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Investigating routes toward atomic layer deposition of silicon carbide: Ab initio screening of potential silicon and carbon precursors

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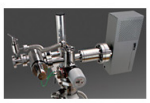
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Investigating routes toward atomic layer deposition of silicon carbide: *Ab initio* screening of potential silicon and carbon precursors

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Silicon carbide (SiC) is a promising material for electronics due to its hardness, and ability to carry high currents and high operating temperature. SiC films are currently deposited using chemical vapor deposition (CVD) at high temperatures 1500–1600 °C. However, there is a need to deposit SiC-based films on the surface of high aspect ratio features at low temperatures. One of the most precise thin film deposition techniques on high-aspect-ratio surfaces that operates at low temperatures is atomic layer deposition (ALD). However, there are currently no known methods for ALD of SiC. Herein, the authors present a first-principles thermodynamic analysis so as to screen different precursor combinations for SiC thin films. The authors do this by calculating the Gibbs energy ΔG of the reaction using density functional theory and including the effects of pressure and temperature. This theoretical model was validated for existing chemical reactions in CVD of SiC at 1000 °C. The precursors disilane (Si_2H_6), silane (SiH_4), or monochlorosilane (SiH_3Cl) with ethyne (C_2H_2), carbontetrachloride (CCl_4), or trichloromethane ($CHCl_3$) were predicted to be the most promising for ALD of SiC at 400 °C. © *2016 American Vacuum Society*.
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I. INTRODUCTION

Silicon carbide (SiC) is a promising material for electronic devices. It is harder than Si and can sustain higher voltages, carry higher currents, and operate at higher temperatures. There is a need to deposit SiC-based films on the surface of high aspect ratio features for various applications for electronics, e.g., low-k spacers/liners and air gap liners for interlayer dielectric, exploiting the low dielectric constant (<5) and low wet etch rate of SiC.

SiC occurs naturally in different crystal polytypes. The most common polytypes being developed for electronics are 3C, 4H, and 6H.[1]

SiC-based films are currently deposited using chemical vapor deposition (CVD). This technique is operated at elevated temperatures 1500–1600 °C and may suffer from nonuniformity due to fast surface reactions.[2] One of the most precise thin film growth techniques is a variant of CVD called atomic layer deposition (ALD). Thin films deposited by ALD or plasma-enhanced ALD (PEALD) are highly conformal even on high-aspect-ratio surfaces and are grown at low temperatures (e.g., <400 °C). However, there are currently no known low temperature methods for ALD of SiC.

The most commonly used precursors in SiC CVD growth are silane (SiH_4)[3–5] as a silicon precursor, and propane (C_3H_8)[3,5–8] or ethylene (C_2H_4)[9,10] as a carbon precursor.[11] They provide a better morphology and higher growth rate than other precursors.[12] However, many different precursors apart from those mentioned above were used for CVD of SiC. Nine different carbon precursors [methane (CH_4), ethane (C_2H_6), ethyne (C_2H_2), ethylene (C_2H_4), propane (C_3H_8), propene (C_3H_6), propadiene (C_3H_4), propyne (C_3H_4), butane (C_4H_{10})] with silane (SiH_4) were analyzed by Hallin *et al.*[4] for the CVD growth of 4H and 6H SiC epitaxial layers, in the temperature range of 1550–1600 °C. The most stable growth at high growth rates was achieved with propane (C_3H_8).[4] For silicon precursors besides silane (SiH_4) the most commonly used are chlorosilanes, such as dichlorosilane SiH_2Cl_2 (DCS),[5] trichlorosilane $SiHCl_3$ (TCS),[9] methyltrichlorosilane $SiCH_3Cl_3$ (MTS),[13] and tetrachlorosilane $SiCl_4$ (TET).[14] TET and TCS are the most common.[12] A review of chloride-based CVD growth of SiC was done by Pedersen *et al.*[15] Single-source precursors (containing both Si and C in the same molecule) have also been used for CVD of SiC.[16] These precursors include: MTS, methylsilane (CH_3–SiH_3),[17] diethylmethylsilane [$(C_2H_5)_2SiHCH_3$],[18] tetramethylsilane [$Si(CH_3)_4$],[19] hexamethyldisilane [$Si_2(CH_3)_6$],[19] silacyclobutane [$SiH_2(CH_2)_3$],[20] and 1,3-disilabutane (SiH_3–CH_2–SiH_2–CH_3).[16]

As was mentioned above, experimentalists are facing difficulties in growing SiC films by ALD or PEALD. Theoretical modeling of ALD using density functional theory (DFT) provides a complementary view to the experimental techniques. DFT is usually used to calculate the pathways for precursor adsorption, ligand migration, and by-product formation on the surface, yielding reaction energies and activation energies for each step of the ALD cycle. A review of previous theoretical studies of Si-based materials can be found in Ref. 21. In this paper, we present a theoretical thermodynamic analysis of different precursor combinations for SiC deposition thin film by calculating Gibbs energy ΔG using DFT as implemented in

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TURBOMOLE (Ref. 22) and VASP (Ref. 23) software. The effects of CVD conditions (1000 °C) and ALD conditions (400 °C) are evaluated. It is found that chemical reactions of disilane (Si_2H_6), silane (SiH_4), monochlorosilane (SiH_3Cl), or DCS (SiH_2Cl_2) precursors with all suggested carbon precursors are thermodynamically favorable. The most negative ΔG are for disilane (Si_2H_6), silane (SiH_4), monochlorosilane (SiH_3Cl), ethyne (C_2H_2), carbontetrachloride (CCl_4), and trichloromethane ($CHCl_3$). Hence, silane (SiH_4), disilane (Si_2H_6), monochlorosilane (SiH_3Cl), ethyne (C_2H_2), carbontetrachloride (CCl_4), and trichloromethane ($CHCl_3$) can be predicted to be the most favorable precursors for ALD of SiC thin films.

II. METHODOLOGY

Atomic-scale modeling was performed to investigate routes toward the ALD of SiC-based films using first principles calculations based on DFT. All precursors were modeled as isolated molecules in vacuum using the TURBOMOLE software.[22] Optimized structures of the Si and C precursors are shown in Fig. 1. The generalized gradient approximation to DFT (Ref. 24) was implemented by using the exchange correlation functional of Perdew, Burke, and Ernzerhof (PBE).[24] The atom-centered basis set def2-TZVPP was used for all the atoms[25] along with an auxiliary basis set for the density within the resolution of identity (RI) approximation.[26,27]

The energy for SiC-3C bulk was obtained using the Vienna *ab initio* simulation package (VASP)[23] also with the PBE exchange-correlation functional. The projector augmented wave method[23,28] was used to describe the core electrons of atoms. A plane wave basis set with a cut-off energy 400 eV was used for the valence orbitals. An 8 × 8 × 8 k-point grid within the Monkhorst–Pack scheme in the Brillioun zone was employed. Full geometry relaxation was carried out using the conjugate gradient method for energy minimization at convergence level of 0.01 eV/Å on each ion.

Reaction energetics for SiC from various silicon and carbon precursors were evaluated using the general formula in Eq. (1), assuming that by-products of the reactions were CH_4, HCl, Cl_2, and H_2 where applicable. Competing reactions to formation of SiC are not considered.

$$\begin{aligned} &n\mathrm{Si}_a\mathrm{X}_b + a\mathrm{C}_n\mathrm{Y}_m \rightarrow an\mathrm{SiC} + amXY + \frac{nb-am}{2}X_2 \\ &\quad \text{if } nb > am; \\ &n\mathrm{Si}_a\mathrm{X}_b + a\mathrm{C}_n\mathrm{Y}_m \rightarrow an\mathrm{SiC} + nbXY + \frac{am-nb}{2}Y_2 \\ &\quad \text{if } nb < am. \end{aligned} \tag{1}$$

For example, for $SiCl_4$ ($X = Cl$, $a = 1$, $b = 4$) and C_2H_6 ($Y = H$, $n = 2$, $m = 6$), Eq. (1) becomes

$$2\mathrm{SiCl}_4 + \mathrm{C}_2\mathrm{H}_6 \rightarrow 2\mathrm{SiC} + 6\mathrm{HCl} + \mathrm{Cl}_2. \tag{2}$$

A list of all the analyzed reactions is presented in Tables I and II in supplementary material.[33]

Gibbs energies ΔG were calculated for these reactions using Eq. (3)

$$\Delta G = \Delta E - T\Delta S + RT\ln Q, \tag{3}$$

where $\Delta E = \sum E_{\text{products}} - \sum E_{\text{reactants}}$ using ground state energies obtained from DFT calculations, ΔS are entropies at temperature T obtained from DFT calculations in TURBOMOLE, assuming that $S_{\text{SiC}} = 0$, and reaction quotient $Q = \prod P^{\mu}_{\text{products}} / \prod P^{\mu}_{\text{reactants}}$, where partial pressures of products are $P_{\text{products}} = 0.01$ Torr, partial pressures of reactants $P_{\text{reactants}} = 1$ Torr and μ are stoichiometric coefficients. Partial pressures were chosen in correspondence with experimental ALD data. ΔG indicates whether a reaction is thermodynamically favorable.

In VASP, the one-electron orbitals are expressed in plane wave basis sets, which make it inefficient and time-consuming for calculating gas-phase molecules, while bulk SiC can be easily simulated with VASP. Therefore, we use a reference gas-phase molecule to estimate energies for bulk SiC in TURBOMOLE. We choose gas-phase tetramethylsilane $Si(CH_3)_4$ as a reference molecule for SiC. It contains Si–C bonds like SiC. First ΔE_1 is computed with VASP for decomposition of the reference molecule using Eq. (4)

$$\mathrm{Si(CH_3)_4(g)} \rightarrow \mathrm{SiC(s)} + 3\mathrm{CH_4(g)}. \tag{4}$$

Calculations for $Si(CH_3)_4$(g) and CH_4(g) molecules were done at single Γ-point in the Brillioun zone at convergence level for the forces on each ion of 0.01 eV/Å. The size of the cell was chosen as 15 × 15 × 15 Å. ΔE_1 is calculated only once. Then, ΔE_2 is computed for the gas-phase reaction to the reference molecule with TURBOMOLE for each X and Y using

$$\begin{aligned} &n\mathrm{Si}_a\mathrm{X}_b\mathrm{(g)} + a\mathrm{C}_n\mathrm{Y}_m\mathrm{(g)} + 3an\mathrm{CH_4(g)} \rightarrow an\mathrm{Si(CH_3)_4(g)} \\ &\quad + amXY\mathrm{(g)} + \frac{nb-am}{2}X_2\mathrm{(g)} \quad \text{if } nb > am; \\ &n\mathrm{Si}_a\mathrm{X}_b\mathrm{(g)} + a\mathrm{C}_n\mathrm{Y}_m + 3an\mathrm{CH_4(g)} \rightarrow an\mathrm{Si(CH_3)_4(g)} \\ &\quad + nbXY\mathrm{(g)} + \frac{am-nb}{2}Y_2\mathrm{(g)} \quad \text{if } nb < am. \end{aligned} \tag{5}$$

In the example above, Eq. (5) becomes

$$2\mathrm{SiCl_4(g)} + \mathrm{C_2H_6(g)} + 6\mathrm{CH_4(g)} \rightarrow 2\mathrm{Si(CH_3)_4(g)} + 6\mathrm{HCl(g)} + \mathrm{Cl_2(g)}. \tag{6}$$

The final corrected ΔE_3 that we use for calculating Gibbs energy ΔG in Eq. (3) will be a sum of ΔE_2 and ΔE_1. This approach can be represented as a Hess cycle; see Fig. 2 for the example of $2SiCl_4 + C_2H_6 \rightarrow 2SiC + 6HCl + Cl_2$. The difference between ΔE computed in VASP and in TURBOMOLE for this sample reaction of Eq. (6) is just 0.0002 eV, well within the precision of the method.

Including the effects of temperature allowed us to validate the approach for known precursor combinations for CVD at 1000 °C. Furthermore, reaction energetics were calculated at 400 °C to predict precursors for ALD of SiC at around this temperature.

ΔG [A(g) + B(g) → AB(s) + C(g)] reflects the actual thermodynamics of the CVD reaction. If $\Delta G < 0$, the reaction is permitted and $\Delta G > 0$ means that it is not permitted.

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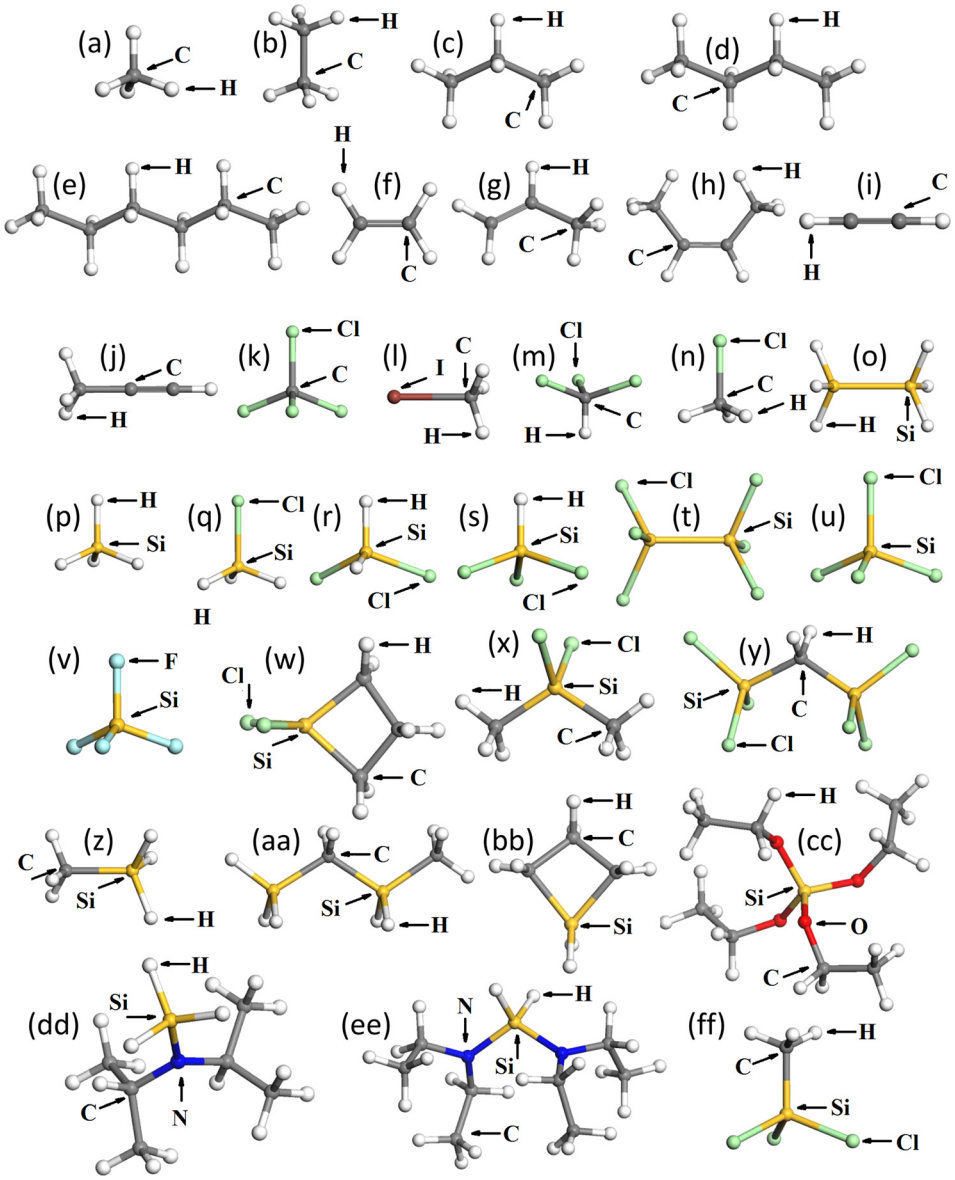


FIG. 1. (Color online) Optimized structures for the possible precursors for ALD of SiC performed in TURBOMOLE with PBE functional. (a) methane (CH_4), (b) ethane (C_2H_6), (c) propane (C_3H_8), (d) *n*-butane (C_4H_{10}), (e) *n*-hexane (C_6H_{14}), (f) ethylene (C_2H_4), (g) propene (C_3H_6), (h) -2-butene (C_4H_8), (i) ethyne (C_2H_2), (j) propyne (C_3H_4), (k) carbontetrachloride (CCl_4), (l) iodomethane (CH_3I), (m) trichloromethane ($CHCl_3$), (n) chloromethane (CH_3Cl), (o) disilane (Si_2H_6), (p) silane (SiH_4), (q) monochlorosilane (SiH_3Cl), (r) DCS, (s) TCS, (t) hexachlorodisilane (Si_2Cl_6), (u) TET, (v) tetrafluorosilane (SiF_4), (w) dichlorosilacyclobutane [$SiCl_2(CH_2)_3$], (x) dimethyldichlorosilane [$Si(CH_3)_2Cl_2$], (y) bis(trichlorosilyl)methane [$(SiCl_3)_2CH_2$], (z) methylsilane (CH_3–SiH_3), (aa) 1,3-disilabutane(SiH_3–CH_2–SiH_2–CH_3), (bb) silacyclobutane [$SiH_2(CH_2)_3$], (cc) tetraethylorthosilicate $Si(OEt)_4$, (dd) DIPAS, (ee) bis(diethylamino)silane $H_2Si[N(Et)_2]_2$, and (ff) MTS. (Et)—ethyl group $^-CH_2\ ^-CH_3$; (iPr)—iso-propyl group $–CH_2–CH_2–CH_3$.

Kinetics is less important at high *T*. By contrast, in an ALD process, reactants A(g) and B(g) do not meet in the reactor, but ΔG [A(g) + B(g) → AB(s) + C(g)] is still relevant for describing the ALD process. Our finding so far with ALD has been that the formation of A-B bonds in the solid product is the main driving force for the process (and that the formation of by-product C plays a secondary role). The A + B reaction is thus a way of measuring this driving force.[21] The actual surface reaction steps in each ALD cycle are (1) unknown for SiC, (2) expected to be quite complex, and (3) dependent on kinetics of each step (because ALD is performed at lower *T* than CVD). It is therefore not possible to screen a wide range of chemicals for their actual detailed behavior in ALD. Instead, we use the simple ΔG model. However, we bear in mind that the absolute value of ΔG has no meaning for the ALD reaction, i.e., $\Delta G > 0$ does not necessarily mean that ALD will not work and $\Delta G < 0$ does not necessarily mean that all the individual surface reactions take place.

Therefore, the same gas-phase reactions were used to investigate ALD and CVD processes. In both cases, a surface was not introduced in the model.

III. RESULTS AND DISCUSSION

Different Si and C precursors for ALD of SiC were screened with respect to their thermodynamic reactivity

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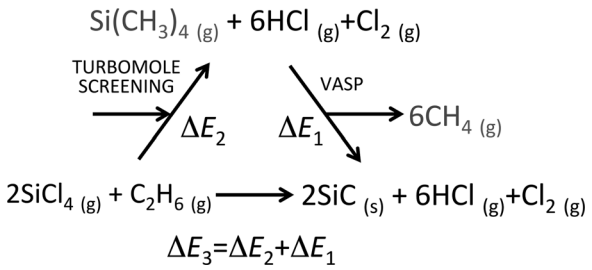


FIG. 2. Hess cycle representing screening approach for calculating ΔE using gas-phase cluster software (in our case TURBOMOLE) and periodic software (in our case VASP) with tetramethylsilane [$Si(CH_3)_4$] as a reference molecule for SiC. ΔE_3 is the desired energy, which is used to calculate Gibbs energy in Eq. (3).

toward forming SiC. Gibbs energies ΔG of chemical reactions between different Si and C precursors were calculated to investigate which chemical reactions are more thermodynamically favorable (Figs. 3 and 4 and Tables I and II in supplementary material). First, Gibbs energies were calculated at CVD conditions $T = 1000\,^{\circ}\mathrm{C}$ and partial pressures $P_{\mathrm{products}} = 0.01$ Torr and $P_{\mathrm{reactants}} = 1$ Torr of products and reactants, respectively, to validate the proposed theoretical model for screening (see Fig. 3, Table I supplementary material). At $T = 1000\,^{\circ}\mathrm{C}$, ΔG is negative for reactions of disilane (Si_2H_6), silane (SiH_4), monochlorosilane (SiH_3Cl), DCS, and TCS with all the analyzed carbon containing precursors. That corresponds very well with experimental results, where silane is the most common silicon precursor for SiC CVD.[3–5] Monochlorosilane together with propane (C_3H_8) gave a growth rate of SiC of 20 μm/h (Ref. 8) and, consistent with this, the calculated ΔG for monochlorosilane (SiH_3Cl) and propane is negative ($\Delta G = -3.3$ eV/SiC). Besides, for CVD of SiC using DCS with propane growth rates up to 100 μm/h were achieved at 1750 °C,[5] where we estimate $\Delta G = -4.8$ eV for DCS reacting with propane at 1750 °C.

The most positive ΔG are computed for reactions of TET and tetrafluorosilane (SiF_4). For tetrafluorosilane (SiF_4), ΔG is positive for reactions with all suggested carbon precursors and is also positive for TET with ethylene, propene, -2-butene, propyne, and carbon tetrachloride. In the experiment, TET together with TCS are the most commonly used chlorosilane precursors for CVD of SiC.[15] The use of TET with hexane (C_6H_{14}) for epitaxial growth of 6H-SiC was demonstrated at 1850 °C with a growth rate of 3.6–7.2 μm/h.[29] Propane was also used with TET at high temperatures up to 1850 °C yielding growth rates up to 200 μm/h.[30] Our model shows near-zero exothermicity for TET reacting with propane and hexane at 1000 °C (ΔG −0.3 and 0.0 eV, respectively), but much more negative values at 1850 °C (−2.9 and −2.6 eV, respectively, not shown in the tables), corresponding very well with the experimental finding.

Experimentally, SiC films were grown by CVD using TCS and ethylene (C_2H_4) precursors with a growth rate of 100 μm/h at 1600 °C.[9] Our calculations found TCS reacting with all of the carbon precursors to be thermodynamically favorable.

The above data include the effects of pressure via the *RTlnQ* term of Eq. (3). We find that this is important: in general, including the effects of pressure makes the reactions more thermodynamically favorable, as seen in ΔG becoming more negative by an average of 0.6 eV/SiC at $T = 1000\,^{\circ}\mathrm{C}$ and by 0.3 eV/SiC at $T = 400\,^{\circ}\mathrm{C}$.

It is also important to include the effects of entropy. The above data include the effects of entropy via $T\Delta S$. Including $T\Delta S$ makes the reactions more thermodynamically favorable by decreasing ΔG by an average of 1.3 eV/SiC for $T = 1000\,^{\circ}\mathrm{C}$ and 1.0 eV/SiC for $T = 400\,^{\circ}\mathrm{C}$ depending on the size of the molecules. For example, for small C_2H_2 reacting with different silicon precursors, including $T\Delta S$ decreased ΔG by an average of 0.1 eV/SiC for $T = 1000\,^{\circ}\mathrm{C}$ and 0.2 eV/SiC for $T = 400\,^{\circ}\mathrm{C}$, while for the bigger molecule C_6H_{14} including $T\Delta S$ decreased ΔG by an average of 1.8 eV/SiC for $T = 1000\,^{\circ}\mathrm{C}$ and 1.2 eV/SiC for $T = 400\,^{\circ}\mathrm{C}$.

To evaluate the viability of these precursors for ALD of SiC, Gibbs energies ΔG at $T = 400\,^{\circ}\mathrm{C}$ and partial pressures $P_{\mathrm{products}} = 0.01$ Torr and $P_{\mathrm{reactants}} = 1$ Torr of products and reactants, respectively, were calculated and are presented in Fig. 4 and Table II in supplementary material. In general, we can see that most of the reactions are less favorable at this lower T, compared to ΔG at higher T presented in Fig. 3, which may be one reason why ALD of SiC is difficult. Nevertheless, direct chemical reactions of disilane (Si_2H_6), silane (SiH_4), monochlorosilane (SiH_3Cl), or DCS Si precursors with all suggested carbon precursors are thermodynamically favorable which suggests that these precursor combinations may give viable indirect reactions in ALD. The most negative ΔG are for ethyne (C_2H_2), carbontetrachloride (CCl_4), and trichloromethane ($CHCl_3$).

ΔG, [eV]/SiC unit, 1000°C (CVD)		methane	ethane	propane	n-butane	n-hexane	ethylene	propene	-2-butene	ethyne	propyne	carbon-tetrachloride	iodo-methane	trichloro-methane	chloro-methane
		CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_6H_{14}	C_2H_4	C_3H_6	C_4H_8	C_2H_2	C_3H_4	CCl_4	CH_3I	$CHCl_3$	CH_3Cl
disilane	Si_2H_6	-3.5	-3.7	-3.8	-3.8	-3.8	-3.1	-3.3	-3.5	-5.5	-2.9	-6.8	-4.3	-6.5	-4.5
silane	SiH_4	-3.9	-4.0	-4.0	-4.0	-4.0	-3.4	-3.5	-3.7	-5.8	-3.2	-8.1	-4.7	-6.9	-4.9
monochlorosilane	SiH_3Cl	-3.2	-3.3	-3.3	-3.3	-3.4	-2.7	-2.8	-3.0	-5.1	-2.5	-5.5	-4.0	-6.2	-4.2
dichlorosilane (DCS)	SiH_2Cl_2	-2.5	-2.6	-2.6	-2.6	-2.7	-2.0	-2.1	-2.3	-4.4	-1.8	-2.9	-3.3	-3.6	-3.5
trichlorosilane (TCS)	$SiHCl_3$	-1.8	-1.9	-2.0	-2.0	-2.0	-1.3	-1.5	-1.6	-2.8	-0.5	-0.3	-2.6	-1.0	-2.8
hexachlorodisilane	Si_2Cl_6	-1.6	-1.7	-1.5	-1.3	-1.2	-0.1	-0.3	-0.5	-1.6	0.7	1.0	-1.4	0.3	-1.6
tetrachlorosilane (TET)	$SiCl_4$	-1.5	-0.6	-0.3	-0.2	0.0	1.0	0.8	0.6	-0.5	1.8	2.0	-1.2	1.3	-0.6
tetrafluorosilane	SiF_4	0.6	3.2	4.0	4.5	4.9	6.5	6.3	6.1	6.7	8.4	8.6	2.6	8.5	3.2

FIG. 3. (Color online) Gibbs energies ΔG for reactions of various Si and C precursors at CVD temperature 1000 °C. The most favorable reactions are those with the most negative ΔG. The least favorable reactions have the most positive ΔG.

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ΔG, [eV]/SiC unit, 400°C (ALD)		methane	ethane	propane	n-butane	n-hexane	ethylene	propene	-2-butene	ethyne	propyne	carbon-tetrachloride	iodo-methane	trichloro-methane	chloro-methane
		CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_6H_{14}	C_2H_4	C_3H_6	C_4H_8	C_2H_2	C_3H_4	CCl_4	CH_3I	$CHCl_3$	CH_3Cl
disilane	Si_2H_6	-1.5	-1.8	-1.9	-1.9	-2.0	-1.9	-1.9	-2.1	-5.0	-2.0	-4.8	-2.3	-4.5	-2.5
silane	SiH_4	-1.8	-2.0	-2.0	-2.0	-2.1	-2.0	-2.0	-2.2	-5.1	-2.1	-6.0	-2.5	-4.8	-2.8
monochlorosilane	SiH_3Cl	-1.1	-1.3	-1.3	-1.3	-1.4	-1.3	-1.3	-1.5	-4.4	-1.4	-3.4	-1.8	-4.1	-2.1
dichlorosilane (DCS)	SiH_2Cl_2	-0.3	-0.5	-0.6	-0.6	-0.6	-0.6	-0.6	-0.8	-3.7	-0.7	-0.8	-1.1	-1.4	-1.3
trichlorosilane (TCS)	$SiHCl_3$	0.4	0.2	0.1	0.1	0.1	0.1	0.1	-0.1	-2.1	0.6	1.8	-0.4	1.2	-0.6
hexachlorodisilane	Si_2Cl_6	0.5	0.2	0.5	0.6	0.7	1.1	1.1	0.9	-1.0	1.6	2.9	0.7	2.3	0.5
tetrachlorosilane (TET)	$SiCl_4$	0.7	1.5	1.8	1.9	2.0	2.4	2.4	2.2	0.2	2.9	4.1	1.0	3.4	1.6
tetrafluorosilane	SiF_4	1.8	4.6	5.5	6.0	6.4	7.4	7.5	7.2	7.3	9.3	10.9	4.1	10.5	4.7

FIG. 4. (Color online) Gibbs energies ΔG for reactions of various Si and C precursors at ALD temperature 400 °C. The most favorable reactions are those with the most negative ΔG. The least favorable reactions have the most positive ΔG. Silane (SiH_4), disilane (Si_2H_6), monochlorosilane (SiH_3Cl), ethyne (C_2H_2), carbontetrachloride (CCl_4), and trichloromethane ($CHCl_3$) are predicted to be the most favorable precursors for ALD of SiC thin films.

A quite different process for low temperature silicon carbide ALD was proposed by Thompson using silicontetrachloride and trimethylaluminium as precursors.[31] We postulated that the corresponding chemical reaction is $3SiCl_4 + Al(CH_3)_3 \rightarrow 3SiC + AlCl_3 + 9HCl$ and found that ΔG for this reaction at 400 °C is −0.54 eV per SiC. This is of the same magnitude as ΔG for the other ALD processes that we have computed to be viable and thus provides further validation for our approach.

To assess single-source precursors, the thermodynamics of their decomposition into SiC and by-products was calculated at $T = 400$ °C and $T = 1000$ °C. The corresponding ΔG are presented in Fig. 5 and in the supplementary material. We find that unimolecular decomposition of most of these precursors is thermodynamically favorable at low temperature. The most negative ΔG are for decomposition of diisopropylaminosilane [DIPAS, $SiH_3N(iPr)_2$] and silacyclobutane [$SiH_2(CH_2)_3$]. The most positive ΔG is for dichlorosilacyclobutane [$SiCl_2(CH_2)_3$].

Experimentally, growth of SiC by CVD using single-source precursors was shown for 1,3-disilabutane (SiH_3–CH_2–SiH_2–CH_3) (low pressure CVD, 750 °C),[16] silacyclobutane [$SiH_2(CH_2)_3$] ($T = 800$–1200 °C),[20] methylsilane (CH_3–SiH_3) ($T = 800$ °C),[17] and MTS ($T = 1570$ °C).[32] Our calculations show that decomposition of 1,3-disilabutane, silacyclobutane, and methylsilane is thermodynamically favorable at $T = 1000$ °C with $\Delta G = -3.5$, −4.5, and −3.8 eV/SiC, respectively. For decomposition of the MTS precursor, we obtained negative $\Delta G = -1.8$ eV/SiC at 1000 °C. Experimentally, it was shown that growth of SiC using MTS is favorable only at 1570 °C. Indeed our theoretical estimation of the Gibbs energy for MTS at 1570 °C gives negative $\Delta G = -3.4$ eV/SiC. This shows that our theoretical results correspond to experimental studies in all of the cases.

Unimolecular decomposition is undesirable as a reaction strategy for ALD because it does not allow surface reactions to self-limit. It is therefore important to check whether proposed ALD precursors can decompose and lead to non-ALD growth. The data in Fig. 5 show that the precursors that are the most resistant toward decomposing at 400 °C are dichlorosilacyclobutane [$SiCl_2(CH_2)_3$] and MTS with $\Delta G = 0.9$ and 0.2 eV/SiC, respectively. On the other hand, the precursors silacyclobutane [$SiH_2(CH_2)_3$] and DIPAS are the most likely to decompose at 400 °C.

In conclusion, we carried out a theoretical thermodynamic analysis of different precursor combinations for SiC thin film by calculating Gibbs energy ΔG, including the effects of pressure and temperature ($G = \Delta E - T\Delta S + RT\ln Q$). The theoretical model was validated for existing chemical reactions in CVD of SiC process at 1000 °C and partial pressures $P_{\text{products}} = 0.01$ Torr and $P_{\text{reactants}} = 1$ Torr. In all of the cases, our theoretical results correspond to experimental studies. For ALD of SiC at 400 °C and

		ΔG, [eV]/SiC unit, 1000°C (CVD)	ΔG, [eV]/SiC unit, 400°C (ALD)
dichlorosilacyclobutane	$SiCl_2(CH_2)_3$	0.1	0.9
dimethyldichlorosilane	$Si(CH_3)_2Cl_2$	-2.6	-0.6
bis(trichlorosilyl)methane	$(SiCl_3)_2CH_2$	-2.4	-0.4
methylsilane	CH_3-SiH_3	-3.8	-1.9
1,3-disilabutane	SiH_3-CH_2-SiH_2-CH_3	-3.5	-1.7
silacyclobutane	SiH2(CH2)3	-4.5	-3.8
TEOS	$Si(OEt)_4$	-8.0	-2.3
DIPAS	$SiH_3N(iPr)_2$	-6.7	-4.6
BDEAS	$H_2Si[N(Et)_2]_2$	-5.4	-0.9
methyltrichlorosilane (MTS)	$SiCH_3Cl_3$	-1.8	0.2

FIG. 5. (Color online) Gibbs energies ΔG for decomposition reactions of single-source precursors containing both Si and C at CVD temperature 1000 °C and at ALD temperature 400 °C. The most favorable reactions are with the most negative ΔG. The least favorable reaction is with the positive ΔG. (Et)—ethyl group $^-CH_2\ ^-CH_3$; (iPr)—iso-propyl group $^-CH_2\ ^-CH_2\ ^-CH_3$.

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$P_{products} = 0.01$ Torr and $P_{reactants} = 1$ Torr, the precursors disilane (Si_2H_6), silane (SiH_4) or monochlorosilane (SiH_3Cl) with ethyne (C_2H_2), carbontetrachloride (CCl_4), or trichloromethane ($CHCl_3$) are predicted to be the most promising.

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