	41*	4.8–14.5	0.8–2.4	3–10	1000–1200	[14]
1	Ar	0.32	1, 4	2	5–11	950–1150	[15]

*Flow rate in mmole/s.

Table 2. Reported experimental standard conditions.

P 10^5 Pa	Carrier Gas	Flow Rate mole/(m² s)	$p(BBr_3)$ Pa	B/Ti	Temp. K	Ref.
1	H_2	0.3–4.6	?	0.6–1.4	1073	[16]
1	H_2	?	950, 1150	1, 1.8	973–1173	[17]

Kamiya [13] have observed a maximum in the growth rate as a function of B/Ti between seven and twelve within the temperature region from 1073 K to 1423 K where the ratio H/Cl was fifteen, and the sum of the feed rates of the metal chloride and boron chloride reactants was kept constant. They have reported an increase in growth rate with increasing ratio H/Cl up to a ratio of sixty within the temperature region from 1073 K to 1473 K where the ratio B/Ti was two. These differences in the growth rate at similar reactant ratios as observed by Pierson and Mullendore [10] and Takahashi and Kamiya [13] are probably a consequence of the different reactant concentrations used. The apparent activation energy of the process varies between 90 kJ/mole and 210 kJ/mole where a combination of feed rate and surface reaction limitation occurs [10,12–15]. One should be aware that a codeposition of TiB_2 and amorphous boron may occur at low reaction temperatures or at B/Ti ratios of more than ten [10,13].

The reported experimental standard conditions for the formation of TiB_2 using BBr_3, $TiCl_4$, and H_2 in a hot-wall CVD reactor are summarized in Table 2. The data are converted into SI units for comparison.

Zeman et al. [16] have varied the B/Ti ratio by increasing the feed rate of BBr_3 at a constant feed rate of $TiCl_4$, and they have observed an increase in growth rate with increasing B/Ti ratio. The growth rate as a function of deposition parameters is discussed only qualitatively by Van der Valk and Grondel [17].

In the present work, growth rates as a function of reaction time, reactor temperature, and reactor pressure using BBr_3, $TiCl_4$, and H_2 as reactants were determined. Furthermore, thermodynamic equilibria are calculated in order to get a better understanding of the process. These calculations are used to evaluate the differences between BCl_3 and BBr_3 as reactants for the synthesis of TiB_2.

EXPERIMENTAL ASPECTS

A hot-wall reactor is used for the experiments. The principle of the gas distribution system of the apparatus is given in a schematic drawing in Figure 1. Argon is purified over a copper catalyst and a 0.4 nm zeolite. H_2 is purified over a palladium catalyst and a 0.4 nm zeolite. A controlled amount of the flow is bubbled through heated liquid $TiCl_4$ and cooled liquid BBr_3 in order to saturate the carrier gas with the reactant vapours. The reactant concentration is calculated assuming the vapour pressure to be in equilibrium with the liquid. The deviation in $TiCl_4$ and BBr_3 gas concentration is less than 14 percent of the calculated values, as checked by monitoring the volume decrease in time of the liquids. The $TiCl_4$ is further diluted by a hydrogen stream before it is introduced into the reactor. The BBr_3 vapour is introduced into the reactor separately because of its high reactivity towards $TiCl_4$. It is observed that a mixing of the reactants below 373 K does result in the formation of a liquid which is probably $TiBr_4$. Therefore, the mixing of the reactants must be at a temperature far above the boiling point of $TiBr_4$ to prevent condensation of the precursor. The reactor consists of a quartz tube with a length of 740 mm and an inner diameter of 49 mm. Inside the quartz tube is a conus with a length of 260 mm, and an expanding diameter from 4 mm to 46 mm to minimize depletion of reactants in the first half of the reactor.

The growth rates are measured on α-alumina, and on TiB_2 pre-coated α-alumina substrates. These substrates are placed in the hot-zone of the reactor where the temperature difference over the length of the

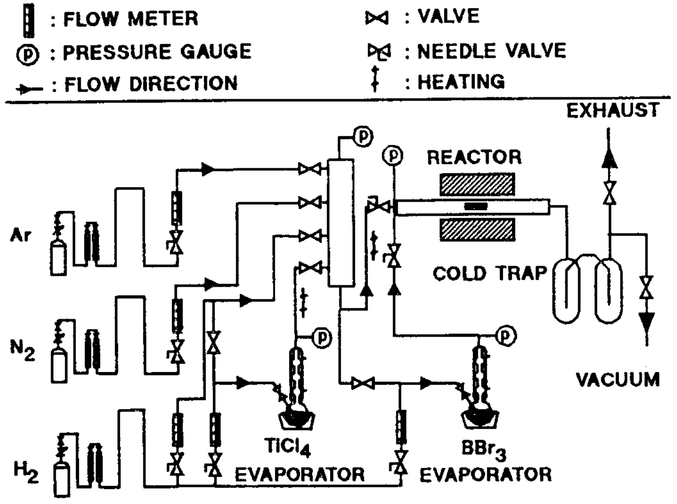

Figure 1. Schematic drawing of the gas distribution system of a hot-wall CVD apparatus for the synthesis of TiB_2.

Table 3. Species considered for thermodynamic calculations.

Thermochemical Data Obtained from References [20] to [22]					
B(g)	BBr_2(g)	BBrCl(g)	Cl_2(g)	$TiCl_2$(g)	Ti(s)
B_2(g)	BBr_3(g)	$BBrCl_2$(g)	HCl(g)	$TiCl_3$(g)	TiB(s)
BH(g)	$BHBr_2$(g)	BBr_2Cl(g)	Ti(g)	$TiCl_4$(g)	TiB_2(s)
BH_2(g)	BCl(g)	Br(g)	TiBr(g)	Ti_2Cl_6(g)	$TiBr_2$(s)
BH_3(g)	BCl_2(g)	Br_2(g)	$TiBr_2$(g)	H(g)	$TiBr_3$(s)
B_2H_6(g)	BCl_3(g)	HBr(g)	$TiBr_3$(g)	H_2(g)	$TiCl_2$(s)
B_5H_9(g)	B_2Cl_4(g)	BrCl(g)	$TiBr_4$(g)	Ar(g)	$TiCl_3$(s)
BBr(g)	$BHCl_2$(g)	Cl(g)	TiCl(g)	B(s)	TiH_2(s)
Estimated Thermochemical Data					
$TiBr_3Cl$	$TiBr_3Cl$	$TiBrCl_2$	BH_2Br	BHBrCl	
$TiBr_2Cl_2$	$TiBr_2Cl$	TiBrCl	BH_2Cl		

sample was always less than 3 K. The experiments are conducted as a function of reaction time, reactor pressure, and reaction temperature. Before each deposition experiment, the reactor is evacuated to 1×10^3 Pa, and filled again with H_2 at a reactor temperature between 373 K and 423 K in order to remove oxygen and water vapour from the reactor. This procedure is repeated three times. After the removal of oxygen, the reactor is kept at atmospheric pressure, and a H_2 flux is applied during the heating procedure.

The $TiCl_4$ feed rate of 0.3 percent of the total feed rate, the BBr_3 feed rate of 0.6 percent of the total feed rate, and the total flow rate of 0.66 mole/(m^2s) are kept constant. The H_2/Ar ratio is kept constant at one. The process time is varied between 3600 s and 28.8×10^3 s, the reaction temperature is varied between 823 K and 1073 K, and the reactor pressure is varied between 1×10^4 Pa and 1×10^5 Pa. A mass balance with an accuracy of 5 μgr is used to determine the mass increase of the samples. Finally, the phase of the layers is determined by XRD analysis.

THERMODYNAMIC CALCULATIONS

Thermodynamic calculations can provide additional information concerning the thermo-chemistry of the TiB_2 CVD process [11,19]. The relevant thermodynamic equilibria can be computed with the SOLGASMIX and Chemsage programmes [20,21]. These programmes are based on a minimization procedure of the total Gibbs energy of the species which is used as input for the calculations. The thermochemical data of the species in Table 3, which are necessary for the thermodynamic equilibrium calculations, are obtained from thermodynamic reference tables [20–22] or are approximated. For example, the thermochemical data of $TiCl_xBr_y$ species are unknown. The thermochemical data of these species can be approximated from the titanium containing species available in the reference tables [20–22] by a linear interpolation of the standard formation enthalpy and the standard entropy at temperature T concordant to Equations (4) and (5):

$$(\Delta H^0_{f,T})_{TiCl_xBr_y} = \frac{x}{x+y}(\Delta H^0_{f,T})_{TiCl_{x+y}} + \frac{y}{x+y}(\Delta H^0_{f,T})_{TiBr_{x+y}} \tag{4}$$

$$(S^0_T)_{TiCl_xBr_y} = \frac{x}{x+y}(S^0_T)_{TiCl_{x+y}} + \frac{y}{x+y}(S^0_T)_{TiBr_{x+y}} \tag{5}$$

where x and y are stoichiometric numbers. Furthermore, the thermochemical data of BH_2Cl and BH_2Br are obtained from the literature [11,23]. The accuracy of the estimated thermochemical data of these species is unknown. Hence, the results of the thermodynamic equilibrium calculations can only be used for a qualitative discussion of the experiments. The species listed in Table 3 are considered for the thermodynamic equilibrium calculations.

Gas phase equilibrium calculations are performed to evaluate the differences between the influence of bromide and chloride species on the overall equilibrium. Furthermore, the solid state stability is studied as a function of input concentration of the species and temperature.

RESULTS

Synthesis Experiments

All deposits are crystalline TiB_2 as identified by XRD analysis. The mass increase as a function of process time is presented in Figure 2. There is a linear mass increase in time at reactor pressures of 5×10^4 Pa and 1×10^5 Pa, and a reaction temperature of 903 K.

The growth rate as a function of reactor temperature at a process time of 3600 s and a reactor pressure of 1×10^5 Pa is presented in an Arrhenius plot in Figure 3. The apparent activation energy of the process is 139 kJ/mole between 823 K and 973 K.

The growth rate as a function of reactor pressure at a process time of 3600 s and a reaction temperature of 903 K is presented in Figure 4. There is an increase in growth rate with increasing reactor pressure from 1×10^4 Pa to 1×10^5 Pa.

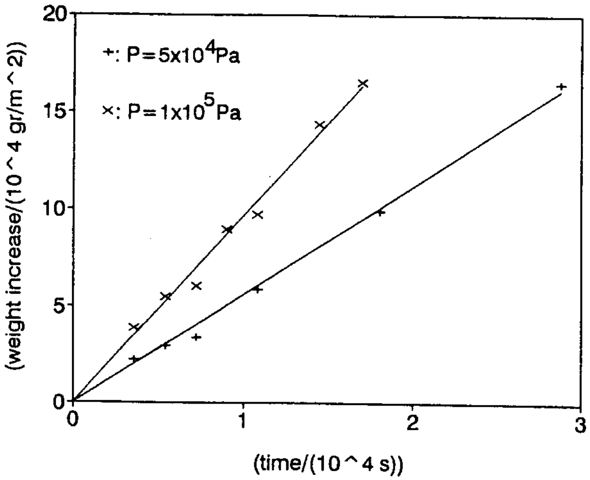

Figure 2. Mass increase of TiB_2 as a function of reaction time at two different reactor pressures. A temperature of 903 K is used.

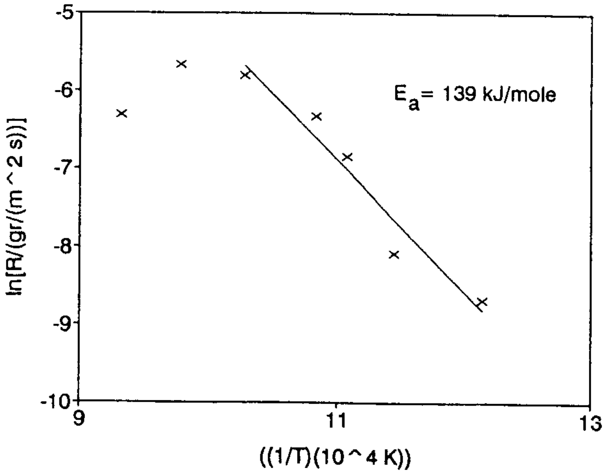

Figure 3. Arrhenius plot of the growth rate of TiB_2 with a reactor pressure of 1 × 10^5 Pa. A reaction time of 3600 s is used.

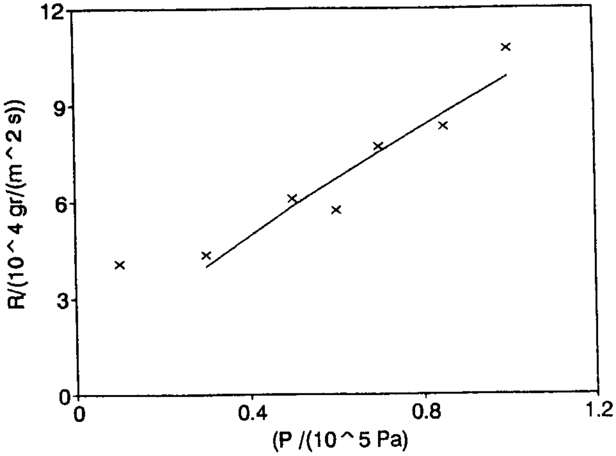

Figure 4. Growth rate of TiB_2 as a function of reactor pressure. A reaction time of 3600 s and a reaction temperature of 903 K are used.

Thermodynamic Calculations

The equilibrium partial pressures of various species of the homogenous gas phase equilibrium $TiCl_4$, BCl_3, H_2, and Ar as input species are presented in Figure 5. The argon and hydrogen concentrations are unaffected by the thermodynamic equilibrium calculations because of their large excess. $TiCl_4$ or $TiCl_3$ and BCl_3 or $BHCl_2$ are the most abundant reactant containing species in the gas phase.

The homogenous gas phase equilibrium using $TiCl_3$, BBr_3, H_2, and Ar as input species is presented in Figure 6. The equilibrium partial pressures of boron containing species are presented in Figure 6a, and the equilibrium partial pressures of titanium containing species are presented in Figure 6b. The argon and hydrogen concentrations are unaffected by the thermodynamic equilibrium calculations because of their large excess. These calculations reveal that $BHCl_2$ is the most abundant boron containing species in the gas phase, and that $TiBr_4$ or $TiBr_3$ is the most abundant titanium containing species in the gas phase. Furthermore, the presence of a titanium bromine binding in the species results in a more stable species than the presence of a titanium chlorine binding.

The solid state stability diagram of three different reactant compositions is presented in Figure 7. At a large excess of boron with respect to titanium, a two phase region is present. The phase boundary shifts

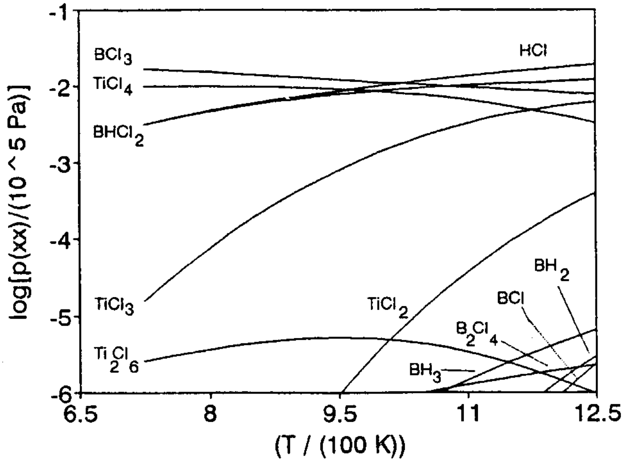

Figure 5. Homogeneous gas phase equilibrium partial pressures of various species as a function of temperature at a pressure of 1 × 10^5 Pa where $p(BCl_3)_{input}$ is 2 × 10^3 Pa, $p(TiCl_4)_{input}$ is 1 × 10^3 Pa, $p(H_2)_{input}$ is 4.85 × 10^4 Pa, and $p(Ar)_{input}$ is 4.85 × 10^4 Pa.

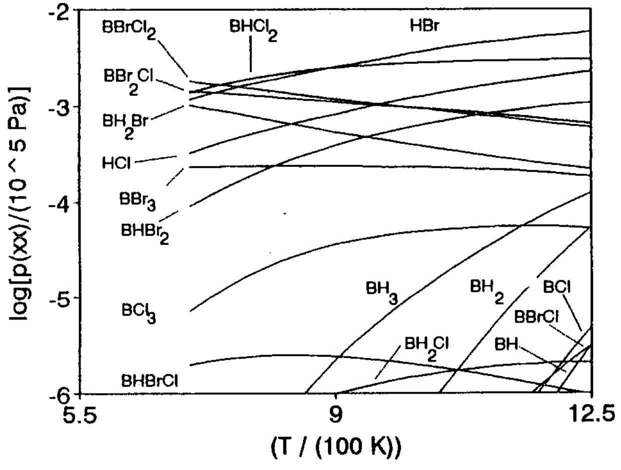

Figure 6a. Homogeneous gas phase equilibrium partial pressures of boron containing species as a function of temperature at a pressure of 1 × 10^5 Pa.

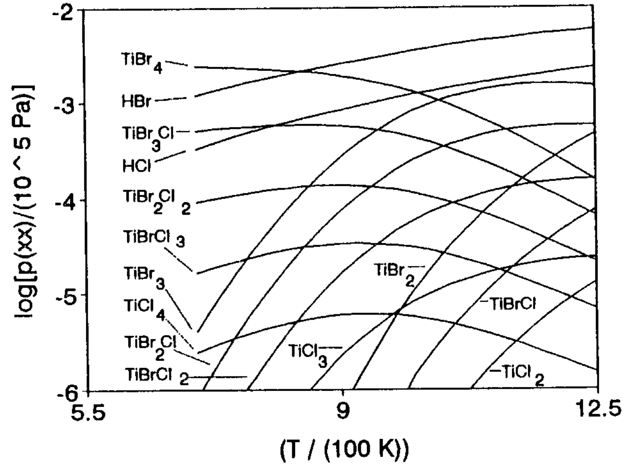

Figure 6b. Homogeneous gas phase equilibrium partial pressures of titanium containing species as a function of temperature at a pressure of 1 × 10^5 Pa where $p(BBr_3)_{input}$ is 6 × 10^2 Pa, $p(TiCl_4)_{input}$ is 3 × 10^2 Pa, $p(H_2)_{input}$ is 4.955 × 10^4 Pa, and $p(Ar)_{input}$ is 4.955 × 10^4 Pa.

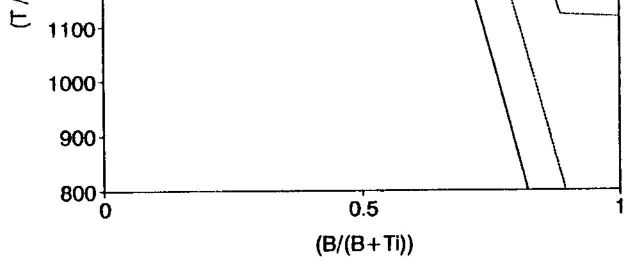

Figure 7. Solid state stability diagram for three different chemical systems where H/(Br + Cl) is kept constant at 18, and the pressure is kept constant at 1 × 10^5 Pa. $TiBr_4$, BBr_3, H_2, and Ar are used as input-species for the chloride system, $TiCl_4$, BBr_3, H_2, and Ar are used as input species for the mixed system, and $TiCl_4$, BCl_3, H_2, and Ar are used as input species for the chloride system.

to higher values of the ratio B/(B + Ti) by replacing the bromide compounds by chloride compounds as input species.

DISCUSSION

Synthesis of TiB_2 Using BCl_3 as Boron Reactant

No studies have been reported on the kinetics of the synthesis of TiB_2 using $TiCl_4$, BCl_3, and H_2. However, a growth rate expression can be obtained by evaluating the reported growth rates as a function of the ratios B/(B + Ti) and H/Cl. Only the results where an excess of BCl_3 of less than ten with respect to $TiCl_4$ is applied can be used to evaluate the kinetics of the growth of TiB_2; otherwise, the deposition of amorphous boron cannot be excluded [13]. The possibility of such a codeposition is predicted also by the solid state stability calculations at B/Ti ratios of more than four, i.e., equal to a value of the ratio B/(B + Ti) of more than 0.8, as can be seen in Figure 7.

Takahashi and Kamiya [13] observed a decrease in growth rate with a simultaneous decrease of the BCl_3 and increase of the $TiCl_4$ concentration, and an increase in growth rate with a simultaneous decrease of the BCl_3 and $TiCl_4$ concentrations at a constant B/Ti ratio. This implies that the growth rate has a positive order dependence with respect to BCl_3, and a negative order dependence with respect to $TiCl_4$. Pierson and Mullendore [10] reported a decrease in growth rate with an increase of the Ti/B ratio. For many CVD processes using halide precursors, H_2 has a positive effect on the growth rate [2,23,24]. Using this information, it can be concluded that the growth rate has a positive order dependence in BCl_3, and a negative order dependence in $TiCl_4$. This negative order behaviour in $TiCl_4$ probably originates from a Langmuir type of adsorption with a mutual displacement of boron and titanium containing species at the surface, which is covered almost fully by a titanium containing intermediate species. Thus, the growth rate can be written according to reaction (6):

$$R \propto \frac{p^{b}_{BCl_3} p^{c}_{H_2}}{p^{d}_{TiCl_4}} \tag{6}$$

where R is the growth rate, p_{xx} is the partial pressure of species xx in the direct vicinity of the substrate, and b, c, and d are positive real values. In this case, d has to be greater than b because otherwise, no increase in growth rate could be observed with decreasing reactant concentrations at a constant B/Ti ratio [13]. At high reaction temperatures, the reduction of BCl_3 in the gas phase might become considerable, as is predicted by the thermodynamic equilibrium calculations presented in Figure 5. Consequently, such a gas phase intermediate species can determine the growth rate. Hence, $BHCl_2$ might also be the boron containing species which is responsible for the observed positive order. However, there are not enough data available on the kinetics of the growth of TiB_2 using $TiCl_4$, BCl_3, and H_2 to propose a more precise growth rate expression.

Synthesis of TiB_2 Using BBr_3 as Boron Reactant

The linear mass increase as a function of reaction time clearly indicates that the synthesis experiments are performed under steady state conditions, as can be seen in Figure 2. The observed apparent activation energy of 139 ± 7 kJ/mole is higher than the apparent activation energy of 100 ± 24 kJ/mole as derived from the reported growth rate experiments as a function of temperature between 973 K and 1073 K [18]. It should be noted that these apparent activation energies are measured using different reactant concentrations, which might explain the different observed activation energies. In addition, such a difference can very well be a consequence of the presence of a feed rate limitation because the apparent activation energy of a process that can be described by a Langmuir isothermal behaviour is concentration dependent [25].

The growth rate as a function of reactor pressure reveals a positive order dependence at a constant feed rate of reactants. Provided that there is a negligible feed rate limitation, then the presented slope of 0.75 in Figure 4 is equal to the sum of the individual reactant orders. The decrease in the slope by lowering the reactor pressure has to be a result of a change in the growth mechanism because one can never observe an increase in the overall apparent reaction order with increasing reactor pressure at a constant feed rate. However, if there is a considerable depletion of a reactant which has, for the growth rate, a negative order dependence, then there can be an increase in overall apparent growth rate order behaviour with respect to the reactor pressure. In this case, the minority reactant $TiCl_4$ might have a negative order dependence with respect to the growth rate. For the growth rate, a first order dependence with respect to the BBr_3 concentration can be derived from the figures reported by Zeman et al. [17]. The gas phase thermodynamic equilibrium calculations suggest that there is an exchange in halogen species between $TiCl_4$ and BBr_3 in the gas phase.

Using this information, a growth rate expression for the synthesis of TiB_2 using $TiCl_4$, BBr_3, and H_2 is proposed:

$$R \propto \frac{p^{u}_{BHCl_2} p^{v}_{H_2}}{p^{w}_{TiBr_4}} \tag{7}$$

where u, v, and w are positive real values. The sum of u and v has to be approximately equal to w if there is a considerable feed rate limitation present at high reactor pressures, or $u + v - w$ has to be equal to 0.75 if a negligible feed rate limitation occurs at high reactor pressures. In principle, u is expected to be one, as derived from the growth rate experiments reported by Zeman et al. [16].

CONCLUSIONS

Based on literature data on the growth of TiB_2 by CVD using $TiCl_4$, H_2, and BCl_3, we propose that the growth rate has a positive order dependence with respect to the H_2 and BCl_3 concentration, and a negative order dependence with respect to the $TiCl_4$ concentration. The gas thermodynamic equilibrium calculations suggest that $BHCl_2$ and $TiCl_4$ or $TiCl_3$ are the most abundant intermediate gas phase species. $BHCl_2$ might be the boron containing gas phase species that determines the growth rate. However, there are not enough experimental data available to decide as to whether BCl_3 or $BHCl_2$ is the boron containing intermediate gas phase species that determines the growth rate.

The growth rate experiments as a function of reaction temperature using $TiCl_4$, H_2, and BBr_3 reveal that all growth rate experiments are conducted under steady state conditions. An apparent activation energy of 139 kJ/mole is derived from synthesis experiments as a function of reaction temperature. Growth rate measurements as a function of reactor pressure reveal that the sum of the individual reactant orders has to be equal to 0.75 if a negligible feed rate limitation occurs, or the sum of the individual reactant orders is likely to be approximately equal to zero if a considerable feed rate limitation occurs. From literature data, it can be concluded that the growth rate has a first order dependence in the BBr_3 input concentration. Moreover, we suggest that the growth rate has a negative order dependence with respect to a titanium containing gas phase species. This species is probably $TiBr_4$ because gas phase thermodynamic equilibrium calculations suggest that there is a considerable exchange in halide species between $TiCl_4$ and BBr_3 in the gas phase at the reaction temperature.

LIST OF SYMBOLS

b, c, d	reaction order constants
E_a	activation energy (kJ/mole)
P	reactor pressure (Pa)
p_{xx}	equilibrium partial pressure of species xx (Pa)
R	growth rate [gr/(m^2 s)]
$(S_T^0)_{xx}$	standard entropy at temperature T of species xx [J/(mole K)]
T	reaction temperature (K)
u, v, w	reaction order constants
x, y, z	stoichiometric numbers
$(\Delta H_T^0)_{xx}$	standard formation enthalpy at temperature T of species xx (J/mole)

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