stants, combination rules for the evaluation of repulsion parameters, etc.

In the interaction potential, the main part is the electrostatic one and the calculated frequencies are strongly dependent on the charge values. The other terms (dispersion, second order of the polarization and dispersion) are less significant. In fact, the validity of the potential is only verified by the position of the minimum (compared to the X-ray crystallographic data). This is not sufficient to test the validity of each term in a potential model but we have no other experimental data which can be compared to the calculation. The other set of experimental data is the set of vibrational frequencies, and these later are related to the second derivatives of the potential.

Nevertheless, this simple model shows that the ionic charges on the atoms lead to very high frequency values compared to the experimental data. On the contrary, charge values deduced from the electronegativity orbital method developed by Mullay, Mortier, and Ghosh give a better agreement with experiment when we take for monovalent cations a charge value of 0.9 e and for  $Ca^{2+}$  a value of 1.5 e. Furthermore, we notice that in the totally exchanged potassium zeolite, it seems that some Na<sup>+</sup> cations remain because of the presence of a band at  $214 \text{ cm}^{-1}$ .

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# Thermal Stability of Methyl Groups on Si(100) Generated by the Decomposition of Tetramethylgermane

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The adsorption and thermal decomposition of tetramethylgermane on Si(100) have been studied by ultraviolet photoelectron spectroscopy, static secondary ion mass spectrometry, temperature-programmed desorption, and Auger electron spectroscopy. Tetramethylgermane adsorbs molecularly on Si(100) at 110 K. In temperature-programmed desorption experiments, most of the tetramethylgermane reversibly desorbs at  $141 \pm 4$  K. The remaining tetramethylgermane decomposes at higher surface temperatures by breaking of a C-Ge bond resulting in the formation of a methyl group and  $Ge(CH_3)_3$ , the latter evolving into the gas phase. Further heating causes decomposition of the methyl group. The hydrogen atoms released by methyl group decomposition form surface Si monohydrides, which later combine to desorb molecular H2. The methyl groups decompose with a pseudo-first-order preexponential of  $(1 \pm 5) \times 10^8$  s<sup>-1</sup> and an activation energy of  $29 \pm 1$  kcal mol<sup>-1</sup>.

## Introduction

The ability to deposit layers with atomic control is of fundamental importance, and there are several methods to form these layers from gas-phase organometallic precursors. These methods include organometallic chemical vapor deposition,<sup>1-3</sup> atomic layer epitaxy,<sup>4-6</sup> and chemical beam epitaxy.<sup>7,8</sup> One system that is receiving considerable attention is the growth of silicon-germanium alloys and heterostructures on Si. The use of heterostructures has been widely exploited in group III-V compounds, but recently heterojunctions compatible with silicon technology are being explored for possible new uses. Silicon-germanium structures are currently being investigated for integrated optoelectronic devices,<sup>9-12</sup> transistors,<sup>13-15</sup> and resonant tunneling diodes.<sup>16-18</sup> We are interested in the surface reactivity of silicon and germanium to gain further insight into the surface processes that may play a role in organometallic chemical vapor deposition of these two elements.

An understanding of the adsorption and decomposition of organic compounds is also important in the study of silicon carbide and diamond film growth. To date, most surface chemistry studies

have dealt with small unsaturated hydrocarbon adsorption on Si.<sup>19-24</sup> Recently, Gutleben and co-workers reported the thermal decomposition of  $CH_3I$  on Si(100) which resulted in the formation of adsorbed methyl groups.<sup>25</sup> The methyl groups were stable to 700 K and decomposed to carbon with hydrogen desorbing into the gas phase at higher temperatures.

In the work presented here we report the low-temperature adsorption results for tetramethylgermane,  $Ge(CH_3)_4$ , on Si(100). The low-temperature adsorption of  $Ge(CH_3)_4$  is studied by ultraviolet photoelectron spectroscopy, Auger electron spectroscopy, and static secondary ion mass spectrometry. The temperature dependence of adsorbed  $Ge(CH_3)_4$  is also examined by temperature-programmed desorption.

## **Experimental Section**

The experiments are carried out in a stainless steel ultrahigh vacuum chamber. The chamber is equipped with a double-pass cylindrical mirror analyzer for Auger electron and photoelectron spectroscopies, a differentially pumped ultraviolet discharge lamp, ion gun, and quadrupole mass spectrometer for both temperature-programmed desorption and secondary ion mass spectrometry. The base pressure of the system is  $4 \times 10^{-11}$  Torr with a typical working pressure of  $1 \times 10^{-10}$  Torr.

Samples are cleaved into  $10 \times 25 \times 0.4$  mm rectangles from two different lots of n-type Si(100) wafers (Virginia Semiconductor,  $\pm 0.25^{\circ}$  of the (100) plane, Sb doped, 5-10 m $\Omega$  cm resistivity) and mounted to a liquid nitrogen cooled manipulator. The sample is held by molybdenum clamps for resistive heating. The silicon surface cleanliness is monitored by Auger electron spectroscopy, ultraviolet photoelectron spectroscopy, and static secondary ion mass spectrometry. The native oxide layer is decomposed by heating to 1225 K in ultrahigh vacuum. The sample is then cooled to 110 K. This procedure left the Si surface free of impurities within the detection limit of Auger electron and ultraviolet photoelectron spectroscopies (impurity level is <6.8  $\times 10^{12}$  cm<sup>-2</sup>). The sample is cleaned by 2-keV Ar<sup>+</sup> sputtering, followed by annealing to 1200 K and rapid cooling to 110 K. This treatment reliably produces a clean Si(100)– $(2 \times 1)$  surface. The sample temperature is monitored by a chromel-alumel thermocouple attached to the back of the sample with Aremco 516 ceramic adhesive.

Ge(CH<sub>3</sub>)<sub>4</sub> (electronics grade, Morton International, Inc.) is further purified by several freeze-pump-thaw degassing cycles, and the purity is carefully monitored by mass spectrometry. Ge(CH<sub>3</sub>)<sub>4</sub> exposures are made through an effusive doser. The flux of Ge(CH<sub>3</sub>)<sub>4</sub> through the doser is sufficient to result in a pressure increase of  $1 \times 10^{-10}$  Torr above the base pressure. The Ge(CH<sub>3</sub>)<sub>4</sub> flux from the effusive doser is not calibrated, and thus all exposures are reported as time exposed. The surface temperature for Ge(CH<sub>3</sub>)<sub>4</sub> exposures is 110 K.

Ultraviolet photoelectron spectra are taken with HeII (40.8 eV) radiation from a He gas discharge lamp, and the analyzer is operated at a fixed pass energy of 20 eV. All the reported binding energies are referenced to the Si valence band edge, which is assigned as 0-eV binding energy.

Temperature-programmed experiments are conducted with a linear temperature ramp of 5.4 K s<sup>-1</sup> with the crystal in lineof-sight of the quadrupole mass spectrometer (nondifferentially pumped). The absolute coverage at saturation for hydrogen on Si(100) near room temperature has been determined using nuclear microanalysis by Feldman and co-workers<sup>26</sup> as 1.5 ML (ML = monolayer, 1 ML =  $6.8 \times 10^{14}$  Si atoms cm<sup>-2</sup>). The temperature-programmed desorption area from a saturation coverage of H atoms is then used as a internal standard for H<sub>2</sub> thermal desorption.

Static secondary ion mass spectrometry measurements are made using a defocused  $Ar^+$  ion beam at 2 keV energy rastered over an area of ~160 mm<sup>2</sup>. The ion current density is typically 12-15 nA cm<sup>-2</sup>.

## **Results and Interpretation**

Characterization of Ge(CH<sub>3</sub>)<sub>4</sub> at Low Temperatures. Figure 1a shows the HeII ultraviolet photoelectron spectrum of the clean Si(100) surface. The low-energy surface states<sup>27</sup> associated with the clean  $(2 \times 1)$  reconstructed surface are observed and can be readily identified. Figure 1b is the ultraviolet photoelectron spectrum of the Si(100) surface exposed to  $Ge(CH_3)_4$  for 300 s at a surface temperature of 110 K. Four distinct features are observed at 4.20, 7.75, 9.60, and 15.60 eV. The clean surface spectrum (Figure 1a) is directly subtracted from Figure 1b, and the difference spectrum is presented as Figure 1c. The four features in Figure 1c are assigned to  $Ge(CH_3)_4$  as follows: 4.20 eV  $(3t_2)$ , 7.75 eV (combination of  $1t_1$  and  $2t_2$ ), 9.60 eV (1e), and 15.60 eV (the C(2s) level). After correction for the vacuum level, these assignments agree well with the gas phase assignments of Jonas and co-workers.<sup>28</sup> The lack of differential shifts when compared with the gas-phase results is indicative of molecular adsorption.

Static secondary ion mass spectrometry can also probe the interaction between  $Ge(CH_3)_4$  and Si at low temperatures. Typical results for a 500-s exposure of  $Ge(CH_3)_4$  to Si are presented in Table I. (For the clean Si surface, only Si-containing secondary



Figure 1. HeII (40.8 eV) ultraviolet photoelectron spectra for (a) the clean Si(100)-(2  $\times$  1) surface, (b) 300-s exposure of (CH<sub>3</sub>)<sub>4</sub>Ge at 110 K, and (c) the difference curve obtained by directly subtracting spectrum a from spectrum b. The molecular orbital assignments are discussed in the text.

TABLE I: Gas-Phase Fragmentation Pattern of Ge(CH<sub>3</sub>)<sub>4</sub> at a Total Pressure of  $1 \times 10^{-7}$  Torr (Ionization Energy 70 eV) and the Secondary Ion Mass Spectrometry (SIMS) Fragmentation Pattern for a 500-s Ge(CH<sub>3</sub>)<sub>4</sub> Exposure to Si(100) at 110 K.

m/z	principle fragment	gas phase	SIMS
15	<sup>12</sup> CH <sub>3</sub> <sup>+</sup>	1.17	123.50
28	<sup>28</sup> Si <sup>+</sup>		313.28
43	SiCH <sub>3</sub> <sup>+</sup>		164.29
58	Si(CH <sub>3</sub> ) <sup>+</sup>		52.13
72	<sup>72</sup> Ge <sup>+</sup>	3.14	3.38
73	$Si(CH_3)_2^+$		156.08
74	$^{74}$ Ge, Si( $^{13}$ CH <sub>3</sub> )( $^{12}$ CH <sub>3</sub> ) <sup>+</sup>	6.06	20.68
87	<sup>72</sup> GeCH <sub>3</sub> +	25.55	18.98
89	<sup>74</sup> GeCH <sub>3</sub> <sup>+</sup>	63.67	43.89
102	$^{72}$ Ge(CH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	1.95	15.85
104	$^{74}\text{Ge}(\text{CH}_{3})_{2}^{+}$	2.23	12.47
117	$^{72}\text{Ge}(\text{CH}_{3})_{3}^{+}$	75.17	77.88
119	$^{74}$ Ge(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup>	100.00	100.00
134	$^{74}\text{Ge}(\text{CH}_{3})_{4}^{+}$	0.07	0.56

ions are detected.) The secondary ion results show that Ge and Si secondary ions containing methyl groups are the strongest signals observed. Also included in Table I is the electron impact ionization fragmentation pattern of gas-phase  $Ge(CH_3)_4$ . The values in Table I are normalized at m/z = 119 to allow for direct comparison of the data. The secondary ion mass spectrometry results and the gas phase fragmentation pattern are similar above m/z = 80. The gas-phase fragmentation pattern also agrees well with the previously published fragmentation pattern of Dibeler.<sup>29</sup> These secondary ion mass spectrometry results are consistent with the photoemission data of Figure 1 and are indicative of molecular adsorption.

**Temperature Dependence.** A series of experiments were conducted in order to determine the various desorption products resulting from the decomposition of  $Ge(CH_3)_4$  during the temperature ramp. The only desorbing products found between m/z = 1 and 150 were  $Ge(CH_3)_4$ ,  $Ge(CH_3)_3$ ,  $CH_3$ , and  $H_2$ . No evidence was observed for the desorption of either  $C_2$  or  $C_3$  hydrocarbon fragments.

The temperature-programmed desorption spectra for various  $Ge(CH_3)_4$  exposures to an initially clean Si(100) surface at 110 K are presented in Figure 2. The <sup>74</sup>Ge(CH<sub>3</sub>)<sub>3</sub> ion, m/z = 119,



Figure 2. Temperature-programmed desorption spectra for  $(CH_3)_4$ Ge exposed to Si(100) at a surface temperature of 110 K. The ion at m/z = 119 was used to monitor  $(CH_3)_4$ Ge as discussed in the text. The temperature ramp rate is 5.4 K s<sup>-1</sup>. The exposure times are (a) 15, (b) 30, (c) 100, (d) 200, (e) 300, and (f) 500 s.

 TABLE II:
 C1 Fragmentation Pattern of the Species Desorbing

 between 145 and 250 K Compared to the Fragmentation Patterns of

 Methyl Radicals<sup>30,31</sup> and Methane (Measured in Our System)

m/z	f(145-250 K) <sup>a</sup>	f(methyl) <sup>b</sup>	f(methyl) <sup>c</sup>	f(methane) <sup>a</sup>
12	0.03	0.03	0.04	0.02
13	0.09	0.10	0.11	0.06
14	0.48	0.54	0.49	0.14
15	1.00	1.00	1.00	0.85
16	0.06			1.00

<sup>a</sup> This work. <sup>b</sup> Reference 30. <sup>c</sup> Reference 31.

is used to monitor the desorption of  $Ge(CH_3)_4$ . The masses corresponding to <sup>74</sup>Ge(CH<sub>3</sub>)<sub>2</sub> and <sup>74</sup>Ge(CH<sub>3</sub>) are also monitored at the same time. The ratio of the desorption signals is determined and compared to the electron impact fragmentation pattern to ensure that a single species is desorbing. Two thermal desorption peaks are observed. The low-temperature peak occurs at 141 ± 4 K, is present at the smallest exposures, increases as the exposure time increases, and does not saturate. This low-temperature peak is attributed to reversibly adsorbed Ge(CH<sub>3</sub>)<sub>4</sub>. A second, smaller peak is observed over a broad temperature range between 200 and 300 K. This peak shifts to lower temperatures with increasing exposure and saturates for exposures  $\geq 500s$ .

Figure 3 is a typical temperature-programmed desorption spectrum for a 150-s exposure of  $Ge(CH_3)_4$ . Curve 3a is the  $^{74}$ Ge(CH<sub>3</sub>)<sub>3</sub><sup>+</sup> cracking fragment of Ge(CH<sub>3</sub>)<sub>4</sub> and exhibits two peaks at 141 and 270 K. The high-temperature  $Ge(CH_3)_4$  state at 270 K is multiplied by a factor of 10 and is shown as Figure 3b. Figure 3c is the m/z = 15 signal multiplied by a factor of 6. Desorption of m/z = 15 is observed over a wide temperature range (130 to  $\sim$  500 K). A careful analysis of the fragmentation pattern at m/z = 12, 13, 14, 15, and 16 during desorption reveals that the low-temperature portion of this desorption state (130-145 K) is due to the fragmentation of  $Ge(CH_3)_4$  in the ionizer of the mass spectrometer. Between 145 and 250 K, the fragmentation pattern changes. Table II summarizes the C<sub>1</sub> fragmentation pattern after subtraction of the  $Ge(CH_3)_4$  contribution in the low temperature state (13C effects are neglected). Also shown in Table II are the previously measured fragmentation pattern for methyl radicals, from the gas-phase pyrolytic decomposition of tetra-



Figure 3. Temperature-programmed desorption spectra for two different masses for a 150-s exposure of  $(CH_3)_4$ Ge to Si(100). The surface temperature was 110 K, and the temperature ramp rate was 5.4 K s<sup>-1</sup>. (a) Temperature dependence of the m/z = 119 ion. (b) High-temperature state of the m/z = 119 ion amplified by a factor of 10. (c) Temperature dependence of the m/z = 15 ion amplified by a factor of 6 with respect to curve a.

methyllead by Osberghaus and Tauber,<sup>30</sup> and the fragmentation pattern for methane measured in our system. Recently, Creighton<sup>31</sup> also observed the desorption of methyl radicals from the decomposition of trimethylgallium on GaAs(100), and these data are included in Table II. The observed fragmentation pattern between 145 and 250 K agrees well with the previously published results for methyl radicals. Above 250 K, the m/z = 15 signal decays slowly, and this may be due to pumping effects inside the mass spectrometer ionization region.

The species desorbing in the state between 200 and 300 K (Figure 3b) is less clear. The mass fragmentation pattern of the desorbing species is similar to that of the low-temperature Ge- $(CH_3)_4$  state with one difference. The difference is in the  $C_1$  fragmentation region. The  $C_1$  fragment region is less intense compared to that observed for Ge(CH<sub>3</sub>)<sub>4</sub>. This can be observed directly in Figure 3 where the m/z = 15 (Figure 3c) signal is not following the m/z = 119 (Figure 3b) signal between 200 and 350 K at the same ratio as in the 145. K desorption state. Mass balance considerations force us to consider a different species to be desorbing in the temperature range 200-300 K, and this is discussed further below. Auger spectra taken after completion of the temperature-programmed desorption experiments show that carbon is the only remaining surface species from Ge(CH<sub>3</sub>)<sub>4</sub> decomposition. No Ge Auger signal is observed.

Above 500 K,  $H_2$  is the only desorbing species observed. The hydrogen desorption peak is centered near 800 K (see Figure 5a).

A second set of experiments to consider the role of vacancy defects on the Si(100) surface is also considered. The clean Si(100) surface is exposed to Si<sub>2</sub>H<sub>6</sub> at an apparent pressure of  $5 \times 10^{-8}$  Torr through an effusive doser at a surface temperature of 1000 K for various periods of time. This procedure will deposit Si onto to the surface in an epitaxial manner and lower the vacancy defect density. The Si<sub>2</sub>H<sub>6</sub> flow is shut off after a period of time, and the sample is then annealed at 1200 K. No difference in Ge(CH<sub>3</sub>)<sub>4</sub> adsorption and decomposition is observed for samples prepared in this fashion versus those prepared by sputtering and annealing as outlined in the Experimental Section. This is interpreted as vacancy defects having a negligible effect on the observed surface phenomena reported here.



Figure 4. HeII (40.8 eV) ultraviolet photoelectron spectra of a 150-s exposure of  $(CH_3)_4$ Ge to Si(100) at an initial surface temperature of 110 K and then annealed to higher temperatures. (a) Clean Si(100) surface before the exposure. (b)  $(CH_3)_4$ Ge exposure surface at 110 K, (c) annealed to 150 K, (d) annealed to 250 K, and (d) annealed to 350 K.

Ultraviolet photoelectron spectra as a function of temperature for a 150-s  $Ge(CH_3)_4$  exposure to Si(100) are presented in Figure 4. The spectrum of the clean surface (Figure 4a) is included for reference. In this series of experiments,  $Ge(CH_3)_4$  is adsorbed at 110 K (Figure 4b), annealed to a predetermined temperature, and the ultraviolet photoelectron spectrum is then recorded. Figure 4b is the ultraviolet photoelectron spectrum of the  $Ge(CH_3)_4$ covered surface at 110 K. Heating to 150 K (Figure 4c) desorbs the low-temperature molecular  $Ge(CH_3)_4$  state. The four features due to molecular  $Ge(CH_3)_4$  are still observed; only the intensity has diminished. Increasing the annealing temperature to 250 K (Figure 4d) results in the removal of the  $3t_2$  and 1e molecular orbitals and in a lower intensity of the C(2s) level. The peak that contains 1t<sub>1</sub> and 2t<sub>2</sub> molecular orbitals has now broadened in energy, and the center of the peak is shifted 0.40 eV toward lower binding energies. Heating the surface to 350 K (Figure 4e) results in the removal of the molecular orbitals due to  $Ge(CH_3)_4$ . There is a small amount of intensity due to C at 15.6 eV and a broad feature centered at 7.15 eV. Static secondary ion mass spectra of the surface, taken immediately after the photoemission experiment, indicate the presence of carbon and hydrogen and the secondary ion mass fragmentation pattern is consistent with that of adsorbed methyl groups.

Surface Reaction Kinetics. Static secondary ion mass spectrometry is employed to monitor the surface decomposition of methyl groups and the desorption of hydrogen from the silicon surface. The  $CH_3^+$  secondary ion is used as a monitor of methyl groups on the Si surface. The  $CH_3^+$  signal is followed as a function of  $Ge(CH_3)_4$  coverage, and the signal intensity increases linearly with exposure. The H<sup>+</sup> secondary ion is used to monitor hydrogen on the Si surface and also is a linear function of  $Ge(CH_3)_4$  coverage.

The secondary ion signal is followed as the surface temperature is changed for a given  $Ge(CH_3)_4$  exposure. Some of these temperature-programmed static secondary ion mass spectrometry results are presented in Figure 5. In Figure 5a, the H<sub>2</sub> thermal desorption for a 150-s exposure of  $Ge(CH_3)_4$  is shown. The thermal desorption peak exhibits a single desorption state near 800 K. This desorption state has been previously attributed to the decomposition of SiH(a) groups on the Si surface.<sup>32-36</sup> Curves 5b and 5c are the temperature-programmed secondary ion signals



Figure 5. Superposition of temperature-programmed secondary ion mass spectrometry data and temperature-programmed desorption data for a 150-s  $(CH_3)_4$ Ge exposure at 110 K. (a) H<sub>2</sub> thermal desorption signal from the decomposition of  $(CH_3)_4$ Ge. (b)  $CH_3^+$  and (c) H<sup>+</sup> secondary ion signals as a function of temperature from the decomposition of  $(CH_3)_4$ Ge on Si(100).

for  $CH_3^+$  and  $H^+$ , respectively.

The CH<sub>3</sub><sup>+</sup> temperature-programmed secondary ion signal (Figure 5b) is multiplied by a factor of 10 relative to the H<sup>+</sup> secondary ion intensity. The CH<sub>3</sub><sup>+</sup> signal is constant from 100 to 125 K and then decreases sharply (not shown in the figure). The decrease occurs as Ge(CH<sub>3</sub>)<sub>4</sub> desorbs in the low-temperature desorption state. Between 150 and 525 K, the CH<sub>3</sub><sup>+</sup> signal is slowly decaying. Above 525 K, the CH<sub>3</sub><sup>+</sup> signal sharply drops and is gone by 750 K. No desorption products are observed between 525 and 700 K during thermal desorption experiments.

The H<sup>+</sup> temperature-programmed secondary ion signal is also constant between 110 and 125 K, before the desorption of Ge- $(CH_3)_4$  (not shown in Figure 5) at 141 K. The H<sup>+</sup> signal drops quickly during the desorption of  $Ge(CH_3)_4$  and the signal continues to gradually decrease up to  $\sim$  500 K. The slowly decreasing H<sup>+</sup> (and  $CH_3^+$ ) signal(s) is consistent with the slow desorption of methyl radicals observed over the temperature range 150-500 K (see Figure 3). Above 525 K, the H<sup>+</sup> signal increases sharply and reaches a maximum by 700 K. This is the temperature range during which the  $CH_3^+$  secondary ion signal is dropping rapidly. We interpret the increase in H<sup>+</sup> intensity due to the decomposition of methyl groups on the Si surface and the formation of SiH groups. The H<sup>+</sup> signal decreases rapidly above 700 K and desorption of  $H_2$  from the surface in observed (Figure 5a). By 900 K, the H<sup>+</sup> signal is zero. The rapid decrease in the H<sup>+</sup> secondary ion signal above 700 K is due to the decomposition of the SiH groups. Similar behavior has been observed previously for the decomposition of SiH groups on Si(100).<sup>28</sup>

Kinetic information for the decomposition of the CH<sub>3</sub> and SiH groups is obtained from the shape and magnitude of the temperature-programmed secondary ion signals.<sup>37-38</sup> The H<sup>+</sup> temperature-programmed secondary ion signal from Figure 5 is reproduced as Figure 6a. Overlaying the H<sup>+</sup> signal (Figure 6b) is the kinetic fit to the data using the method of Zhou and White.<sup>38</sup> Between 525 and 700 K, the increase in the H<sup>+</sup> signal is best described by an activation energy of  $29 \pm 1$  kcal mol<sup>-1</sup> and a preexponential factor of  $(1 \pm 5) \times 10^8$  s<sup>-1</sup>. The decrease in signal above 700 K is governed by an activation energy of  $48 \pm 1$  kcal mol<sup>-1</sup> and a preexponential factor of  $(5 \pm 5) \times 10^{11}$  s<sup>-1</sup>. The error bars in the measurement are the standard deviation of four or five



Figure 6. (a) H<sup>+</sup> temperature-programmed secondary ion signal from a 150-s (CH<sub>3</sub>)<sub>4</sub>Ge exposure. (b) Kinetic fit to the experimental curve as discussed in the text for the formation of SiH(a) by the decomposition of methyl groups;  $E_f = 29$  kcal mol<sup>-1</sup>,  $\nu = 1 \times 10^8 \text{ s}^{-1}$ . Kinetic fits for the decomposition of SiH: (c)  $E_d = 47$  kcal mol<sup>-1</sup>,  $\nu = 1 \times 10^{12} \text{ s}^{-1}$ , (d)  $E_d = 48.5$  kcal mol<sup>-1</sup>,  $\nu = 6 \times 10^{11} \text{ s}^{-1}$ , and (e)  $E_d = 49$  kcal mol<sup>-1</sup>,  $\nu = 1 \times 10^{11} \text{ s}^{-1}$ .

TABLE III: First-Order Kinetic Parameters for the Decomposition of CH<sub>3</sub> and SiH on Si(100)

system	secondary ion	coverage, ML	$E_{\rm a}$ , kcal mol <sup>-1</sup>	$\nu, s^{-1}$
CH3	CH <sub>3</sub> <sup>+</sup> H <sup>+</sup>	0.06-0.10	$28 \pm 2$ 29 \pm 1	$1 \times 10^{8\pm 1}$ (1 ± 5) × 10 <sup>8</sup>
SiH LIDª	H+	0.18-0.28	$48 \pm 1$ 45 ± 2	$(5 \pm 5) \times 10^{11}$ 2.2 × 10 <sup>11</sup>

<sup>a</sup>Reference 34.

replicate experiments at each coverage studied that are then averaged together. A least-squares error analysis of the curve fit to the data yields a deviation that is less than the abovementioned error bars.

The kinetic parameters for the decomposition of the methyl and SiH groups are summarized in Table III. Shown in Table III are the average values for the decomposition of SiH, as measured by secondary ion mass spectrometry, and these values are compared with the laser-induced desorption results of Sinniah et al.<sup>34</sup> The secondary ion mass spectrometry and laser-induced desorption results yield the same kinetic parameters within experimental error. The H<sub>2</sub> thermal desorption area for a given exposure is used to determine the coverage of SiH groups decomposing. The coverage accessible by our system is  $\theta = 0.18-0.28$  SiH groups/first layer Si atom. The kinetic parameters are constant within experimental error over the coverages studied.

The decomposition of the methyl groups is monitored by the decrease of the m/z = 15 and by the increase in the m/z = 1 signal. The kinetic analysis using either secondary ion signal yield the same activation energies and preexponential factors as indicated in Table III. The coverage of methyl groups was obtained by assuming that each methyl groups yielded three hydrogen atoms in the H<sub>2</sub> thermal desorption peak at 800 K (Figure 5).

#### Discussion

The Si(100)- $(2 \times 1)$  surface is a reconstructed surface in which Si surface atoms form dimers with a dangling bond on each of the Si atoms in the dimer pair.<sup>39</sup> This unique bonding configuration gives rise to an intrinsic surface state in ultraviolet photoelectron spectroscopy. The surface state is at 0.80-eV binding energy for our samples. Adsorption of  $Ge(CH_3)_4$  at 110 K did not quickly quench the surface state. The intensity of the surface decreased with increasing exposure, and the ultraviolet photoelectron results reveal that the  $Ge(CH_3)_4$  molecule adsorbs molecularly on Si(100) at 110 K. This is consistent with the majority of  $Ge(CH_3)_4$  molecules condensing on the Si surface without preferential adsorption at Si dangling bonds. Preferential adsorption at the dangling bond sites would have shown a rapid decrease in surface state intensity with increasing  $Ge(CH_3)_4$  exposure. The condensation of  $Ge(CH_3)_4$  on the Si surface is also consistent with temperature programmed desorption experiments, as evidenced by the low-temperature reversible desorption state for  $Ge(CH_3)_4$ .

A fraction (15% as estimated by thermal desorption) of the  $Ge(CH_3)_4$  is irreversibly adsorbed. All Ge-containing products desorb in either the low-temperature peak centered at 141 K or in the broad desorption state at 250 K. No Ge was found on the surface by Auger electron spectroscopy after the temperature ramp. Above 140 K, at least one Ge-C bond is broken to generate methyl radicals. Some of the methyl radical desorb directly into the gas phase. A fraction of the radicals stay adsorbed on the surface. Quantification of the amount of decomposing Ge(CH<sub>3</sub>)<sub>4</sub> is difficult by temperature-programmed desorption. If one takes into account the desorption of methyl radicals and the change in the fragmentation pattern during the desorption state between 145 and 250 K, a second Ge-containing species must be desorbing. The species must have a fragmentation pattern similar to that of  $Ge(CH_3)_4$  for the Ge-containing portion of the fragmentation pattern to be consistent with the data. One possible desorption product is  $Ge(CH_3)_3$ . The gas-phase electron impact fragmentation pattern of  $Ge(CH_3)_3$  has not been measured; however, the fragmentation pattern is expected to be similar to that of Ge(C- $H_3$ )<sub>4</sub>. This proposed surface reaction would also account for the loss of methyl from  $Ge(CH_3)_4$  to the gas phase and to the surface.

The concentration of surface methyl groups is not dependent on the number of vacancy defects on Si(100) as determined by the experiments on epitaxially grown Si surfaces. In this set of experiments, where the defect density should be lower, no difference is observed between the sputtered-annealed surface or the epitaxial Si surface. This means that the branching ratio for methyl chemisorption versus methyl desorption should then be governed by the number of available chemisorption sites. This suggests that methyl desorption should be favored at high initial Ge(CH<sub>3</sub>)<sub>4</sub> coverages over methyl chemisorption. The data qualitatively support this hypothesis as the coverage of methyl groups on Si(100) saturates quickly with Ge(CH<sub>3</sub>)<sub>4</sub> exposure and is constant for the largest exposures.

The adsorbed methyl groups are stable to  $\sim 600$  K. The decomposition of the methyl group yields C(a) and 3 H(a). The hydrogen atoms recombine at higher temperatures and desorb as molecular H<sub>2</sub> near 800 K and carbon remains on the surface. It is interesting to compare the decomposition of methyl here with the recent results of Gutleben et al.<sup>25</sup> In Gutleben's work, CH<sub>3</sub>I was used as a source of methyl groups on Si(100)–(2 × 1). CH<sub>3</sub>I was found to thermally dissociate to I(a) and  $CH_3(a)$ . The  $CH_3$ group was stable to near 700 K. This is 100 K higher than what is measured here. One possible explanation is that in our study, at 600 K, methyl is the only surface species present. In Gutleben's study iodine atoms are coadsorbed with the methyl groups. The iodine atoms may serve to block sites for methyl decomposition. Indeed, CH<sub>3</sub> decomposition was not observed until I(a) was thermally removed from the surface above 700 K. Thus, the presence of the coadsorbate stabilizes the CH3 group. In our case, the methyl coverage is relatively low (0.06-0.10 ML), and it is the only surface species present. So there are a number of open Si surface sites available to facilitate CH<sub>3</sub> decomposition.

It is also interesting to consider the origin of the low preexponential factor obtained for CH<sub>3</sub> decomposition  $((1 \pm 5) \times 10^8 \text{ s}^{-1})$ . This preexponential is well below the "normal" value of  $10^{13} \text{ s}^{-1}$  often attributed to simple first-order processes. Consider the following two-step reaction

$$CH_3(a) \xleftarrow{k_1}{k_{-1}} CH_3^*(a)$$
(1)

$$CH_3^*(a) \xrightarrow{k_2} C(a) + 3 H(a)$$
 (2)

In eq 1 species  $CH_3(a)$  reacts to form  $CH_3^*(a)$ . This equation is written as an equilibrium and can be thought of as a diffusional step where  $CH_3(a)$  diffuses to the orientation (or site) needed for eq 2 to occur. Equation 2 is the decomposition reaction of CH<sub>3</sub>\* to the final products. Since we detect only SiH during our experiments, we believe eq 2 to be applicable. However, if CH<sub>3</sub>\* decomposes by sequential loss of H, then only the overall rate of eq 2 is important. As long as the overall rate of eq 2 is faster than that of eq 1, the conclusion reached below is not affected by either mechanism of CH<sub>3</sub>\* decomposition. At steady state the rate of eq 2 is given by

$$R_2 = [k_2 k_1 / (k_2 + k_{-1})] \Theta_{\rm CH_3^*}$$
(3)

Equation 3 clearly contains preexponentials and activation energies from more than one elementary reaction step. Because preexponential factors for surface diffusion processes are typically small, the anticipated effect of  $k_1$  in eq 3 is an overall preexponential factor well below 10<sup>13</sup> s<sup>-1</sup>.

#### Conclusions

The significant results of this work may be summarized as follows:  $Ge(CH_3)_4$  adsorbs molecularly on Si(100)-(2 × 1) at 110 K. Decomposition of Ge(CH<sub>3</sub>)<sub>4</sub> begins at low temperature with the evolution of methyl radicals into the gas phase between 145 and 250 K. All Ge-containing species desorb from the surface by 325 K with only methyl groups remaining on the Si surface. The surface methyl groups decompose with an activation energy of 29 kcal mol<sup>-1</sup> and represent, to our knowledge, the first kinetic measurements of methyl decomposition on Si(100).

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