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# GeH<sub>x</sub> (x = 0-3) and Ge<sub>n</sub>H<sub>x</sub> (n = 2-7) in flash pyrolysis of GeH<sub>4</sub>

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#### Abstract

Gas-phase thermal decomposition of germane, GeH<sub>4</sub>, has been studied using a flash pyrolysis technique (~ 20 µs reaction time), coupled with a vacuum-ultraviolet (VUV) photoionization time-of-flight mass spectrometer (TOFMS). Pyrolysis temperatures ranged from 685 to 1500 K, and resulted in the formation of GeH<sub>2</sub> above 900 K and GeH<sub>x</sub> (x = 0, 1, 3) above 1100 K. In addition, Ge<sub>n</sub> (n = 2-7) and a small amount of highly unsaturated hydrogenated Ge<sub>n</sub>H<sub>x</sub> (n = 2-7) clusters were observed above 1100 K. © 2002 Elsevier Science B.V. All rights reserved.

#### 1. Introduction

GeH<sub>4</sub> is an important precursor in chemical vapor deposition (CVD) of  $Si_{1-x}Ge_x$  thin films. Due to their improved thin-film transistor (TFT) characteristics over Si films and the lower thermal budget for their deposition, the polycrystalline  $Si_{1-x}Ge_x$  alloys (poly-SiGe) are a promising replacement for poly-Si in heterojunction bipolar transistors, MOSFETs, and pixel drives for active matrix liquid crystal displays (AMLCD) [1].

While many CVD processes of  $Si_{1-x}Ge_x$  film growth are carried out under high to ultra-high vacuum (UHV) conditions [2–6] which are costly and limit production, reduced pressure [1,7–10] and atmospheric CVD have also been studied [11,12]. UHV deposition essentially eliminates the contribution of gas-phase reactions and can be considered exclusively a surface process, while in higher-pressure deposition processes ( $10^{-5}$  Torr to 1 atm), gas-phase reactions must be taken into consideration.

The morphology, Si and Ge content, particle size and smoothness [13], and free carrier mobilities [6,14] of Si<sub>1-x</sub>Ge<sub>x</sub> (amorphous and polycrystalline) films grown using SiH<sub>4</sub> or Si<sub>2</sub>H<sub>6</sub> and GeH<sub>4</sub> precursors have been well characterized at low Ge levels (x < 0.35). The growth mechanisms involved, however, are not well understood. In low temperature film deposition (T = 400-600 °C), growth rates increased with increasing GeH<sub>4</sub> partial pressure, which was attributed to the lower activation energy of hydrogen desorption from Ge surface sites versus Si sites [15]. In this temperature regime, the increase in the Ge:Si ratio did not increase linearly with the increase in GeH<sub>4</sub> : SiH<sub>4</sub>

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		This work <sup>a</sup>	Das <sup>b</sup>	Ruscic <sup>c</sup>	Newman <sup>d</sup>	Botintsev <sup>e</sup>
$GeH_4 \rightarrow GeH_2 + H_2$	$\Delta H_0$	36.0		≥ 35.1		
	$E_{\rm a}$				50-54.3	$52.1\pm3.1$
$GeH_2 \rightarrow Ge + H_2$	$\Delta H_0$	28.2		$\leq 28.9(26.4)$	$17.5\pm10$	≥ 15.5
	$E_{\rm a}$					≤ 35.1
$GeH_4\rightarrowGeH_3+H$	$\Delta H_0$	83.1	85.2	$< 85.5(82 \pm 2)$		$87.0\pm5.0$
$GeH_3 \rightarrow GeH + H_2$	$\Delta H_0$	21.6		≤ 31.4		
$GeH_3  \rightarrow  GeH_2 + H$	$\Delta H_0$	56.6	56.9	> 56.4(59)		
$GeH_2\rightarrowGeH+H$	$\Delta H_0$	68.7	69.2	< 68.9(66)	$45\pm10$	$44.5\pm6.5$
$GeH\rightarrowGe+H$	$\Delta H_0$	63.2	63.2	> 53.7(63)		

Table 1 Heats of reaction,  $\Delta H_0$ , and activation energies,  $E_a$ , for thermal decomposition reactions of germane

All values are in kcal/mol.

<sup>a</sup>  $\Delta H_0$  (0 K) values are calculated at G3 level of theory with geometries and zero-point energies (ZPEs) at QCISD/cc-pvTZ level of theory. See [25] for more information of G3 theory and calculations.

<sup>b</sup> Ref. [27]. No ZPE correction.

<sup>c</sup> Ref. [22]. More probable values are in parentheses.

<sup>d</sup> Ref. [20].

<sup>e</sup> Ref. [21].

ratio. Instead, the Ge:Si ratio leveled off and amorphous  $Si_{1-x}Ge_x$  films were limited to  $x < \sim 0.35$ . The growth rate was not limited by adsorption of growth species, and was instead attributed to other factors such as surface nucleation or gas-phase kinetics [15,16].

Understanding homogeneous thermal decomposition of the precursors may help explain the limitations of amorphous  $Si_{1-x}Ge_x$  growth and allow for increased Ge incorporation into amorphous  $Si_{1-x}Ge_x$  films. The flash pyrolysis technique is able to isolate and detect the initial reactive intermediates and primary pyrolysis products formed upon gas-phase thermal decomposition [17–19], thus revealing the mechanisms involved in pyrolysis of the precursors.

The homogeneous thermal decompositions of  $SiH_4$  and  $Si_2H_6$  have been studied extensively. Our recent experimental work on thermal decomposition pathways for silane and disilane have confirmed the following initiation steps [19]:

$$SiH_4 \rightarrow SiH_2 + H_2$$
 (1)

 $Si_2H_6 \rightarrow SiH_4 + SiH_2$  (2)

$$Si_2H_6 \rightarrow Si_2H_4 + H_2$$
 (3)

The thermal decomposition of  $GeH_4$  has been studied experimentally [20,21], and similar initial dissociation mechanisms have been proposed:

$$GeH_4 \rightarrow GeH_2 + H_2$$
 (4)

$$GeH_2 \rightarrow Ge + H_2$$
 (5)

The activation energy of reaction (4) has been determined to be 50–54 kcal/mol, while H atom loss from GeH<sub>4</sub> was considered unlikely due to the large H<sub>3</sub>Ge–H bond dissociation energy of  $82 \pm 2$  kcal/mol [20–22]. Energetics of the relevant reactions are listed in Table 1 and shown in Fig. 1.

In this Letter, direct experimental evidence of the formation of  $\text{GeH}_2$  at T > 900 K and  $\text{GeH}_x$ 



Fig. 1. Energy diagram for the homogeneous thermal decomposition of GeH<sub>4</sub>. Energies are those calculated in this work. Indicated activation energies,  $E_a$ , are from [21]. See Table 1 for more details.

(x = 0, 1, 3) species at T > 1100 K is presented. These results are in good qualitative agreement with the literature. Also reported here is the first observation of production of gas-phase Ge<sub>n</sub> (n = 2-7) and highly unsaturated hydrogenated Ge<sub>n</sub>H<sub>x</sub> (n = 2-7) clusters in GeH<sub>4</sub> pyrolysis above T = 1100K. In general, the thermal decomposition and small cluster growth involved in pyrolysis of GeH<sub>4</sub> behave similarly to those of silane and disilane.

#### 2. Experimental

The pyrolysis experiment and the experimential setup have been described previously [17–19]. The pyrolysis nozzle was based on that of Chen and coworkers [17]. Flash pyrolysis was carried out by flowing a gas mixture of 1% germane (99.997+%, Aldrich Chemicals) in argon at a total backing pressure of 1.3 atm through a short, heated SiC tube (10 mm heated length, 2 mm o.d., 1 mm i.d., Carborundum). The residence time of the gas species in the heated zone of the SiC tube was on the order of  $\sim 20 \ \mu s$  [17]. The precursor and thermal decomposition products exited the heated tube and supersonically expanded into the vacuum chamber (held at  $< 5 \times 10^{-4}$  Torr with the molecular beam on), and then passed through a skimmer into the photoionization region of a Wiley-McLaren type linear time-of-flight mass spectrometer (TOFMS) [18,19,23]. The pyrolysis products were ionized by single VUV photon ionization at  $\lambda = 118.2$  nm (10.49 eV). TOF mass spectra were recorded on a multi-channel scaler (EG&G, Turbo-MCS), and were accumulated with 2000 laser shots. The 118.2 nm radiation was produced by frequency tripling the 355 nm output from an Nd:YAG laser in a Xe cell. The VUV radiation was focused by an MgF<sub>2</sub> lens through a small aperture into the photoionization zone, while the fundamental 355 nm UV beam diverged in this region, thereby minimizing multi-photon ionization (MPI) and the amount of UV radiation scattered in the ionization zone. When the tripling medium was removed, no ion signal was observed at all pyrolysis temperatures, indicating negligible MPI or secondary electron-impact ionization (EI) from the fundamental UV radiation.

#### 3. Results and discussion

Ionization potentials (IPs) of Ge and  $GeH_n$ (n=2-4) have been determined experimentally [22,24]. The adiabatic IP of GeH<sub>4</sub> is  $\leq 10.53$  eV, slightly above the 10.49 eV available from the VUV source, thus the cold GeH<sub>4</sub> in the molecular beam should not be detectable by 118.2 nm VUV photoionization. The experimental IPs for Ge, GeH<sub>2</sub>, and GeH<sub>3</sub> are 7.90, 9.25, and 7.94 eV, respectively. The IP of GeH was calculated by using CCSD(T,Full)/avg-cc-pvTZ//QCISD//cc-pvTZ+ ZPE//QCISD/cc-pvTZ method [25], and was determined to be 7.71 eV, close to previous theoretical values [26,27]. Thus, all GeH<sub>x</sub> (x = 0-3) species can be ionized by a single photon at 118.2 nm. The appearance energies of  $Ge^+$  (with  $2H_2$ ),  $GeH^+$ (with  $H_2 + H$ ),  $GeH_2^+$  (with  $H_2$ ), and  $GeH_3^+$  (with H) from ionization fragmentation of GeH<sub>4</sub> are 10.7, 11.3, 10.8, and 10.8 eV, respectively [22,28]. Thus, photoionization fragmentation of GeH<sub>4</sub> should not occur at 10.49 eV (118.2 nm). Note that the appearance energy of  $GeH^+$  (with  $H_2$ ) from ionization fragmentation of GeH<sub>3</sub> radical is  $\leq 9.0 \text{ eV}$  [22].

The results of GeH<sub>4</sub> pyrolysis and germanium cluster production are shown in Figs. 2–4. The small peaks between m/e 70 and m/e 76 at low pyrolysis temperatures are attributed to a minor



Fig. 2. Mass spectra of pyrolysis of germane (1% in Ar) between 685 and 1500 K, detected using 10.49 eV photoionization/TOFMS. Baselines of the mass spectra are offset for clarity.



Fig. 3. Enlarged view of mass spectra for pyrolysis of germane (685-1500 K) for the monomer. The mass spectra are offset for clarity.



Fig. 4. Enlarged view of mass spectra for  $\text{Ge}_n\text{H}_x$  (n=2-7) formation upon flash pyrolysis of germane (1% in Ar) between 1160 and 1500 K. Baselines of the TOF mass spectra are offset for clarity.

amount of EI of GeH<sub>4</sub> precursors (discussed below), and these peaks remain nearly constant up to 800 K. Above 900 K, the peaks between m/e 70 and 79 begin to grow, and steadily increase up to T=1500 K, indicating thermal decomposition of GeH<sub>4</sub> (Fig. 3). Contributions to these mass peaks from each GeH<sub>x</sub> (x=0-3) species are deconvoluted by the method discussed below. In addition, Ge<sub>n</sub> and Ge<sub>n</sub>H<sub>x</sub> (n=2-7) clusters are produced above  $T \sim 1100$  K, as indicated by the higher mass peaks between 140 and 550 (Fig. 4).

The small mass peaks at m/e 70–76 present below 800 K, before significant thermal decomposition takes place in the  $\sim 20 \ \mu s$  time scale, are due to a minor amount of EI and/or photoionization fragmentation of the GeH<sub>4</sub> precursors. The EI is caused by a small number of photoelectrons resulting from scattered light in the photoionization region. Every effort has been made to minimize the contribution from EI, such as by minimizing the 118.2 nm spot size and by masking the photoionization region from 355 nm radiation, but it cannot be eliminated completely without losing the photoionization signal as well. A mass spectrum for the EI fragmentation pattern of GeH<sub>4</sub> was modeled by using the monoisotopic EI mass spectrum of GeH<sub>4</sub> [28,29] and the relative Ge isotopic abundances. The calculated spectrum, however, is not similar to our observed mass spectra below 800 K. This might be due to different temperatures of GeH<sub>4</sub> and electron-energy-dependent EI fragmentation [30,31] (with a range of electron energy from 0 to 300 eV and a most probable energy of 150 eV due to the location of the molecular beam in this experiment). Alternatively, photoionization fragmentation of GeH<sub>4</sub> by both the VUV and the fundamental UV photons (at a total photon energy  $\sim 14 \text{ eV}$ ) could occur, although the mass pattern modeled based on photoionization efficiency curves of GeH<sub>4</sub> [22] is different from the observed as well.

The contribution from EI and/or photoionization fragmentation, which is small and constant up to 800 K, is subtracted out as described below. If the extent of EI is assumed to be nearly constant at all pyrolysis temperatures (i.e., the products and precursors were efficiently cooled upon supersonic expansion), the mass spectra at low pyrolysis temperatures ( $T \leq 800$  K, before significant thermal dissociation) can be used as a baseline and subtracted from the higher temperature spectra to eliminate the EI contribution. If supersonic cooling is less efficient, ion fragmentation would be expected to increase with temperature as the internal energy of the products increases. If this were the case, the resulting peaks, after background subtraction, would represent the upper limit to

photoionization products. However, it is generally believed that the supersonic cooling is efficient and the temperature of the molecular beam is  $\leq 100$  K [17]. This is largely consistent with the nearly constant peak intensities up to T = 800 K.

Experimentally, evaluating the pyrolysis products of germane is more complicated than silane due to the existence of five stable isotopes of germanium with similar isotopic abundances: <sup>70</sup>Ge  $(20.5\%), {}^{72}\text{Ge} (27.4\%), {}^{73}\text{Ge} (7.8\%), {}^{74}\text{Ge} (36.5\%),$ and  $^{76}$ Ge (7.8%), while silicon is primarily present as <sup>28</sup>Si (~ 92%). Mass peaks in the TOF mass spectra are first fitted with Gaussian peaks in order to determine the experimental intensities of each mass peak, and the baseline contributions from EI fragmentation are removed. The contributions of the GeH<sub>x</sub> (x = 0-3) products are then deconvoluted in a process using the relative abundances of Ge isotopes. As the m/e 70 peak is exclusively due to <sup>70</sup>Ge, the contributions of <sup>72</sup>Ge, <sup>73</sup>Ge, <sup>74</sup>Ge, and <sup>76</sup>Ge to m/e 72, 73, 74, and 76 peaks can be calculated from the m/e 70 peak using isotope abundances. Similarly, the contributions of GeH species can be calculated using m/e 71, which is exclusively <sup>70</sup>GeH, and isotope abundances. The Ge and GeH components are then subtracted from the experimental peaks, leaving the contributions from GeH<sub>2</sub> and GeH<sub>3</sub>. The remaining intensity at m/e 72 is exclusively due to <sup>70</sup>GeH<sub>2</sub>, which can be used to determine all isotope contributions of GeH<sub>2</sub>. Another iteration of this process effectively separates the contributions of all GeH<sub>x</sub> (x = 0-3) species to the experimental spectra. A similar deconvolution process is performed by starting with m/e peaks 78 and 79, which result from <sup>76</sup>GeH<sub>2</sub> (with no or little contribution from parent  $^{74}$ GeH<sub>4</sub>) and <sup>76</sup>GeH<sub>3</sub> exclusively. The results from both calculations are in reasonable agreement, and the

average values are listed in Table 2. As absolute photoionization cross-sections of the various  $\text{GeH}_x$  (x = 0-3) species at 118.2 nm are not known, no correction is made for the photoionization efficiencies. Nevertheless, the deconvolution results starting from Ge and GeH and from GeH<sub>2</sub> and GeH<sub>3</sub> are similar, implying that this correction is not very significant.

At 900 K, the initial pyrolysis products are GeH<sub>2</sub> and H<sub>2</sub> (reaction (4)). At ~ 1100 K, Ge is formed as per reaction (5), and it becomes the predominant product at 1500 K. The large increase of Ge implies efficient subsequent decomposition of GeH<sub>2</sub> to Ge and H<sub>2</sub> [although an intersystem crossing is needed in going from GeH<sub>2</sub>( $\tilde{X}^1A_1$ ) to Ge(<sup>3</sup>P)]. These two steps are the lowest energy pathway to Ge product (Table 1 and Fig. 1). Also above ~ 1100 K, the higher energy channel is identified

$$GeH_4 \rightarrow GeH_3 + H$$
 (6)

A small amount of GeH product is also observed above  $\sim 1100$  K, presumably due to:

$$GeH_2 \rightarrow GeH + H$$
 (7)

$$GeH_3 \rightarrow GeH + H_2$$
 (8)

Some GeH<sup>+</sup> ions could be produced from photoionization fragmentation of GeH<sub>3</sub>, as the appearance energy of GeH<sup>+</sup>(GeH<sub>3</sub>) is  $\leq 9.0$  eV and the relative photoion yield of GeH<sup>+</sup>/GeH<sub>3</sub><sup>+</sup> from GeH<sub>3</sub> at 118.2 nm is ~ 0.2 [22]. The GeH<sub>3</sub> and GeH intensities reported in Table 2 have not been corrected for this relatively minor ion fragmentation process, and the GeH<sub>3</sub> and GeH values at a given temperature can be considered as minimum and maximum values, respectively. Other ion fragmentation processes, such as GeH<sub>2</sub><sup>+</sup> from

Table 2

Calculated relative intensities of GeH<sub>4</sub> pyrolysis products, averaged from both procedures of deconvolution (see text for more details)

Temperature (K)	GeH <sub>3</sub>	GeH <sub>2</sub>	GeH	Ge	
900	0	2	0	0	
1020	5	6	1	3	
1160	4	20	6	14	
1320	15	32	16	46	
1500	58	52	29	146	

All values have been corrected for baseline as described in the text. Relative errors are typically within  $\pm 25\%$  of the listed values.

Temperature (K)	Relative intensity of $Ge_2 + Ge_2H_x$	$Ge_2H_x$ : $Ge_2$ ratio
1160	55	0.17
1320	148	0.10
1500	343	0.18

Table 3 Total intensity of both  $Ge_2$  and  $Ge_2H_x$  clusters and estimated  $Ge_2H_x$ :  $Ge_2$  ratio versus temperature

Intensity of m/e 140 peak and Ge isotope abundances are used to obtain the contribution exclusively from the Ge<sub>2</sub> cluster.

GeH<sub>3</sub>, were not observed by Ruscic et al. [22]. In summary, the predominance of the Ge product implies that reactions (4) and (5), rather than the higher energetic pathways (reactions (6)–(8)), are the main initial steps in pyrolysis of GeH<sub>4</sub>. This conclusion is consistent with the literature [20,21].

At temperatures above  $\sim 1100$  K, the formation of  $\operatorname{Ge}_n \operatorname{H}_x$  (n = 2-7) clusters was detected (Figs. 2 and 4). As before, the presence of five germanium isotopes greatly complicates determining the extent of hydrogenation of these clusters. However, similar to the deconvolution process of  $GeH_x$ (x=0-3), by using the intensity of m/e 140 peak (due to only  $^{70}$ Ge<sub>2</sub>) and Ge isotope abundances, the contribution exclusively from the Ge<sub>2</sub> cluster and thus the  $Ge_2H_x$ :  $Ge_2$  ratio can be calculated, and the results are presented in Table 3. These results indicate that most of the  $Ge_2H_x$  clusters are pure Ge<sub>2</sub> with only a small amount of highly unsaturated hydrogenated  $Ge_2H_x$  species. The low intensity of m/e 141 peak (due to <sup>70</sup>Ge<sub>2</sub>H exclusively) also suggests that Ge<sub>2</sub>H cluster is minimal. Determining the  $Ge_nH_x$ :  $Ge_n$  ratio for  $Ge_nH_x$  $(n \ge 3)$  is more difficult, and due to lack of resolution of these larger clusters, the extent of hydrogenation in these species is not estimated. Nevertheless, the mass peak envelopes of  $Ge_nH_x$  $(n \ge 3)$  indicate predominant contributions from bare  $\text{Ge}_n$  ( $n \ge 3$ ) clusters (Fig. 4). This behavior in GeH<sub>4</sub> pyrolysis is similar to the pyrolysis of both SiH<sub>4</sub> and Si<sub>2</sub>H<sub>6</sub> [32]. The silicon clusters formed upon pyrolysis of the SiH<sub>4</sub> and Si<sub>2</sub>H<sub>6</sub> precursors were found to be largely bare Sin clusters and a small amount of highly unsaturated  $Si_nH_x$  clusters. For example,  $Si_6H_r$  clusters were predominantly bare (x=0), but had a small fraction which were mono- or di-hydrogenated species (x = 1, 2). With smaller Ge-H bond strengths compared to those for Si-H, complete dehydrogenation of GeH<sub>4</sub> to Ge seems to be more efficient, also a lower hydrogen content is expected in the  $Ge_nH_x$  clusters. The  $Ge_nH_x$  clusters could be produced by efficient dehydrogenation of polygermanes that might be formed by insertion of  $GeH_2$  to  $GeH_4$ , similar to the pyrolysis of SiH<sub>4</sub> [19,32]. In addition, the  $Ge_n$ clusters could be formed directly from condensation of Ge atoms generated in the pyrolysis of GeH<sub>4</sub>. Indeed, a strong correlation between the concentrations of reactive species GeH<sub>2</sub> and Ge and the particle production has been observed in RF discharges of GeH<sub>4</sub> [33].

# 4. Conclusion

The formation of GeH<sub>x</sub> (x = 0-3) species upon flash pyrolysis of germane was directly observed by VUV–TOFMS. The initial primary product was GeH<sub>2</sub>, and at higher temperatures Ge, GeH, and GeH<sub>3</sub> were also formed, with atomic Ge being the predominant product. These observations are in good agreement with previous studies on germane pyrolysis, and provide direct experimental evidence to support the thermal decomposition mechanisms, shown in reactions (4)–(8) and Fig. 1.

Subsequent reaction of pyrolysis products resulted in the formation of  $\text{Ge}_n\text{H}_x$  (n = 2-7) clusters at temperatures above 1100 K. Although the exact extent of hydrogenation of these clusters is difficult to define, they are largely pure  $\text{Ge}_n$  clusters, with only a small amount of highly unsaturated  $\text{Ge}_n\text{H}_x$ species.

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