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A Thermodynamic Estimation of the Chemical Vapor Deposition of Some Borides

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The temperature dependencies of the change in Gibbs energy for a series of probable reactions of chemical vapor deposition (CVD) of TiB_2, ZrB_2, NbB_2, TaB_2, and LaB_6 using BCl_3, BBr_3, B_2H_6, B_5H_9, and $B_{10}H_{14}$ as boron sources have been plotted on the basis of thermodynamic data from the literature. It has been shown that from a thermodynamic point of view the deposition of these borides should proceed in all cases under milder conditions when boron hydrides are the boron sources. Is has been established that of the two boron halides BBr_3 is the more suitable boron precursor in the CVD of the borides under consideration. Due to its properties this boron halide would probably prove especially appropriate for technological processes of transition metal diboride deposition. © 2000 Academic Press

Key Words: **borides; chemical vapor deposition; thermodynamic estimation; boron halides; boron hydrides.**

INTRODUCTION

Chemical vapor deposition (CVD) is one of the most effective techniques for the synthesis and crystal growth of refractory compounds and especially for the preparation of thin films and protective coatings of these compounds. In CVD gaseous reactants pass over a heated substrate where chemical reactions occur and solid material deposits and grows.

Boride films are of significant interest for various applications (1) but the number of investigations concerning the use of CVD for the preparation of such films is relatively small. In the majority of these studies reactions of simultaneous reduction of the corresponding metal chloride and boron trichloride with hydrogen were used (2).

Diborane has been used as a boron source in CVD of TiB_2 (3–5) and TaB_2 (6). Recently J. T. Spencer and colleagues proposed some higher boranes as alternative boron precursors in the preparation of Ni_3B (7), GdB_6 (8), and LaB_6 (9) thin films by vacuum copyrolysis of these boranes and the chlorides of the corresponding metals.

Chemical vapor deposition processes are complex. Chemical thermodynamics, mass transfer, reaction kinetics, and crystal growth all play important roles (10). Equilibrium thermodynamic analysis is the first step in understanding any CVD processes. However, it should be taken into account that the results of this analysis serve as an estimation alone because in dynamic CVD systems equilibrium is rarely achieved and kinetic factors often govern deposition rate behavior.

In the present work the temperature dependencies of the change in Gibbs energy for a series of probable reactions of chemical vapor deposition of TiB_2, ZrB_2, NbB_2, TaB_2, and LaB_6 during the interaction of metal halides and different volatile boron precursors have been plotted on the basis of thermodynamic data from the literature. The borides have been chosen on the basis of their importance with respect to the different applications and the availability of a sufficient amount of reliable data. The purpose of this paper is to use the results obtained for a preliminary comparative estimation of the expedience and conditions of the reactions with the participation of the different precursors.

THERMODYNAMIC CALCULATIONS

The probability for the deposition of each of the above borides to take place within the range of 298–2000 K was evaluated thermodynamically by calculating the temperature dependence of Gibbs energy according to the well-known equation

$$\Delta G_T^0 = \Delta H_{298}^0 - T\Delta S_{298}^0 - T \int_{298}^{T} \frac{dT}{T^2} \int_{298}^{T} \Delta C_p \, dT, \quad [I]$$

where ΔG_T^0 is the change in Gibbs energy (kJ/mol), ΔH_{298}^0 denotes the standard change of the reaction enthalpy (kJ/mol), ΔS_{298}^0 is the standard change of the reaciton entropy (J/mol degree), T is the temperature (K), and C_p is the molar heat capacity (J/mol degree).

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TABLE 1
Thermodynamic Data on the Substances Participating in the Reactions Investigated

				$C_p = A + B \times 10^{-3}T + C \times 10^{5}T^{-2} + D \times 10^{-6}T^{2}$ (J/mol deg)					
No.	Substance	ΔH_{298} (kJ/mol)	S_{298} (J/mol deg)	A	B	C	D	Temperature range (K)	Ref.
1	$TiCl_{4,g}$	– 763.16	354.84	134.706	4.44	5.543	—	298–2000	12, 17
2	$TiBr_{4,g}$	– 550.20	398.58	107.835	0.167	– 6.368	—	298–2000	12, 17
3	$ZrCl_{4,g}$	– 869.98	367.69	107.668	0.259	– 8.068	—	298–2000	12, 17
4	$ZrBr_{4,g}$	– 644.48	414.48	107.990	0.092	– 4.819	—	298–2000	12, 17
5	$NbCl_{5,g}$	– 703.33	404.07	132.3	0	– 15.5	—	No data	12, 17
6	$TaCl_{5,g}$	– 764.83	412.94	132.3	0	– 7.9	—	No data	12, 17
7	$LaCl_{3,g}$	– 741.0	364.7	80.3	0.25	– 2.9	—	298–2000	12, 14
8	$LaBr_{3,g}$	– 586.1	396.5	80.8	—	—	—	298	14
9	$BCl_{3,g}$	– 403.23	290.262	78.456	1.394	– 15.499	—	298–2000	12
10	$BBr_{3,g}$	– 204.18	324.19	80.403	1.440	– 11.962	—	298–2000	12, 17
11	$B_2H_{6,g}$	41.00	233.17	11.308	180.199	– 3.441	– 55.358	298–1500	12, 17
12	$B_5H_{9,g}$	73.22	275.40	95.5	—	—	—	298	13, 17
13	$B_{10}H_{14,g}$	47.28	352.12	179.70	—	—	—	298	15, 17
14	$H_{2,g}$	0	130.67	27.30	3.27	0.50	—	298–3000	12
15	$TiB_{2,s}$	– 279.49	28.53	30.224	4.802	—	—	298–1073	16, 17
16	$ZrB_{2,s}$	– 322.59	35.84	49.32	41.809	—	– 16.864	298–1073	16, 17
17	$NbB_{2,s}$	– 247.0	36.0	49.45	—	—	—	298	15, 16
18	$TaB_{2,s}$	– 190.1	47.3	58.53	—	—	—	298	15
19	$LaB_{6,s}$	129.8	83.23	90.98	85.4	—	—	298–1483	14, 16
20	HCl_g	– 92.37	186.911	26.54	4.60	1.09	—	298–2000	12
21	HBr_g	– 36.44	198.591	26.17	5.86	1.09	—	298–1600	12, 17

Using data from the literature on the enthalpy of formation, ΔH^0_{298}, and the entropy S^0_{298} under standard conditions, as well as data on the temperature dependence of the molar heat capacity ($C_p = A + B \times 10^{-3}T + C \times 10^{5}T^{-2} + D \times 10^{-6}T^{2}$) for each of the substances participating in the reaction (see Table 1), we calculated the change of the Gibbs energy by the method of Temkin and Schwartzmann, according to which the above equation can be written as

$$\Delta G^0_T = \Delta H^0_{298} - T\Delta S^0_{298} - T(M_0\Delta A + M_1\Delta B + M_2\Delta D + M_{-2}\Delta C). \qquad [II]$$

The values of the constants M_0, M_1, M_2, and M_{-2} for the different temperatures investigated have been tabulated (11).

CHOICE OF BORON SOURCES

Boron trichloride, BCl_3, is the most commonly used boron source in CVD of borides. However, the low boiling temperature of this compound (12.5°C) causes some inconveniences during CVD processes. The experimental procedures would perhaps be simplified by using BBr_3 which has a boiling point of 90°C and a price comparable to that of BCl_3. It is, however, interesting to compare the results of thermodynamic estimations of the reactions with BCl_3 and BBr_3, which will be made in what follows.

The third boron source in CVD of borides, which is the subject of the present work, is diborane, B_2H_6. It is known (18) that, during thermal dissociation of B_2H_6, a series of higher boranes can be obtained, pentaborane (9), B_5H_9, and decaborane (14), $B_{10}H_{14}$, being among the most stable. It might be accepted that in a CVD process with the participation of diborane the real boron source would be one of these two compounds (with boiling points of 333°C and 213°C, respectively). This is indicated by the data in Fig. 1 which

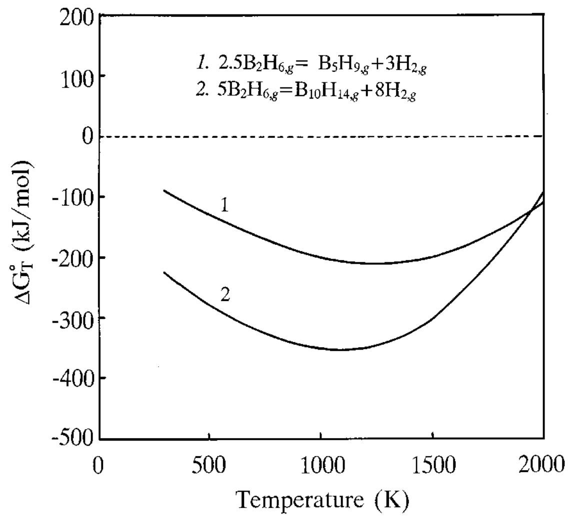

FIG. 1. Gibbs free energy vs temperature plots for reactions of thermal dissociation of B_2H_6 to B_5H_{10} (1) and $B_{10}H_{14}$ (2).

present the changes in Gibbs energy with rising temperature during the dissociation of B_2H_6, the resulting products being B_5H_9 or $B_{10}H_{14}$. It is obvious that from a thermodynamic viewpoint the decomposition should not be hindered up to 1200 K and 1100 K, respectively, and the formation of decaborane (14) is more probable. Above these temperatures the ΔG^0 values begin to grow, which evidences the occurence of the reverse processes.

Pentaborane (9) and decaborane (14) are commercially available products. It can be supposed that their use in CVD processes of metal borides would be more convenient from an experimental point of view than is the case of gaseous diborane which is highly toxic and burns explosively in air.

THERMODYNAMIC ANALYSIS OF CHEMICAL VAPOR DEPOSITION REACTIONS OF BORIDES

1. CVD of Titanium and Zirconium Diborides

In chemical vapor deposition of TiB_2 and ZrB_2 the following reactions were studied:

$$MeX_{4,g} + 2BX_{3,g} + 5H_{2,g} = MeB_{2,s} + 10HX_g \quad [1]$$

$$MeCl_{4,g} + B_2H_{6,g} = MeB_{2,s} + 4HCl_g + H_{2,g} \quad [2]$$

$$MeCl_{4,g} + 0.4B_5H_{9,g} + 0.2H_{2,g} = MeB_{2,s} + 4HCl_g \quad [3]$$

$$MeCl_{4,g} + 0.2B_{10}H_{14,g} + 0.6H_{2,g} = MeB_{2,s} + 4HCl_g \quad [4]$$

Here, $Me = \mathrm{Ti}$ or Zr and $X = \mathrm{Cl}$ or Br.

It may be assumed that, in addition to BCl_3, another boron source might be the $HBCl_2$ appearing as a result of the interaction of BCl_3 with the hydrogen available in the system according to the reaction

$$BCl_{3,g} + H_{2,g} = HBCl_{2,g} + HCl_g. \quad [5]$$

The thermodynamic analysis, however, has shown that the occurrence of this reaction is less probable than that of reaction [1]. Even less probable is, in the temperature range investigated, the process of partial BCl_3 reduction,

$$BCl_{3,g} + 0.5H_{2,g} = BCl_{2,g} + HCl_g. \quad [6]$$

As to BCl_3 dissociation,

$$BCl_{3,g} = BCl_{2,g} + 0.5Cl_{2,g}, \quad [7]$$

its probability is negligible.

There is an analogous situation when the boron source used is BBr_3.

The plots $\Delta G^0 = f(T)$ for CVD reactions of TiB_2 and ZrB_2 are given in Figs. 2 and 3, respectively. Obviously, in the chloride systems the thermodynamic equilibrium should set in at a lower temperature when ZrB_2 is deposited, whereas with bromide systems the opposite situation is observed. The simplificaton of the experiments by using BBr_3 instead of BCl_3 has also been pointed out above. Since the chlorides of titanium and zirconium are more accessible and cheaper than the corresponding bromides, it was of interest to study the temperature dependence of the Gibbs free energy change in reactions with the participation ofmetal tetrachlorides where the boron source is BBr_3:

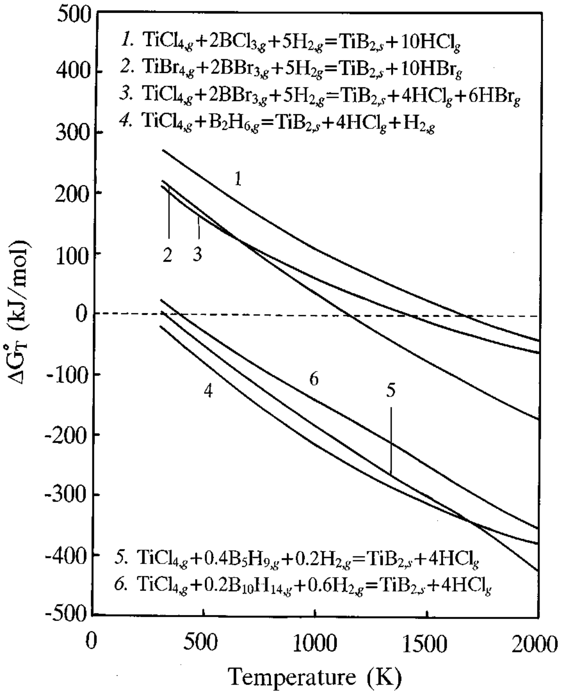

FIG. 2. Gibbs free energy vs temperature plots for reactions of TiB_2 deposition.

$$MeCl_{4,g} + 2BBr_{3,g} + 5H_{2,g} = MeB_{2,s} + 4HCl_g + 6HBr_g. \quad [8]$$

The data in Fig. 3 evidence that with ZrB_2 this dependence practically coincides with that of a pure bromide system. However, when TiB_2 is deposited, the thermodynamic equilibrium in the system with $TiCl_4$ is reached at a temperature higher than that needed for the bromide system, but lower than that for the chloride system (Fig. 2).

As the data in Figs. 2 and 3 show, the systems with the participation of boron hydrides are very attractive from a thermodynamic viewpoint primarily due to the much lower temperatures at which deposition should take place. The differences observed with the three boron sources are not essential. The most suitable precursor offering the best

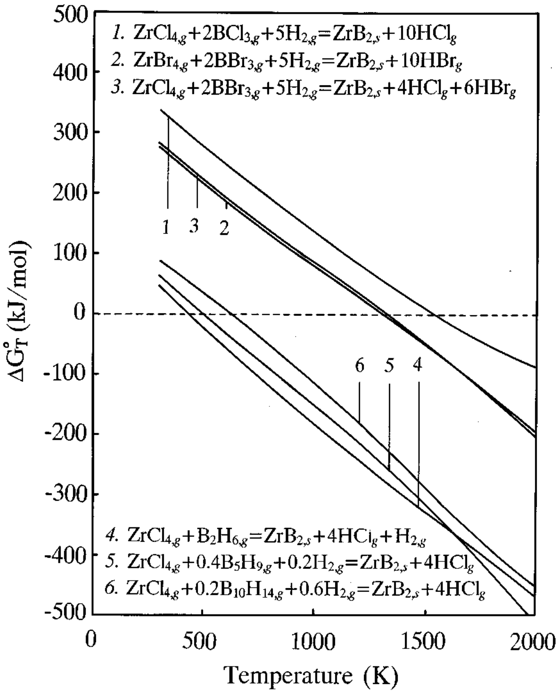

FIG. 3. Gibbs free energy vs temperature plots for reactions of ZrB_2 deposition.

technological advantages and the highest quality products should be chosen experimentally.

2. *CVD of Niobium and Tantalum Diborides*

The absence of sufficient data on the thermodynamic functions of $NbBr_5$ and $TaBr_5$ prohibited an investigation of the behavior of systems in which bromides only participate. Data were obtained on the temperature dependence of the change in Gibbs free energy of the reactions

$$MeCl_{5,g} + 2BCl_{3,g} + 5.5H_{2,g} = MeB_{2,s} + 11HCl_g \quad [9]$$

$$MeCl_{5,g} + 2BBr_{3,g} + 5.5H_{2,g} = MeB_{2,s} + 5HCl_g + 6HBr_g \quad [10]$$

$$MeCl_{5,g} + B_2H_{6,g} = MeB_{2,s} + 5HCl_g + 0.5H_{2,g} \quad [11]$$

$$MeCl_{5,g} + 0.4B_5H_{9,g} + 0.7H_{2,g} = MeB_{2,s} + 5HCl_g \quad [12]$$

$$MeCl_{5,g} + 0.2B_{10}H_{14,g} + 1.1H_{2,g} = MeB_{2,s} + 5HCl_g. \quad [13]$$

In the above reactions Me = Nb or Ta.

The curves in Figs. 4 and 5 indicate that from a thermodynamic point of view the reactions with BBr_3 as a boron source are more favorable than those using BCl_3.

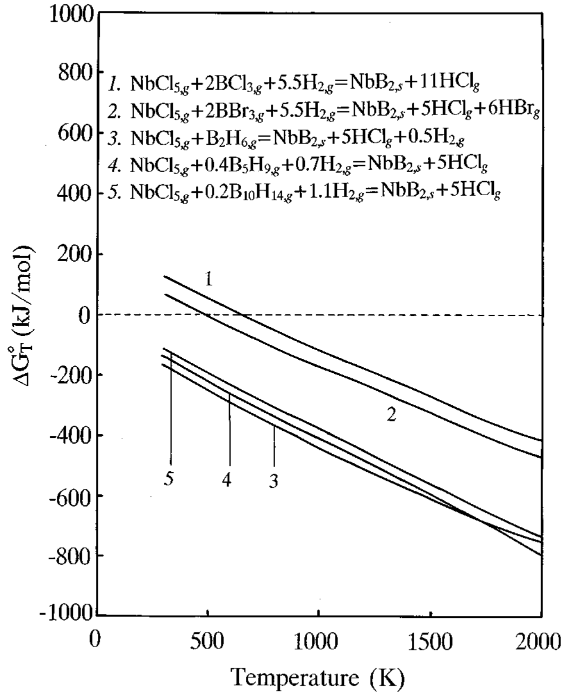

FIG. 4. Gibbs free energy vs temperature plots for reactions of NbB_2 deposition.

As to reactions with the participation of boron hydrides, similarly to the cases of TiB_2 and ZrB_2 deposition, they would ensure the occurrence of CVD processes of prepara-

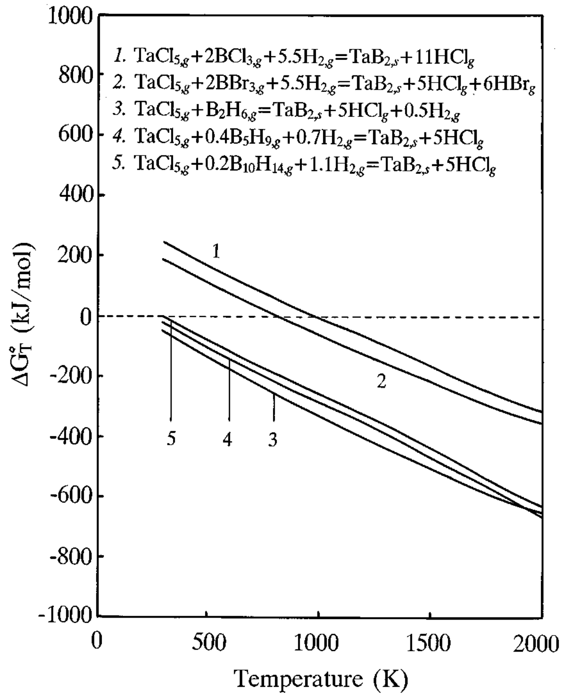

FIG. 5. Gibbs free energy vs temperature plots for reactions of TaB_2 deposition.

tion of niobium and tantalum diborides under conditions milder than those needed for reactions using a halide as a boron source.

3. *CVD of Lanthanum Hexaboride*

Figure 6 presents the $\Delta G^0 = f(T)$ dependencies obtained by thermodynamic calculations for the reactions

$$\mathrm{LaCl_{3,g} + 6BCl_{3,g} + 10.5H_{2,g} = LaB_{6,s} + 21HCl_g} \quad [14]$$

$$\mathrm{LaBr_{3,g} + 6BBr_{3,g} + 10.5H_{2,g} = LaB_{6,s} + 21HBr_g} \quad [15]$$

$$\mathrm{LaCl_{3,g} + 6BBr_{3,g} + 10.5H_{2,g} = LaB_{6,s} + 3HCl_g + 18HBr_g} \quad [16]$$

$$\mathrm{LaCl_{3,g} + 3B_2H_{6,g} = LaB_{6,s} + 3HCl_g + 7.5H_{2,g}} \quad [17]$$

$$\mathrm{LaCl_{3,g} + 1.2B_5H_{9,g} = LaB_{6,s} + 3HCl_g + 3.9H_{2,g}} \quad [18]$$

$$\mathrm{LaCl_{3,g} + 0.6B_{10}H_{14,g} = LaB_{6,s} + 3HCl_g + 2.7H_{2,g}}. \quad [19]$$

The above dependencies clearly show that reaction [14] could hardly be effective in the deposition of LaB_6. This is also confirmed by the small number of published experiments (2). Better results might be expected from CVD processes according to reactions [15] and [16] with the participation of BBr_3. However, it is evident that the most promising boron sources for future experiments on CVD of LaB_6 and, above all, on chemical deposition of the extremely interesting thin films of this boride are the boron hydrides.

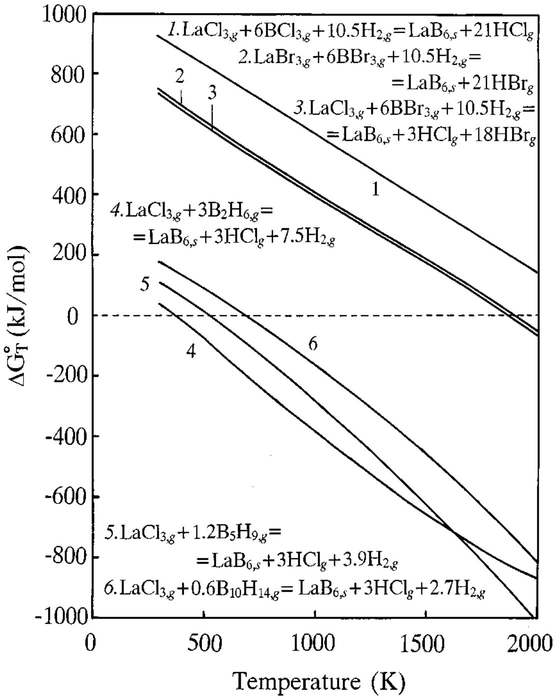

FIG. 6. Gibbs free enegy vs temperature plots for reactions of LaB_6 deposition.

CONCLUSION

The results of the thermodynamic calculations presented in this work have shown that the processes of chemical vapor deposition of TiB_2, ZrB_2, NbB_2, TaB_2, and LaB_6 should take place under much milder conditions when boron hydrides such as B_2H_6, B_5H_9, and $B_{10}H_{14}$ are used as boron sources. In experiments on these processes diborane should be dissociated and an efficient boron precursor would be a higher boron hydride, most probably decaborane (14).

From a thermodynamic point of view, boron tribromide is a more efficient boron source than is boron trichloride. Processes of CVD chiefly of transition metal diborides might be realized with the participation of BBr_3 according to a rather simplified technological procedure as compared to that using BCl_3 due to the favorable boiling point of BBr_3. The latter is also superior to boron hydrides in a technological respect since, in contrast to them, it is characterized neither by a high toxicity nor by an explosive behavior.

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