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Reaction kinetics and mechanisms of inorganic hydrides on germanium surfaces

Cohen, Stephen Michael, Ph.D.

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REACTION KINETICS AND MECHANISMS OF INORGANIC HYDRIDES ON GERMANIUM SURFACES

by

STEPHEN MICHAEL COHEN

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE
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APPROVED, THESIS COMMITTEE:

M.P. D’Evelyn, Assistant Professor Chemistry

K.H. Whitmire, Associate Professor Chemistry

P. Nordlander, Assistant Professor Physics

Houston, Texas
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ABSTRACT

Reaction Kinetics and Mechanisms of Inorganic Hydrides on Germanium Surfaces

by

Stephen Michael Cohen

The surface reactivity of germanium is of interest because of novel $\text{Si}_x\text{Ge}_{1-x}$ heterostructure applications and the insight into semiconductor surface chemistry attainable through comparative studies on silicon and germanium. The adsorption of the inorganic hydrides $\text{H}_2\text{S}$, $\text{H}_2\text{O}$, $\text{NH}_3$, and $\text{HX}$ ($X = \text{Cl}, \text{Br}$) on Ge(100) was investigated by temperature-programmed desorption (TPD) for the first time. The initial sticking probability $S_0$ for $\text{H}_2\text{S}$ exhibits at most only a minor temperature effect, remaining roughly constant at $\sim 0.23$ within the temperature range $173 \text{ K} \leq T \leq 373 \text{ K}$. Adsorbed $\text{H}_2\text{S}$ decomposes upon heating into $\text{H}_2$ and GeS, which desorb at 570 K and 660 K, respectively. The initial sticking probability for $\text{H}_2\text{O}$ depends strongly upon substrate temperature, dropping from 0.28 at 173 K to $\sim 0.02$ at 273 K. Adsorbed water decomposes to yield $\text{H}_2$ and GeO, which desorb at peak temperatures of 570 K and 660 K, respectively. Both HCl and HBr adsorb on Ge(100), and desorb upon heating to 570 K as $\text{H}_2$ and to 580 K as $\text{HX}$ in roughly equal proportions. The remaining $X(a)$ desorbs as Ge$X_2$ at 680–760 K. The initial sticking probability for HBr is 0.77 at 273 K, falling slightly to 0.55 at 373 K, whereas $S_0$ for HCl falls from 0.30 at 273 K to 0.066 at 373 K. The peak shapes and independence of peak temperature with coverage for $\text{H}_2$ and $\text{HX}$ for all adsorbates indicate approximately first-order desorption kinetics, but Ge$X_2$ desorption follows second-order desorption kinetics. Adsorption of $\text{NH}_3$ was not observed, implying $S_0 \leq 6 \times 10^{-5}$. The adsorption and desorption behavior of these molecules can be
understood by regarding the Ge(100) dimer atoms as being linked by a strained double bond and examining analogous addition and elimination reactions of molecular germanium compounds.
Acknowledgements

Within the realm of the laboratory, the most important person responsible for this project is my advisor, Mark D'Evelyn. It is he, of course, who introduced me to that mysterious specialty of scientific study where chemistry, physics, and materials engineering meet, namely, surface science. It is he who set my fellow students and me the daunting task of creating the ultimate ultra-high vacuum chamber, and all the difficulties involved therein. It is also he who, I hope, imparted to me a modicum of understanding of “scientific thought,” typically not taught at the undergraduate level, and probably best learned under the auspices of graduate school apprenticeship.

Other people, without whom this project would still be a gleam in the National Science Foundation’s eye, are my colleagues Lisa Ulvick and Yuemei Yang, for collaborating on building, care, and feeding of the monster vacuum chamber, and Terttu Hukka, for assisting me with collection of the hydrogen halide data, as well as providing me with more Finnish postage stamps than I knew what to do with. Though not in my research group, Meg Fraelich probably has done more than any other fellow chemistry graduate student to show me that life and conversation is more than Chemistry; to her I say “pilamiyaye ye.” Her colleague, Jennie Weston, probably doubled the size of my postage-stamp collection through her generous contributions. Jack Moss, my fiancée’s father, actually slogged through several early drafts of this work and offered valuable proofreading advice.

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even when the tunnel’s exit seemed eternally blocked. Through them I have come to realize that wisdom flows from the mouths of those without advanced degrees, and, conversely, possession of initials after one’s name does not automatically confer the title of khakham. My cousins, the Entman clan, and Aunt Rose Entman provided me with a surrogate family plus Friday night dinners that sustained me for more than a week. Their generosity from even before my acceptance into Rice University has been unbounded. Through Rabbi Stuart Federow and the B’nai B’rith Hillel Foundation in Houston I found friends, spiritual nourishment, and yidishkayt, sources for Jewish culture, discussions, and values.

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1. Introduction

With the invention of the transistor in the late 1940s by Bardeen and Brattain, the study of semiconductors suddenly jumped from more than a peculiar intermediate between insulators and metals into a full-blown topic of serious research. Invention, extraction, purification, and production of materials with tailor-made band-gaps became the object of intense investigation. In the 1950s, germanium was the elemental semiconductor of value, but as the utility of silicon in solid-state device technology became apparent, interest in germanium flagged. Silicon has a larger bandgap (1.12 eV) than germanium (0.66 eV) at 300 K, thus reducing leakage current and increasing the maximum operating temperature of solid-state devices from 90 °C (Ge) to nearly 200 °C (Si). Silicon, furthermore, has a passivating oxide layer (SiO₂) useful as a dopant diffusion barrier and for integrated-circuit patterning, whereas the corresponding oxide of germanium, GeO₂, is water-soluble and dissociates at ~ 800 °C. Availability and price also work in favor of silicon.

Germanium has always found use as a far-infrared-detector and discrete-device material, yet within the past decade research into the chemistry and physics of germanium has gained momentum as more potential uses for this element have been uncovered. Research into the properties of strained layers of silicon-germanium alloys grown epitaxially on silicon has expanded rapidly in the past decade. By varying the elemental proportions of the alloy, the bandgap can be adjusted for production of novel types of photodiodes and -detectors, as well as integrated optoelectronics. The high quality of the alloy's interface with the silicon substrate allows fabrication of better field-effect and bipolar transistors.

With this new interest come new questions into the detailed structure of such layers, the properties of clean surfaces, and the chemistry that can be performed on these surfaces. Given the technological advances in the last thirty years, particularly in the fields of vacuum technology and computerized data acquisition, many of these new questions can be tackled.
The present, systematic, study of inorganic hydrides on germanium is derived from such a background.

1.1. Ge(100) surface

Most research is performed on the (111) and (100) surfaces of silicon and germanium, because these are the wafer orientations upon which integrated circuits are fabricated. Elemental Group 14 crystals break easily along the {111} family of planes. For the (100) surface orientation, facile cleavage along {111} planes provides convenient cleavage of a (100) wafer into rectangles, preferred for metal-oxide-semiconductor device fabrication. Breakage along {111} within crystals oriented to the (111) plane, however, is six-fold (at 60° angles); this surface tends to be preferred for bipolar technology, that is, devices in which both electrons and holes flow internally.2,6

The history of research on the (100) crystal face of germanium began with the pioneering work of Schlier and Farnsworth nearly four decades ago,7 who “rediscovered” the tool of low-energy electron diffraction (LEED) invented by Davisson and Germer in the 1920s, and used it to interpret the (2×1) reconstruction on the clean (100) surfaces of germanium and silicon. If a crystal with tetrahedral structure is cut to expose the (100) face, each exposed atom has two unpaired electrons (often termed “dangling bonds”), as shown in Fig. 1.1.1. The (2×1) reconstruction, so called because the surface layer “reconstructs” to form an overlayer whose unit cell’s dimensions are 2a × 1a (where a is the lattice constant), lowers the number of unpaired electrons by causing nearest-neighbor upper-level atoms to bond together, creating a more stable, less reactive surface, with only one “dangling bond” per atom, as shown in Fig. 1.1.2. Such a situation exists with the Group 14 elements carbon (as diamond), silicon, and germanium. In recent years attempts have been made to clarify the precise structure of these paired-atom arrangements, called “dimers”. Levine9 modified Schlier and Farnsworth’s model to include displacement of the
two "dangling bonds" per unreconstructed surface atom

Figure 1.1.1. Unreconstructed diamond-lattice (100) surface.

one "dangling bond" per reconstructed surface atom

Figure 1.1.2. Reconstructed (100)-(2×1) diamond lattice.

dimers toward the bulk for the Si(100) surface. Soon thereafter, Appelbaum and Hamann\textsuperscript{10} performed kinematic analysis of LEED data, confirming the subsurface distortions Levine predicted for Si, and also noting that these distortions are expected for Ge(100) and diamond(100) as well. Tong and Maldonado subsequently supported Appelbaum and Hamann by taking intensity-voltage spectra of LEED patterns of Si(100).\textsuperscript{11}
Later work has focused on whether the dimers are symmetrical\textsuperscript{12} or asymmetrical,\textsuperscript{13} or possibly containing vacancies,\textsuperscript{14} all due to longer-range interaction between the dimers. It is also unclear how far down surface reconstruction into the bulk material occurs,\textsuperscript{15} but the basic picture involving dimers remains unchanged.

The type (\( \sigma \) or \( \pi \)) and strength of the bond between the dimers is a long-standing yet incompletely-answered question. Charge-density calculations by Appelbaum and coworkers indicated \( \pi \) and \( \pi^* \) orbitals across the Si(100) dimer atoms\textsuperscript{16}; the multiple-bond character of the Si dimer bond was confirmed through the calculations of Yin and Cohen.\textsuperscript{17} Recently Avouris and Boland showed evidence in scanning-tunneling microscope images for both occupied (i.e., \( \pi \)-states) and unoccupied (i.e., \( \pi^* \)-states) when scanning at \(-2\) V and \(+1.2\) to \(+1.7\) V, respectively.\textsuperscript{18} Various values for the strength of the proposed \( \pi \)-bond include Boland's scanning-tunneling spectroscopy estimate\textsuperscript{18b} of \(~75\) kJ mol\(^{-1}\), Nachtigall, and colleagues' \textit{ab initio} computations\textsuperscript{19} suggesting \(21\) kJ mol\(^{-1}\), a lattice-gas model by D'Evelyn and coworkers\textsuperscript{20} indicating a \( \pi \)-bond strength near \(~30\) kJ mol\(^{-1}\), and isothermal desorption measurements by Höfer, \textit{et al.},\textsuperscript{21} providing an energy of \(~25\) kJ mol\(^{-1}\) as well. Though similar measurements concerning the Ge(100) dimer bond strength have not been made, it is reasonable to assume similar bonding characteristics occur between Ge atoms.

1.2. Hydrides on Germanium

Semiconductor wafer processing involves inorganic hydrides, i.e., molecules with the chemical formula \( H_nX \). Probably the main hydride used is ultrapure water during rinsing and oxide growth. Another hydride used in the etching and cleaning process is HF, typically in combination with ammonium fluoride, phosphoric acid, or acetic acid. Numerous hydrides, including AsH\(_3\), PH\(_3\), and B\(_2\)H\(_6\) are used to dope As, P, or B, respectively, into semiconductors. In chemical vapor deposition, layers of semiconductor
are deposited via reactions producing HCl as a byproduct. To create silicon nitride, silane or trichlorosilane is reacted with NH₃ in the presence of the substrate. Clearly, then, it is essential to understand the detailed surface chemical mechanisms underlying these important industrial processes.

While molecular oxygen and hydrogen have been studied since the very first germanium-surface experiments, relatively little else has been investigated until the 1970s because of the overwhelming influence of silicon. Even as recent as the late 1980s, as Froitzheim put it, “[m]ost of the available data, based on indirect methods, are interpreted by analogy with the much better investigated Si properties, assuming similar behaviour for Ge due to the strong similarities between the structures of the two materials.” It is, of course, by no means clear that such analogies are justified.

In the 1960s, several primitive experiments involving adsorption on the surface of crushed germanium powder—believed to be primarily Ge(111) surfaces, for Ge(111) is the cleavage plane—were undertaken, most notably by Burshtein, et al., Novototskii-Vlasov and Sinyukov, Neizvestnyi, and Spaarnay and Boonstra, using water, alcohols, diethyl ether, substituted benzenes, and inorganic hydrides as adsorbates. These studies generally involved uptake and surface electrical-property measurements, and almost nothing was learned about surface structure or chemistry. Perhaps the most interesting of these works, for our purposes, was Boonstra’s, in which an attempt was made to systematically characterize hydride uptake on Ge powder. His results are summarized in Table 1.2.1.

Boonstra found that H₂ desorbed at ~ 350 °C for all the di- and trihydrides adsorbed on Ge powder. Dinitrogen was observed to desorb above 450 °C from adsorbed ammonia, while sulfur and selenium were removed from adsorbed H₂S or H₂Se by annealing the Ge powder to 650 °C. For hydrogen halides, evolution of H₂ was slower and did not even start until the surface temperature reached 200 °C. The data were explained by postulating complete dissociation of each adsorbate molecule on the Ge surface.
Table 1.2.1. Adsorption of H$_a$X ($a = 1-4$) on crushed Ge by Boonstra$^{27b,c}$

<table>
<thead>
<tr>
<th>$a$</th>
<th>molecule</th>
<th>molecules/Ge surface atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>GeH$_4$, SiH$_4$</td>
<td>0 (&lt; 0.01 monolayer)</td>
</tr>
<tr>
<td>3</td>
<td>NH$_3$, PH$_3$, AsH$_3$, SbH$_3$</td>
<td>1/6</td>
</tr>
<tr>
<td>2</td>
<td>H$_2$O, H$_2$S, H$_2$Se</td>
<td>1/4</td>
</tr>
<tr>
<td>1</td>
<td>HCl, HBr, HI</td>
<td>1/2</td>
</tr>
<tr>
<td>HF</td>
<td>&lt;&lt;1/2</td>
<td></td>
</tr>
</tbody>
</table>

In the early 1970s, Madix and coworkers$^{28}$ performed reactive scattering experiments of halogens (Cl$_2$, Br$_2$, and I$_2$) on Ge(111) and (100) surfaces, reporting dissociative adsorption, with $S_0 \sim 0.3$ at $T > 600$ K for Cl$_2$/Ge(100). Contemporaneously, Henzler and Töpler$^{29}$ adsorbed water on \textit{in-vacuo}-cleaved Ge(111), and observed, through LEED and Auger electron spectroscopy (AES), that a single H$_2$O molecule bonds to two sites on that surface, but blocks an area of 3–4 sites from adsorption by other molecules. An initial sticking coefficient $S_0$ of $\sim 5 \times 10^{-4}$ was also derived. Schnell and coworkers$^{30}$ adsorbed chlorine and bromine on the Ge(100)-(2×1)surface, and determined through core-level photoemission studies of the Ge 3$d$ state that the saturation coverage of Cl was unity, corresponding to one Cl attached to each top-most Ge atom.

Substantial interest in hydrides adsorbed on Ge(100) surfaces did not develop until the 1980s. Ranke and colleagues performed a series of experiments$^{31}$ concerning the adsorption of H$_2$S on Ge surfaces as studied by ultraviolet photoelectron spectroscopy and AES, and determined that the initial sticking coefficient $S_0 = 0.2$ at $T = 300$ K, with a saturation coverage of 0.5 from dissociation of the H$_2$S into adsorbed H and SH species. Leung, \textit{et al.} similarly found, by means of high-resolution electron-energy spectroscopy (HREELS) and AES, that H$_2$S dissociatively adsorbs at $T = 300$ K, but furthermore that
the adsorbed SH species dissociated into 2H(a) + S(a) at 573 K, and by $T = 673$ K all hydrogen had desorbed, leaving only sulfur on the surface.\textsuperscript{32}

Adsorption of water on Ge(100) also became of interest to various research groups, including Ranke, \textit{et al.}, who found that water dissociatively adsorbs at $T = 300$ K with $S_0 = 2 \times 10^{-4}$ at a saturation coverage of 0.5, forming H(a) + OH(a) on the Ge(100) surface.\textsuperscript{31b} Lapeyre and coworkers\textsuperscript{33} used HREELS to observe both molecular and dissociative adsorption of water at 100 K, but found no adsorption at 300 K for exposures up to 100 L. Upon heating to 345 K, the water completely dissociated into H(a) + OH(a) on the surface, and beyond 450 K the OH(a) itself dissociated. Above 620 K, the Ge—H modes vanished because of H$_2$ desorption, leaving only an oxidized Ge(100) surface. Using photoelectron spectroscopy, Larsson, Flodström, and colleagues\textsuperscript{34} investigated water on the Ge(100) surface, and observed molecular adsorption at 160 K but dissociation upon heating to 300 K, with a sticking probability for water that was "several orders of magnitude" smaller at 300 K than at 160 K.

There have been several studies\textsuperscript{33b,35} of water on alloys of germanium and silicon, Ge$_x$Si$_{1-x}$, which indicate that water likewise dissociates at room temperature on the (100) face of this material.

1.3. Temperature-Programmed Desorption Theory

Temperature-programmed desorption (TPD) is a relatively simple, yet widely-used technique for determining details of desorption kinetics. It began to be used extensively in studies of N$_2$ and H$_2$ on tungsten in the 1950s,\textsuperscript{36} and was extensively developed as a quantitative technique by Ehrlich\textsuperscript{37}. A classic treatment on the interpretation of desorption data was published by Redhead in 1962,\textsuperscript{38} as well as excellent, more recent explanations by King and Madix in 1979.\textsuperscript{39} A detailed examination of TPD from Si(111) was written by Kleint and Brzóska in 1990.\textsuperscript{40}
We begin by considering that desorption of a species $i$ from a surface can be modeled by Arrhenius-like behavior, resulting in the Polanyi-Wigner equation (Eq. 1.3.1) for $k$, the rate of desorption per unit area,

$$k = -\frac{d\theta_i}{dt} = v_i \theta_i^{n_i} e^{(-\Delta E_i / RT)},$$  \hspace{1cm} (1.3.1)

where $n_i$ is the reaction order for desorption of $i$, $v_i$ is the pre-exponential factor, $\Delta E_i$ is the activation energy for desorption, and $\theta_i$ is the surface coverage of $i$. We assume that both $v$ and $\Delta E$ are independent of $\theta$ (which often is not true when adsorbate-adsorbate interactions become important). Given a linear ramping at rate $\beta$ of the sample temperature $T$ with time $t$ (Eq. 1.3.2),

$$T = T_0 + \beta t,$$  \hspace{1cm} (1.3.2)

we can solve Eq. 1.3.1 to find the peak temperature $T_p$, where the desorption rate is at a maximum (i.e., set the second derivative of the coverage to zero with respect to time, $d^2\theta/dt^2 = 0$). We can thus use the peak temperature to extract information about the reaction kinetics.

The general relationship between $T_p$, $\beta$, and Arrhenius parameters $\Delta E$ and $v$ is, at surface coverage $\theta_p$ during the maximum desorption rate (when $T = T_p$),

$$\frac{\Delta E}{RT_p^2} = \frac{n v \theta_p^{n-1}}{\beta} e^{(-\Delta E / RT_p)} \text{ (when } n > 0),$$  \hspace{1cm} (1.3.3)

Redhead$^{38}$ showed that, with numerical approximations accurate to within a few percent,

$$\theta_p^{1-n} = n \theta_0^{1-n} \text{ (when } n \geq 0 \text{ and } n \neq 1)$$  \hspace{1cm} (1.3.4)

$$\theta_p = \theta_0 / e \text{ (when } n = 1)$$

so that we can simplify Eq. 1.3.3 slightly to
\[ \frac{\Delta E}{RT_p^2} = \frac{V_n \theta_0}{\beta} e^{-\frac{\Delta E}{RT_p}} \quad \text{(when } n > 0) \]  \hspace{1cm} (1.3.5)

For zero-order desorption, integration of Eq. 1.3.1 from \( T_0 \) to \( T_p \) and using \( \theta_p = 0 \) when \( n = 0 \) gives approximately

\[ \frac{\Delta E}{RT_p^2} = \frac{V_1}{\theta_0 \beta} \quad \text{(when } n = 0) \]  \hspace{1cm} (1.3.6)

where \( \theta_0 \) is the initial surface coverage. For such a system, increasing the coverage will cause the peak temperature to shift **upward**. Simplifying the case for \( n = 1 \) (first-order desorption),

\[ \frac{\Delta E}{RT_p^2} = \frac{V_1}{\beta} e^{-\frac{\Delta E}{RT_p}} \quad \text{(when } n = 1) \]  \hspace{1cm} (1.3.7)

we see that \( T_p \) is independent of coverage, that is, when varying the coverage of adsorbate on the surface during the course of several experimental runs, the peak temperature **will not vary**. Simplifying the case for \( n = 2 \) (second-order desorption),

\[ \frac{\Delta E}{RT_p^2} = \frac{\theta_0 V_2}{\beta} e^{-\frac{\Delta E}{RT_p}} \quad \text{(when } n = 2) \]  \hspace{1cm} (1.3.8)

shows that the peak temperature will **decrease** as the initial adsorbate coverage is increased.

Information about reaction kinetics also can be extracted from the shape of the desorption peak. Redhead showed that for a first-order reaction \( n = 1 \),

\[ \ln \left( \frac{k_p}{k} \right) = \frac{\Delta E}{R \left( \frac{1}{T} - \frac{1}{T_p} \right)} + \left( \frac{T}{T_p} \right)^2 \exp \left[ -\frac{\Delta E}{R \left( \frac{1}{T} - \frac{1}{T_p} \right)} \right] - 1, \]  \hspace{1cm} (1.3.9)

which gives an asymmetric peak shape. For a second-order reaction \( n = 2 \),

\[ \frac{k_p}{k} = \cosh \left[ \frac{\Delta E}{2R \left( \frac{1}{T} - \frac{1}{T_p} \right)} \right], \]  \hspace{1cm} (1.3.10)

within the immediate vicinity of the desorption peak, giving a symmetric peak shape.\( ^{38} \)}
Typical methods for solving Equations 1.3.7 and 1.3.8 for $\Delta E$ involve noting the $T_p$ dependence on coverage (after recording a series of spectra at a wide variety of coverages) to determine the reaction order, guessing $\nu_1 = 10^{13}$ s$^{-1}$ (for first-order reactions), and substituting in the experimental parameter $\beta$ (usually set anywhere from 1–100 K s$^{-1}$) and the observed $T_p$.

In general, temperature-programmed desorption provides (a) kinetic reaction orders, from peak shapes and temperature shifts; (b) relative reaction rates, from peak temperatures; and (c) amounts of product desorbed, from the peak areas.

1.4. Experimental Objective

Given the surprising lack of systematic knowledge about the interaction of inorganic hydrides with the Ge(100) surface, the goal of this work is to use the technique of temperature-programmed desorption to learn about the adsorption and decomposition of hydrides on the Ge(100) surface, and attempt to explain their resultant kinetics and reactivities. An overall goal, however, is to create a foundation for systematic rules in surface chemistry, in much the same way that organic chemistry has been organized and classified.
2. **Experimental**

2.1. **Chamber**

Basic studies in surface science usually require ultrahigh vacuum (UHV, < 10^{-8} Torr) conditions, so that the surface under study remains clean during the course of an experiment. Kinetic theory of gases shows\(^{41}\) that the number of collisions \(Z_w\) of gas molecules with a surface is given by Eq. 2.1.1:

\[
Z_w = \frac{P}{\sqrt{2\pi MRT}}
\]

(2.1.1)

where \(P\) is the pressure, \(M\) is the molar mass of the gas, \(R\) is the gas constant, and \(T\) is the absolute temperature. Given \(P = 10^{-8}\) Torr of air (\(M = 29\) g mol\(^{-1}\)) at \(T = 273\) K, \(Z_w = 3.94 \times 10^{12}\) collisions cm\(^{-2}\) s\(^{-1}\). For the (100) crystal face of germanium, whose lattice constant \(a = 0.5658\) nm,\(^{42}\) the surface density is \(6.25 \times 10^{14}\) atoms cm\(^{-2}\) (\(= 1\) monolayer) so that at this pressure the gas will be impinging on the surface at a rate of \(3.94 \times 10^{12}\) collisions cm\(^{-2}\) s\(^{-1}\) / \(6.25 \times 10^{14}\) atoms cm\(^{-2}\) = 0.00630 monolayers s\(^{-1}\), and the surface will be covered in 159 s, if all molecules stick solely at vacant sites. Ideally, then, it is preferred to keep the pressure even lower, in the \(10^{-10}\) Torr range, so that the sample remains clean on the order of hours.

A second reason for attaining at least moderate vacuum conditions is to allow the use of ions or electrons as probes of surface structure. These particles need mean free paths comparable to or greater than the probe-to-sample distance (at least several cm), else they will be scattered by the intervening gas.

Our custom-built UHV chamber attains \(10^{-10}\) Torr pressures (\(P_{\text{base}} = 1 \times 10^{-10}\) Torr) easily to solve both cleanliness and ion-transmission problems. It is cylindrically-shaped, constructed of 304-type stainless steel, with an upper level for experimental work, and a lower level for sample loading. The chamber is pumped by a liquid-nitrogen-trapped diffusion pump (Varian, VHS-6) containing polyphenyl ether fluid (Monsanto, Santovac 5,
$P_{\text{vapor}} = 2 \times 10^{-9}$ Torr), which is, in turn, pumped by a two-stage mechanical pump (Edwards, E2M18). Two salt windows (for the transmission of infrared light) are differentially pumped by the mechanical pump, and a rotating platform supporting the sample manipulator is doubly differentially pumped, first by the mechanical pump (outer stage) and then by a small ion pump (inner stage). Fig. 2.1.1 is a schematic of the vacuum chamber pumping system. Attached to the chamber are a number of surface tools and

![Diagram](image)

Letters A, B, C, D connect to points on Fig. 2.4.1 (Gas Manifold).

1. Two-stage rotary vane pump
2. Molecular-sieve trap
3. Pneumatic isolation valve
4. Flexible teflon coupling
5. Flexible steel formed bellows
6. Thermocouple (TC) gauge
7. Manual venting valve
8. Analog TC-gauge controller
9. Diffusion pump
10. Liquid nitrogen trap
11. Pneumatic gate valve
12. UHV chamber
13. Titanium-sublimation pump
14. Nude ionization gauge
15. Differentially-pumped salt window
16. Differentially-pumped rotary-motion stage
17. Manipulator x,y,z-translation stage
18. 1/4-turn manual valve with conductance-limiting aperture (for calibrated dosing)
19. Small ion pump
20. Manual isolation valve
21. Sorption pump
22. Digital ionization-gauge controller
23. Metal-sealed isolation valve
24. Electromagnetic venting valve

**Figure 2.1.1. Ultra-High Vacuum System.**
probes, including a quadrupole mass-spectrometer (Vacuum Generators, SXP-400) mounted on a home-built translation stage, three-grid LEED/ESDIAD optics (N.I.S.T.) incorporating microchannel plates along with a 50° off-axis electron gun, hemispherical analyzer (VSW, HA-100) for Auger electron spectroscopy, a second electron gun (Apex Electronics, CE-406) for use with the hemispherical analyzer, a custom-built ion gun for sputtering the surface, a tungsten filament for dissociating hydrogen molecules, a calibrated doser to allow a known flux of gas into the chamber, an X-ray source (VG Microtech, XR2E2) for photoelectron spectroscopy, a titanium-sublimation pump, and a nude Bayard-Alpert ionization gauge. Both electron guns are powered by a 5-kV power supply (Perkin Elmer, Φ 11-010). Figure 2.1.2 shows a horizontal cross-section of the vacuum chamber at probe level.

The sample itself is mounted on a custom-built manipulator, which includes infrared optics suitable for focusing infrared light onto an internal-reflection element, as well as allied mechanical trains and assemblies designed to bring the optics into alignment with the internal reflection element. The manipulator is hung from an x-, y-, z-translator (U.H.V. Instruments) with a z-motion travel of 26 cm between upper and lower levels. The translator-manipulator assembly is mounted on a doubly-differentially pumped rotary-motion device so that the entire manipulator assembly can be rotated 360° and the samples may face any desired probe.

2.1.1. Attainment of Ultra-High Vacuum

Reaching ultra-high vacuum (< 10^-8 Torr) from full atmospheric pressure requires several steps. We follow a procedure quite similar to that given by Dubois. If all sections of the vacuum system are at 1 atm, the mechanical pump (1, in Fig. 2.1.1, as are the following numbers) is started and the sieve trap (2) is baked (via an integral electrical heater) for 24 h to remove adsorbed oils and water from the molecular sieve, after which
the foreline (extending from 2–9) is evacuated to typically 30-60 mTorr. The liquid-N₂ trap (10) is then baked into the foreline for 24 h, using heating tapes, to remove adsorbed water and diffusion-pump oils. During this time the diffusion pump is started. The chamber is properly sealed and mechanically pumped down to 300-400 mTorr through a connection ("B") to the gas-dosing manifold. At this pressure a sorption pump (21) is used
to continue the process to $\leq 30$ mTorr, at which time the gate valve (11) is opened and the chamber is pumped via the liquid-nitrogen-trapped diffusion pump (9 and 10). The ionization gauge (14) may be used at this vacuum level, and typically shows a reading at $\sim 10^{-6}$ Torr, dropping gradually to $10^{-7}$ Torr. Helium leak-checking is then performed, noting the $m/e = 4$ signal on the quadrupole mass spectrometer. If all seals are tight, no leaks are found, and the vacuum chamber is baked out to a temperature of $\sim 150$ °C, by means of heating tapes and tubular heaters wrapped around various sections of the chamber (consuming on the order of 6 kW), for a period of 24–36 hours.

At the end of the bakeout, the ionization gauge normally reads in the mid-to-high $10^{-8}$-Torr range, and the chamber is allowed to cool to room temperature, so that the pressure becomes $\leq 5 \times 10^{-9}$ Torr. During cooling, hot filaments (ion gun, H$_2$ dissociator, QMS) within the chamber are permitted to outgas. Simultaneously, the ion pump (21) attached to the inner section of the doubly-differentially-pumped rotary stage (16) is started by evacuation into the gas-dosing manifold ("D") to $< 5$ mTorr. At this ion-pump pressure its sorption pump (19) is cooled with a liquid N$_2$ bath until the ion pump starts. When the UHV chamber is completely cooled (18–24 h due to the large thermal load of the hemispherical analyzer), the titanium-sublimation pump (13) is activated several times, approximately 1 min per flash, and the chamber pressure drops to $\sim 1 \times 10^{-10}$ Torr. Base pressures occasionally have been recorded as low as $7 \times 10^{-11}$ Torr.

### 2.1.2. Quadrupole-Mass-Spectrometer Translator

In order to optimize signal-to-noise ratio from sample desorption products it is desirable to bring the mass-spectrometer as close as possible to the sample, but be able to retract the mass spectrometer while rotating the manipulator or performing residual-gas analysis of the vacuum chamber. Accordingly, a precision translation stage (Fig. 2.1.2.1) for the mass spectrometer was designed and built to provide several inches of travel for the mass spectrometer into and out of the chamber, based on a similar system with longer
travel built by M.S. Hammond.44

The mass spectrometer is attached to a movable mating knife-edge flange which is translated via a ball-bearing screw (Warner Electric, R-0308). The position of the mass-spectrometer is manually adjusted by a crank-driven worm-and-wheel assembly (Chicago Gear Works; 48-pitch, 20 teeth). Connection between the movable flange and UHV chamber is made via welded stainless-steel bellows (4.97” O.D., 4” I.D.). For proper alignment throughout its length of travel, the mass-spectrometer assembly is supported on four pillow blocks mounted on twin parallel linear rails (Thomson Linear Motion System, 1CB).
(b) Orthogonal view of translator. Mounting bracket for worm and crank has been omitted for clarity.

Figure 2.1.2.1. (continued) Schematic of QMS translator.

2.1.3. Sample Holder for Temperature-Programmed Desorption

A holder for performing temperature-programmed desorption experiments on semiconductors was designed and constructed, within the requirements that high (> 600 °C) and low (< −100 °C) temperatures were reproducibly attainable on samples. The basic scheme involved simultaneously flowing coolant (liquid or gaseous nitrogen) through the mounting block while resistively heating the sample to bring the temperature up to the desired level.
The mounting block for the holder was machined out of solid copper, and attached to the central manipulator by means of stainless-steel screws and steel shim, to reduce heat transfer between the holder and manipulator. A hole, into which a copper pin brazed to 1/16-in.-O.D. steel cooling tube was fitted, was drilled in the mounting block. With this method the copper mounting block could be cooled to below −100 °C within half an hour, and temperatures as low as −120 °C were often attainable.

Approximately uniform sample heating was achieved by radiatively heating the back of the sample wafer with a glowing 0.001-in. 100 × 100 mesh tungsten screen. In parallel, direct resistive heating of the sample (which takes over once the temperature of the sample has increased enough to cause its resistance to fall) was employed. The sample itself (1–2 cm² in area) was held by tantalum clips attached to the mounting block but insulated by alumina sleeves and washers. Temperature measurement was performed by drilling a small (≤ 0.5 mm) hole near one edge of the sample, and cementing a chromel-alumel thermocouple into the hole with high-temperature ZrO₂-based cement (Aremco 516). A sketch of the sample holder is provided in Fig. 2.1.2.1.

2.1.4. **Calibrated Doser**

In order to dose a known amount of gas into the chamber, a novel calibrated gas-doser was designed and constructed.⁴⁵ Common features of existing doser designs are a large upstream “dead” volume between the valve seat and exit orifice, and small conductance-limiting apertures. This means the time required to terminate a dose is large unless the gas upstream of the aperture is pumped away, and flow rates are limited to ~ 10¹³ molecule Torr s⁻¹. The need to remove gas is inconvenient when repetitive dosing or expensive gases are involved, and a low flow rate may be problematic for species with a low sticking coefficient. To solve these problems, a new doser was built which both reduced the dead volume to ≈ 0.18 cm³ and increased the orifice diameter to ~ 42 μm. The essential features of the doser are a laser-drilled removable insert and a modified diaphragm
valve that can be turned on and off rapidly through a quarter turn.

The insert was fabricated by threading (1/16 in. NPT) a 0.66-in. long stainless steel rod containing a central hole 2 mm in diameter milled to ≤ 0.003 in. of the unthreaded end of the rod. The 0.003-in.-thick membrane was then laser-drilled (Lenox Laser) with a conical hole (entrance diameter of ~ 60 μm as observed under a microscope). The inlet of a stainless-steel diaphragm valve (Nupro, “DL” series) was drilled and tapped to mate with the insert. TFE tape was wrapped around the insert’s threads and the insert was screwed into the valve. The valve’s inlet was bolted via a 1.33-in. knife-edge flange to the ultra-high-vacuum chamber. By using the intended inlet rather than the outlet as the actual outlet, the dead volume between the valve seat and orifice of the insert was reduced to a minimum. Figure 2.1.4.1 shows diagrams of (a) the insert, (b) the valve, and (c) the assembly.

Upstream of the aperture-valve assembly is a capacitance manometer (Datametrics,
Fig. 2.1.4.1. Cut away views of the (a) Insert, (b) modified Nupro valve, and (c) entire assembly, in which the insert is screwed into the valve, using TFE tape as a sealant.
600 A; range = 0–10 Torr) to monitor the backing pressure. Downstream of the assembly, inside the vacuum chamber, is a stainless-steel doser with a linear array of holes arranged so as to produce a uniform flux over a large-area sample.

Under molecular-flow conditions, the conductance of an aperture is independent of the backing pressure behind the the aperture. Typical aperture sizes have been ≤ 10 μm to ensure molecular flow, i.e., the mean free path $\lambda$, defined in Eq. 2.1.4.1, is much greater than the diameter $D$ of the orifice:

$$\lambda = \frac{kT}{2^{1/2} \pi d^2 P},$$

(2.1.4.1)

where $k = $ Boltzmann's constant and $d$ is the molecular diameter. With an aperture whose diameter is several tens of micrometers, flow at pressures near 10 Torr lies somewhat outside of the molecular-flow regime. For H$_2$ and Ar, for example, the molecular diameters are ~ 0.29 and ~ 0.34 nm, respectively, so that when $P = 10$ Torr and $T = 300$ K, $\lambda_{H_2} = 8$ μm and $\lambda_{Ar} = 6$ μm, which is smaller by several times than our orifice.

Tests of whether the conductance is actually independent of the pressure, to show that the flow rate is independent of the pressure, were performed on Ar and H$_2$, by observing the quadrupole mass-spectrometer signal and ion gauge reading as these gases were dosed into the chamber. There was no significant difference between the relative change in ion gauge and mass spectrometer parent ion ($m/e = 40$ for Ar, $m/e = 2$ for H$_2$) signals, indicating that desorption off the chamber walls induced by the incoming gas was an unimportant effect. Fig. 2.1.4.2 shows the relationship between pressure behind the aperture and change in pressure inside the chamber, during a dose. The linear relationship indicates that the conductance is independent of the pressure even at backing pressures slightly beyond the effusive regime.

The conductance $C$ of the orifice was determined by allowing a known volume of gas $V$ (122 ± 3 cm$^3$) to escape through the aperture while monitoring the decay with time $t$ of the backing pressure. Because $C \propto M^{-1/2}$ for molecular flow, the decay rate of the
Fig. 2.4.1.2. Relationship between backing pressure and UHV-chamber pressure rise (uncorrected ion gauge) for argon and hydrogen. Lines are linear least-squares fits.

Pressure, scaled as a function of \( t^* = t M^{-1/2} \), ought to be the same for all gases. Fig. 2.1.4.3 shows the backing pressure as a function of dosing time, fitted to the form

\[
P = P_0 - \frac{t^*}{\tau^*}
\]

(2.1.4.2)

where \( P_0 \) is the backing pressure at \( t = 0 \) and \( \tau^* \) is the reduced time constant for pressure decay for the particular dosing system, \( \tau^* = \tau M^{-1/2} \). The linearity of the plots demonstrates, consistent with Fig. 2.1.4.3, that the conductance of the orifice is pressure-independent up to 10 Torr. The equality of the slopes for Ar and H\(_2\) confirms the expected dependence of the backing-pressure decay on the molecular mass. Averaging data taken over a period of time yields \( \tau^* = 178.6 \pm 9.3 \text{ s mol}^{1/2} \text{ g}^{-1/2} \) at the 95% confidence limit.

We obtain the conductance, flow rate, and effective diameter of the orifice from simple kinetic theory of gases, the definition of \( C \), and the known ballast volume \( V \):
Fig. 2.1.4.3. Relationship between backing pressure and valve-assembly time open. Lines are linear least-squares fits.

\[ C = \frac{V}{\tau} = \frac{V}{\tau^*} M^{-1/2} \]  \hspace{1cm} (2.1.4.3)

\[ = 0.683 \pm 0.040 \, M^{-1/2} \, \text{cm}^3 \, \text{s}^{-1}, \]

where \( M \) is given in g mol\(^{-1}\). With the conductance of an ideal round aperture under molecular-flow conditions,

\[ C = \frac{1}{4} \sqrt{\frac{\pi D_{\text{eff}}^2}{4}} \]  \hspace{1cm} (2.1.4.4)

we obtain \( D_{\text{eff}} = 41.9 \pm 1.2 \, \mu\text{m} \) (at \( T = 297 \, \text{K} \)). This value is probably equal to the exit diameter (which cannot be observed properly) of the conical aperture. The coefficient relating pressure upstream of the aperture to the flow rate is

\[ -\frac{1}{P} \frac{dN}{dt} = \frac{C}{kT} = (2.42 \pm 0.14) \times 10^{16} \, M^{-1/2} \, \text{molecule Torr}^{-1} \, \text{s}^{-1}, \]  \hspace{1cm} (2.1.4.5)

where \(-dN/dt\) is the flow rate.
The answer to how far beyond the rigorous molecular-flow regime \( C \) remains pressure-independent is displayed in Fig. 2.1.4.4 for Ar. A section of the gas manifold

![Graph showing the relationship between backing pressure and time](image)

**Fig. 2.1.4.4.** Relationship between argon backing pressure and valve-assembly time open. The line is fitted by linear regression. Convelectron gauge pressure is corrected for Ar sensitivity.

was filled with Ar at nearly atmospheric pressure. The gas was allowed to flow through the orifice, using a pressure gauge (Granville-Phillips, 275 Convelectron) with tabulated correction factors, to monitor the pressure. As the flow becomes sonic or supersonic at higher backing pressures the conductance undergoes a large increase, but still remains essentially pressure-independent below 43 Torr, where \( \lambda \) is less than \( D_{\text{eff}} \) by a factor of \( \sim 30 \).

The rapid recovery time after dosing within the vacuum chamber is revealed in Fig. 2.1.4.5, in which is shown plots of the mass-spectrometer signal \((m/e = 2 \text{ and } 40)\) versus time while manually opening and closing the valve assembly. The maximum flux and base pressure rapidly reach their steady-state values after only a few seconds. A semilogarithmic plot of \( \ln(\text{mass-spectrometer signal}) \) with respect to \( t \) after valve closure
Fig. 2.1.4.5. Doser response time while manually opening and closing the valve for (a) Ar \((m/e = 40)\) and (b) H\(_2\) \((m/e = 2)\). Dashed lines are merely a guide for the eye.

gave a linear decay \((\tau_{\text{Ar}} = 1.3 \ \text{s} \text{ and } \tau_{\text{H}_2} = 0.45 \ \text{s})\) with a nonlinear tail. The dead volume was then calculated from the relation \(V_{\text{dead}} = \tau C = 0.18 \ \text{cm}^3\).
2.2. Temperature-Programmed Desorption Method

To perform temperature-programmed desorption, several components are necessary: a doser, a sample, a reproducible heating scheme, and a probe of the desorption products. For a sample, Ge(100) (Si-Tech, Inc.), cut 4–6° off the (100) plane towards the [011] direction, 0.25–0.30 mm thick, n-type, $\rho = 5–40 \ \Omega \ cm$, and optically polished, was cut into a $13.4 \times 13.8 \ mm$ rectangle, degreased in acetone and ethanol, and placed into the vacuum chamber. A wafer cut vicinal to the (100) plane was chosen over one cut precisely on the (100) plane because for miscuts $\geq 4^\circ$, a double step forms between surface terraces, leading to dimer rows all in the same direction. For miscuts $<4^\circ$, single steps are formed between terraces, and the dimer rows on adjacent terraces are oriented $90^\circ$ to each other.\textsuperscript{48} (For the purposes of this study such an effect is of little importance, but for infrared absorption experiments bond orientations are crucial, especially when using polarized light.) The sample was cleaned by several sputter-and-anneal cycles ($i_{Ar^+} = 2–3 \ \mu A \ cm^{-2}$, $E_{Ar^+} = 500 \ V$, $T_{anneal} = 823 \ K$). The usable sample size facing the doser, between the clips, is $11.5 \ mm \times 13.4 \ mm$.

The doser is described above (§ 2.1.4), and is calibrated for a flow rate of $(2.42 \pm 0.14) \times 10^{16} \ M^{-1/2} \ molecule \ Torr^{-1} \ s^{-1}$, giving a calculated molecular flux of 17% of the molecules exiting the doser\textsuperscript{49} that strike the sample, when the manipulator is rotated to cause the sample to face the doser at a distance of $\sim 0.5 \ cm$. The heating system is composed of a 35 V, 30 A regulated DC power supply (Kikusui, PAD 35-30L) controlled by a programmable temperature controller (Eurotherm, 818P), with a ramping rate set to 2 K s$^{-1}$. Temperature control is linear to within 2 K of the expected temperature (for $T > 273 \ K$) as measured by a chromel-alumel thermocouple cemented into a small hole in the sample. When dosing into the chamber, H$_2$S (Airco, 99.5%, no further purification), H$_2$O (deionized and triply freeze-pump-thawed), NH$_3$ (M G Industries, 99.99%, no further
purification), HCl (Matheson, 99.0%, no further purification), and HBr (Matheson, 99.8%, no further purification) are used.

After dosing, once the pressure has come down to ~3–4 × 10⁻¹⁰ Torr, the sample is rotated to face the quadrupole mass spectrometer, which can be multiplexed to analyze up to three separate masses. Because germanium is composed primarily of three isotopes⁵⁰, Ge⁷⁰ (21%), Ge⁷² (27%), and Ge⁷⁴ (37%), when observing germanium etch products, the mass spectrometer is detuned slightly to increase sensitivity to all isotopes. The temperature ramp is begun, and, simultaneously, data-taking is started, controlled by an AT-compatible personal computer, up to a maximum temperature of 823 K. While the sample temperature is above 823 K, the titanium-sublimation pump is flashed for about one minute, for H₂S, H₂O, and NH₃ experiments. After flashing, the sample is allowed to slowly cool (2 K s⁻¹). During HCl and HBr experiments the titanium-sublimation pump is flashed immediately after large doses (before the ramp) to avoid chamber-wall desorption effects during detection of products.

2.3. Infrared-Sample Preparation

Because infrared spectroscopy is an important part of our laboratory’s repertoire for determining surface chemical properties, creation of multiple internal-reflection waveguide samples became a priority. Maximization of surface sensitivity was emphasized, meaning that long path lengths (i.e., many bounces inside the reflection element) were required. It was also hoped that a narrow element, similar in shape and size to the detector, would reduce infrared light loss, and so the “standard” internal reflection element became a 2-in.-long sample, 3 mm wide, fabricated from a wafer 0.25–0.35 mm thick, with ends beveled at an angle of 30°, and a trapezoidal profile, as shown in Fig. 2.3.1. Such a geometry results in ~150 bounces of light on each long face of the element.
Fabrication of an optical device out of a semiconductor, however, is a non-trivial matter. Germanium has a Mohs hardness of 6.3,\textsuperscript{51} while silicon has a hardness of 7.0,\textsuperscript{52} and both are rather brittle and fragile. After several generations of evolution, the following scheme emerged.

A semiconductor wafer, 0.25–0.35 mm thick and mirror polished on both faces, was hand-cut, using a glass-cutter fitted with a tungsten-carbide tip, into about half a dozen "blanks," mounted with a thermoplastic glue (Aremco, Crystalbond 509) in a custom-made tool-steel (Mohs hardness 6.75–7.75)\textsuperscript{53} jig with multiple slots (Fig. 2.3.2). The sides of

Figure 2.3.2. Jig for polishing sides of the infrared-capable samples.
the blanks were successively sanded and polished (400- and 600-grit SiC disks, then 15-μm and 6-μm diamond paste on nylon cloth, and finally 1-μm and 0.25-μm diamond paste on felt disks) on a rotary polisher (speed = 1–2 Hz). An hour or two of polishing at each grit size was required, and relative smoothness was judged using a low-power (×50) microscope. A final polish with an alkaline silica suspension (Remet, Syton HT-50) on a felt disk was carried out to attain a mirror finish.

The blanks were then carefully removed from the jig placed on a hot plate (~ 250 °F) so as to remelt the Crystalbond, and the residual glue was removed by dissolution in acetone. The slanted ends of the blanks were sanded and polished (same successive regime as in the previous paragraph) by mounting the blanks in a special two-part tool-steel jig with a triangular cross-section that held the blanks at a 30° angle, as shown in Fig. 2.3.3.

![Diagram of the jig for polishing ends of infrared-capable samples.](image)

**Figure 2.3.3. Jig for polishing ends of infrared-capable samples.**

An hour or two of polishing at each grit size was required once again, and smoothness was judged under a microscope, followed by Syton polishing. (Photomicrographs of samples at various sanding and polishing stages are displayed in Fig. 2.3.4.) The finished waveguides were removed from the triangular jig by mild heating on a hot plate and then dissolving off the Crystalbond residue with acetone.
Fig. 2.3.4. Appearance of germanium sample after polishing for 1–2 h with (a) 600-grit SiC, (b) 15-μm diamond paste, (c) 6-μm diamond paste, (d) 1-μm diamond paste, (e) 0.25-μm diamond paste, and (f) silica suspension (Syton). Magnification = 100 ×.
The resulting yield, using this procedure, was roughly 50–60% of the original blanks, after about 1 week of polishing time. With optimum alignment of the Fourier-transform infrared spectrometer (Mattson, Cygnus 100), optical train, sample, and InSb detector (Infrared Associates), signal-to-noise ratios for the frequency range 2100–2200 cm\(^{-1}\) of about \(1–3 \times 10^4\) were attained, at 4 cm\(^{-1}\) resolution, co-adding 256–1024 scans. For surfaces lacking Syton treatment (polishing stopped at the 0.25-μm-grit step), signal-to-noise ratios of roughly \(0.5–3 \times 10^3\) were seen, also at 4 cm\(^{-1}\) resolution, but co-adding 2048 scans. Though comprehensive studies on the precise improvement afforded by the addition of the Syton-polishing step have not been done, it seems that signal levels were improved substantially (\(> 30–50\%\)) when Syton was included. The infrared-capable samples were not used, however, in the experiments reported here, for technical difficulties prevented reproducible, even heating of the long, thin samples.

2.4. Gas-Handling System and Toxic-Gas Detector

Many of the adsorbates used in these or other experiments performed in this laboratory are highly toxic or explosive (e.g., \(\text{H}_2\text{S}\), \(\text{PH}_3\), \(\text{AsH}_3\), \(\text{PH}_3\), \(\text{H}_2\text{Se}\), \(\text{B}_2\text{H}_6\), \(\text{Si}_2\text{H}_6\)), hence safe handling of these materials is important. An extensive gas-handling system with a warning system was designed and installed to prevent injury from these materials. The system (Fig. 2.4.1) is made of three parts: (a) toxic-gas enclosure; (b) ventilation with blower; and (c) toxic-gas sensor and warning circuit.

The enclosure (~28 in. × 26 in. × 5 in.), which fit under the vacuum chamber, was designed under the assumption that most gases dosed into the chamber are contained in lecture bottles. (The sole exception to this assumption was digermane, \(\text{Ge}_2\text{H}_6\), diluted in helium, sold in a much larger container.) The enclosure was fabricated from sheet aluminum, with lucite doors in front to allow remote observation of the toxic gases in active use. Up to four different lecture bottles could be accommodated at once. The dosing
1. Exhaust blower  
2. Single-stage rotary vane pump  
3. Condensate trap  
4. Electromechanical venting valve  
5. Flexible steel formed bellows  
6. Electromechanical isolation valve  
7. Thermocouple gauge  
8. Manual venting valve  
9. Flexible steel formed bellows  
10. Manual isolation valve  
11. Manual isolation valve  
12. VCR connection (Ni gasket)  
14. Lead gasket seal  
15. Digermane (in helium) tank  
16. Lecture bottle  
17. Toxic-gas enclosure  
18. Convection gauge  
19. Viton O-ring connection  
20. Viton-O-ring-sealed valve  
21. Glass bulb for condensibles  
22. Capacitance manometer  
23. Hydrides sensor

**Figure 2.4.1.** Gas manifold connected to UHV chamber.
system, made of stainless-steel electropolished on the interior, ran through the enclosure, so gaps thus created in the walls of the enclosure were sealed with sheet rubber.

Ventilation to the enclosure was designed so that the enclosure was under negative pressure, i.e., ambient air would flow into the enclosure and up the ventilation stack, avoiding undesirable gas leakage into the laboratory room. With a hood volume of 1728 in$^3$ (2.11 ft$^3$), and assuming the access doors are nearly closed (standard operating condition) so that the open area to the room is 9 in. × 3 in., or 0.188 ft$^2$, we desired a complete air change, using an air velocity of 150 ft min$^{-1}$, of (150 ft min$^{-1}$ × 0.188 ft$^2$) = 28.2 ft$^3$ each minute. A calculation for such a system is shown in Table 2.4.1. To minimize diffusivity of gases through the ductwork walls into the laboratory atmosphere, chlorinated polyvinyl-chloride pipe (4 in. dia.) was run from the enclosure to the existing building hood ventilation system. A small blower (Grainger, 4C761, 46 ft$^3$ min$^{-1}$ at 0.1 in. static pressure) was installed near the junction to the hood system to pull exhaust gases through the enclosure and up the pipe. Because these toxic gases were dosed into the chamber and thus pulled through the various pumps, stainless-steel tubing (1/2 in. O.D.) was strung from the exhausts of the mechanical pumps to the polyvinyl chloride pipe. In this way, no exhaust gases are vented into the laboratory environment.

As a protective measure, a toxic-gas warning circuit (Fig. 2.4.2) was installed to

![Diagram of Toxic-gas warning circuit](image)

**Figure 2.4.2.** Toxic-gas warning circuit.
Table 2.4.1. Calculation of Velocity Pressure for Toxic-Gas Ventilation System.\textsuperscript{54}

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Volume (V)</td>
<td>28.2 ft(^3) m(^{-1})</td>
</tr>
<tr>
<td>Duct Length (L)</td>
<td>25.5 ft</td>
</tr>
<tr>
<td>Duct Diameter</td>
<td>4 in.</td>
</tr>
<tr>
<td>Duct Area (A)</td>
<td>0.0873 ft(^3)</td>
</tr>
<tr>
<td>Duct Velocity (V / A)</td>
<td>323 ft min(^{-1})</td>
</tr>
<tr>
<td>Velocity-Pressure(<em>{duct}) (VP(</em>{duct}))</td>
<td>0.01 in. H(<em>2)O / VP(</em>{duct})</td>
</tr>
<tr>
<td>Straight Duct Friction Factor (F)</td>
<td>12 VP(_{duct}) / 100 ft</td>
</tr>
<tr>
<td>Elbow Radius</td>
<td>1.5 radius / dia.</td>
</tr>
<tr>
<td>Elbow Pressure Loss Factor (E)</td>
<td>0.39 VP(_{duct}) / elbow</td>
</tr>
<tr>
<td>Acceleration Loss</td>
<td>1.2 VP(_{duct})</td>
</tr>
<tr>
<td>Hood Entry Loss</td>
<td>0.5 VP(_{duct})</td>
</tr>
<tr>
<td>Straight Duct Friction Loss (L (\times) F / 100)</td>
<td>3.06</td>
</tr>
<tr>
<td>Elbow Loss (E (\times) 5 elbows)</td>
<td>2.34 VP(_{duct})</td>
</tr>
<tr>
<td>Subtotal (S)</td>
<td>7.1 VP(_{duct})</td>
</tr>
<tr>
<td>Total Loss (S (\times) VP(_{duct}))</td>
<td>0.07 in. H(_2)O</td>
</tr>
<tr>
<td>Fan Static Pressure (Total Loss - VP(_{duct}))</td>
<td>(0.07 - 0.01) in. H(_2)O</td>
</tr>
<tr>
<td></td>
<td>= 0.06 in. H(_2)O</td>
</tr>
</tbody>
</table>

advise workers of any leakage within the toxic-gas enclosure. An electrochemical sensor attached to a hydrides monitor (Bionics Instrument Co., Ltd., TG-4000KA) was hung inside the enclosure. The monitor was equipped with an alarm which was inaudible away from the immediate area, so a remote alarm relay (Acromag, 160A-M-SN-NP-1) was attached to the 0–10 V chart recorder output of the monitor and installed outside the entrance to the laboratory. The relay activated a custom-built light bulb-and-household-
buzzer circuit as an audiovisual warning when the monitor measured hydrides beyond an adjustable chart-recorder-output level.
3. Data and Analysis

Dissociative adsorption on a (100) dimer involves breaking an intramolecular bond, thus creating two fragments, each of which saturates a surface "dangling bond". As sketched in Fig. 1.1.2, there is one monolayer of "dangling bonds" on a semiconductor (100) surface. With two fragments of adsorbate reacting with one monolayer of "dangling bonds," dissociative adsorption saturates the surface at 0.5 monolayer. (We argue in § 4.1, however, that a π-bond model is more appropriate than a "dangling bond" description in these sorts of adsorption reactions.) Examples of this adsorbate-substrate system include water on Ge(100)\textsuperscript{31b,33,34} and Si(100)\textsuperscript{34c,55} as well as on Si\textsubscript{x}Ge\textsubscript{1-x}(100)\textsuperscript{33b,35,56}, H\textsubscript{2}S on Ge(100)\textsuperscript{31,32} and Si(100)\textsuperscript{55g}, halogens on Ge(100)\textsuperscript{28a,30} and Si(100)\textsuperscript{57}, methanol\textsuperscript{58} and formic acid\textsuperscript{59} on Si(100), silane and disilane on Si(100),\textsuperscript{60} ammonia, NF\textsubscript{3}, and PH\textsubscript{3} on Si(100),\textsuperscript{61,62} and triethylgallium on Si(100).\textsuperscript{63} Coverage calibrations have been performed for H\textsubscript{2}S, H\textsubscript{2}O, and halogens on both Ge(100)\textsuperscript{30,31} and Si(100)\textsuperscript{55g,57a}, and NH\textsubscript{3} on Si(100)\textsuperscript{62g}, all of which indicate a saturation coverage of 0.5 monolayer. Therefore, in the following data,\textsuperscript{64} absolute coverages are obtained by assuming dissociative chemisorption, i.e., saturation coverage occurs at θ\textsubscript{sat} = 0.5 monolayers (ML).

3.1. Hydrogen Sulfide/Ge(100)

Fig. 3.1.1 presents a triply-multiplexed TPD spectrum for the desorption of 8.9 ± 1.1 ML of H\textsubscript{2}S from Ge(100) after adsorption at 273 K. Three m/e values were scanned: m/e = 2 (H\textsubscript{2}), 34 (H\textsubscript{2}S), and 104 (GeS). Fig. 3.1.1 clearly shows a desorption peak for H\textsubscript{2} at 570 K and a peak for GeS at 660 K. A weak feature in the m/e = 34 trace is attributed to desorption from supports.

A detailed look at the desorption of H\textsubscript{2} from H\textsubscript{2}S adsorption on Ge(100), as a function of surface exposure to H\textsubscript{2}S at 173 K, is shown in Fig. 3.1.2. A clearly asymmetric peak, whose peak temperature T\textsubscript{p} is invariant with respect to coverage, is easily
Fig. 3.1.1. Multiplexed TPD spectrum for \( H_2S \) desorption products from Ge(100) following a \( H_2S \) dose of 8.9 ± 1.1 ML at 273 K.

Fig. 3.1.2. \( H_2/H_2S/Ge(100) \) desorption at various initial coverages of \( H_2S \) (\( T_{dose} = 173 \) K).
seen again at 570 K, increasing with coverage up to saturation at 0.50 ML. Similar coverage-versus-exposure studies of GeS desorption from Ge(100) were not performed, given the reduced QMS sensitivity relative to hydrogen, as well as the implication from stoichiometry that equal amounts of H₂ and GeS are produced during the desorption reaction.

A comparison of coverage versus exposure for H₂S adsorbed on Ge(100) at several temperatures (173 K, 273 K, and 373 K) is given in Fig. 3.1.3. The data are fit to the function

\[ \theta = \theta_{\text{sat}} \left[ 1 - \exp \left( -\frac{S_0 \Phi t}{\theta_{\text{sat}}} \right) \right]. \]  

(3.1.1)

Fig. 3.1.3. H₂S coverage on Ge(100) as a function of H₂S exposure for dosing temperatures of 173 K (△), 273 K (○), and 373 K (□). \( \theta_{\text{sat}} \) is assumed to be 0.5 ML. Initial sticking probabilities obtained from least-squares fits are 0.28 ± 0.06 at 173 K, 0.19 ± 0.04 at 273 K, and 0.21 ± 0.06 at 373 K.
where $\theta$ is the coverage, $\theta_{\text{sat}}$ is the saturation coverage (0.5 ML), $S_0$ is the initial sticking probability, and $\Phi \cdot t$ (flux $\times$ time) is the dose. This function is appropriate for first-order Langmuir adsorption kinetics, i.e., if $S = S_0 \times (1 - \theta / \theta_{\text{sat}})^n$ such that the reaction order $n = 1$, and was chosen for convenience because present results cannot distinguish clearly between direct and precursor adsorption kinetics. Another reason is that with the given sample (Fig. 2.3.1) and doser configuration the gas flux is nonuniform across the lateral sample dimension. Therefore the only meaningful quantities that can be derived from adsorption kinetics are $S_0$ and $\theta_{\text{sat}}$. (Using the model defined by Eq. 3.1.1, the sticking probability decreases linearly with coverage from $S_0$ at $\theta = 0$ to $0$ at $\theta = \theta_{\text{sat}}$. For precursor kinetics, however, the sticking probability does not fall off so fast from zero coverage, until a critical coverage is reached where the molecules cannot so easily find the chemisorptive well, and so the sticking probability rapidly drops to zero.) For H$_2$S adsorption on Ge(100), there is little dependence of $S_0$ on temperature: $S_0$ decreases only slightly, from 0.28 to about 0.2 between 173 K and 373 K, and the decrease is within the precision of the measurements.

The error bars in the dosage shown in all coverage-versus-exposure graphs are based on an uncertainty in the dosage time $t$ of 0.5 s, with dosages ranging from $\sim 1$–200 s. Additional uncertainty arises from imprecision in doser backing pressure $P$, as measured by the capacitance manometer, of 0.02 Torr, in pressures ranging from 0.05–10 Torr, and the 6.1% uncertainty in the coefficient relating backing pressure in the doser to the flow rate (Eq. 2.1.4.5).

### 3.2. Water/Ge(100)

A triply-multiplexed TPD spectrum for desorption of H$_2$O from Ge(100) is presented in Fig. 3.2.1. The three $m/e$ values scanned are 2 (H$_2$), 18 (H$_2$O), and 88 (GeO). For H$_2$, a desorption peak at 570 K is observed, while for GeO a peak at 660 K is
seen. A large amount of water desorption from supports is evident from the strong increase in the H$_2$ and H$_2$O signals with higher temperatures.

TPD spectra for H$_2$ desorption from H$_2$O on Ge(100) as a function of coverage are shown in Fig. 3.2.2. The desorption peak, at 570 K, is invariant with respect to temperature. No concurrent coverage-versus-exposure experiments for GeO were done due to the reduced QMS sensitivity with respect to hydrogen, as in the case of GeS desorption from H$_2$S/Ge(100) (§ 3.1).

A comparison of coverage versus exposure for H$_2$O adsorbed on Ge(100) at several temperatures (173 K, 223 K, and 273 K) is given in Fig. 3.2.3. Just as for the coverage-versus-exposure data in Fig. 3.1.3 for H$_2$S/Ge(100), the H$_2$O/Ge(100) data are fit to a first-order Langmuirian model (Eq. 3.1.1). As is clear from Fig. 3.2.3, H$_2$O
Fig. 3.2.2. $\text{H}_2/\text{H}_2\text{O}/\text{Ge}(100)$ desorption at various initial coverages of $\text{H}_2\text{O}$ ($T_{\text{dose}} = 173 \text{ K}$).

Fig. 3.2.3. $\text{H}_2\text{O}$ coverage on $\text{Ge}(100)$ as a function of $\text{H}_2\text{O}$ exposure for dosing temperatures of 173 K, 223 K, and 273 K. $\theta_{\text{sat}}$ is assumed to be 0.5 ML. Values for $S_0$ from least-squares fits are $0.229 \pm 0.099$ at 173 K ($\square$), $0.021 \pm 0.013$ at 223 K ($\triangle$), and $0.017 \pm 0.011$ at 273 K ($\circ$).
adsorption on Ge(100) depends strongly on temperature: $S_0$ decreases dramatically, from $0.229 \pm 0.099$ at 173 K to $\leq 0.02$ at 273 K, although there is large scatter within the data sets taken at 223 K and 273 K.

### 3.3. Ammonia/Ge(100)

Numerous attempts were made to cause NH$_3$ to stick to the Ge(100) surface, but even with doses as high as 810 ML no evidence of desorption of H$_2$ or NH$_3$ was seen. Fig. 3.3.1 shows a doubly-multiplexed TPD scan taken observing $m/e = 2$ (H$_2$) and 17

![Graph showing TPD spectrum](image)

**Fig. 3.3.1.** Doubly-multiplexed TPD spectrum of desorption products from Ge(100) after dosing 810 ML of NH$_3$ ($T_{dose} = 173$ K).

(NH$_3$) at $T_{dose} = 173$ K, displaying a null result. If the TPD experiment's sensitivity is $\sim 0.05$ ML of an adsorbate (cf. Fig. 3.1.2), and 810 ML of NH$_3$ produces less than 0.05 ML, then the upper bound on $S_0$ for NH$_3$ at 173 K dosing temperature is $6 \times 10^{-5}$. 
3.4. Hydrogen Chloride/Ge(100)

A triply-multiplexed spectrum of desorption of HCl from Ge(100) is given in Fig. 3.4.1. The \( m/e \) values scanned were \( m/e = 2 \) (H\(_2\)), 36.5 (HCl), and 143 (GeCl\(_2\)), after saturated doses of HCl were applied. An obvious peak attributed to HCl (\( m/e = 36.5 \)) desorption is observed at 580 K; there is a peak from H\(_2\) (\( m/e = 2 \)) desorption at 570 K, and a desorption feature from GeCl\(_2\) (\( m/e = 143 \)) is found at \( \sim 680 \) K.

To determine the absolute saturation coverage of the H\(_2\) desorption product from HX/Ge(100), doses were calibrated against saturated H\(_2\) desorption features from H\(_2\)S/Ge(100). Because the saturation coverage of H\(_2\)S (\( \theta_{H_2S,sat} \)) is believed to be 0.5 monolayer on Ge(100)\(^{31} \), the coverage of H atoms on a H\(_2\)S-saturated surface (\( \theta_{H/H_2S,sat} \)) must be one monolayer. As with other hydrides, we assume HX saturation (\( \theta_{HX,sat} \)) occurs at 0.5 monolayer on Ge(100), so that saturation coverage of both H atoms
(\(\theta_{H/HX,\text{sat}}\)) and X atoms (\(\theta_{X/HX,\text{sat}}\)) also must be 0.5 monolayer. During sample heating, some H(a) and X(a) pair up to desorb as HX, while some H(a) atoms pair up to desorb as H\(_2\). The ratio of the saturated H\(_2\)/HX desorption peak to the saturated H\(_2\)/H\(_2\)S is therefore the fraction of monolayer coverage for H atoms desorbing as H\(_2\) from HX. Once the saturation coverage of H\(_2\) from HX/Ge(100) is known, it is simple to calculate the saturation coverage of the remaining H atoms (and hence HX molecules) from HX/Ge(100) using the relation \(\theta_{HX/HX,\text{sat}} = 0.5 - \theta_{H_2/HX,\text{sat}}\). Finally, any X(a) remaining above \(\sim 610 \text{ K}\) desorbs as GeX\(_2\). Hence, from stoichiometry, for every hydrogen molecule desorbing from HX/Ge(100), there must be a GeX\(_2\) molecule desorbing, so \(\theta_{GeX_2/HX,\text{sat}} = \theta_{H_2/HX,\text{sat}}\).

Fig. 3.4.2, the change in H\(_2\) desorption with HCl coverage on Ge(100), reveals no \(T_p\) shift as coverage increases up to saturation at 0.264 ML in the asymmetrically-shaped peak, indicating that the H\(_2\) desorption process is first-order. Similarly, a comparison of

![Graph showing coverage (monolayers) vs. Ge(100) substrate temperature/K](image)

**Fig. 3.4.2.** H\(_2\)/HCl/Ge(100) desorption at various initial coverages of HCl (\(T_{dose} = 273 \text{ K}\)).
Fig. 3.4.3. HCl/HCl/Ge(100) desorption at various initial coverages of HCl ($T_{dose} = 273$ K). The saturation coverage has been scaled to 0.236 ML.

HCl desorption at various initial coverages (Fig. 3.4.3) is also first order up to saturation at 0.236 ML at a dosing temperature of 273 K. Graphs of the coverage-versus-exposure data for H$_2$ and HCl desorption are exhibited in Figs. 3.4.4 and 3.4.5, from which are calculated the apparent initial sticking probabilities for H$_2$/HCl ($S_0 = 0.142 \pm 0.020$) and HCl/HCl ($S_0 = 0.157 \pm 0.096$). Given a scenario of dissociative chemisorption with subsequent diffusion and mixing of the adsorbed species, to calculate the actual $S_0$ for HCl adsorption the two apparent sticking probabilities must be added. In this manner one gets $S_0$ for HCl adsorption of $0.299 \pm 0.098$ at $T_{dose} = 273$ K.

The higher temperature desorption product, GeCl$_2$, was also investigated. Fig. 3.4.6 shows GeCl$_2$ desorption peaks at various initial coverages, revealing second-order desorption kinetics. A coverage-versus-desorption graph, plotted in Fig. 3.4.7 for a
Fig. 3.4.4. \( \text{H}_2 \) desorption from Ge(100) as a function of HCl exposure for \( T_{\text{dose}} = 273 \) K. Saturation coverage = \( 0.264 \times \theta_{\text{sat,H}_2/H_2S} \). Initial sticking probability obtained from a least-squared fit = 0.142 \( \pm \) 0.020.

Fig. 3.4.5. HCl desorption from Ge(100) as a function of HCl exposure for \( T_{\text{dose}} = 273 \) K. Saturation coverage = 0.236 ML. \( S_0 \) obtained from a least-squared fit = 0.157 \( \pm \) 0.096.
Fig. 3.4.6. GeCl$_2$/HCl/Ge(100) desorption at various initial coverages of GeCl$_2$ from HCl ($T_{\text{dose}} = 273$ K). Due to digitization noise and low signal levels, the data were fit to Gaussian curves.

Fig. 3.4.7. GeCl$_2$ coverage on Ge(100) as a function of HCl exposure for a $T_{\text{dose}}$ of 273 K. $\theta_{\text{sat., GeCl}_2}$ is scaled to 0.264 ML. $S_0$ obtained from a least-squares fit is 0.184 ± 0.014.
dosing temperature of 273 K and stoichiometrically scaled to saturation at 0.264 ML, results in an initial sticking probability of 0.184 ± 0.014. Because it is sufficiently similar to that for H₂ desorption for HCl ($S_{0,H_2/HCl} = 0.142 ± 0.020$), this value confirms the reliability of $S_{0,H_2/HCl}$.

When HCl was adsorbed onto Ge(100) at a higher temperature, 373 K, sticking probabilities fell significantly, along with the saturation coverage of H₂ to 0.218 monolayer. Figs. 3.4.8 and 3.4.9 reveal $S_{0,H_2} = 0.030 ± 0.002$ and $S_{0,HCl} = 0.036 ± 0.001$, respectively, providing an initial sticking probability for HCl adsorption on Ge(100) of 0.066 ± 0.002 at $T = 373$ K.

![Graph](image)

**Fig. 3.4.8.** H₂ coverage on Ge(100) as a function of HCl exposure for a $T_{dose}$ of 373 K. $\theta_{sat,H_2}$ is scaled to $0.218 \times \theta_{sat,H_2/H_2S}$. $S_0$ obtained from a least-squares fit is 0.030 ± 0.002.
3.5. Hydrogen Bromide/Ge(100)

As with HCl, the reaction of HBr with Ge(100) results in several desorption products, as shown in Fig. 3.5.1. A strong $H_2$ ($m/e = 2$) desorption was seen at 570 K, along with HBr ($m/e = 81$) desorption at 580 K. The expected high-temperature etching product analogous to GeCl$_2$, namely, GeBr$_2$, could not be detected, possibly due to loss of mass-spectrometer sensitivity at relatively high mass ($m/e = 244$), but its cracking fraction, GeBr ($m/e = 153$), was observed with the QMS at a peak temperature of $\sim 710$ K, only after extreme detuning of the mass spectrometer and scanning without multiplexing other masses.

Determination of absolute $H_2$ coverage from HBr absorption follows the method outlined for $H_2$ from HCl absorption in the previous section, i.e., comparison to the $H_2$...
Fig. 3.5.1. HBr desorption products from Ge(100) following HBr saturation doses at 273 K. The H$_2$ and HBr scans (dose = 136 ± 8 ML) were multiplexed together; the GeBr scan (dose = 29.1 ± 3.2 ML) was taken separately after extreme detuning of the QMS.

desorption peak area from H$_2$S. At a dosing temperature of 273 K, $\theta_{H_2/HBr, sat} = 0.297 \times \theta_{H_2/H_2S, sat}$, and at 373 K $\theta_{H_2/H_2Br, sat} = 0.277 \times \theta_{H_2/H_2S, sat}$. (An attempt was made to measure $\theta_{H_2/HBr, sat}$ at $T_{dose} = 448$ K, but desorption of H$_2$S was already significant by that temperature, destroying the calibration.) A graph of coverage versus exposure for H$_2$ at a dosing temperature of 273 K is exhibited in Fig. 3.5.2, which clearly shows the hallmarks of first-order desorption: asymmetric peaks and no peak shift with coverage. The saturation coverage for H$_2$ was scaled to 0.297 monolayer. The graph of desorption versus coverage for HBr ($m/e = 80$) is exhibited in Fig. 3.5.3, which, likewise, reveals first-order desorption, and is scaled to $0.5 - 0.297 = 0.203$ monolayer saturation for HBr.

Coverage-versus-exposure data for H$_2$ and HBr desorption at 273 K are given in Figs. 3.5.4 and 3.5.5, respectively. Initial sticking probabilities were calculated to be
Fig. 3.5.2. $H_2/HBr/Ge(100)$ desorption at various initial coverages of HBr ($T_{\text{dose}} = 273$ K). The saturation coverage has been scaled to $0.297$ of $\theta_{H_2,\text{sat}}$ from $H_2S$ at $T_{\text{dose}} = 273$ K.

Fig. 3.5.3. HBr/HBr/Ge(100) desorption at various initial coverages of HBr ($T_{\text{dose}} = 273$ K).
Fig. 3.5.4. $H_2$ desorption from Ge(100) as a function of HBr exposure for $T_{\text{dose}} = 273$ K. Initial sticking probability obtained from a least-squared fit = 0.572 ± 0.058.

$S_{0,\text{H}_2/\text{HBr}} = 0.572 \pm 0.058$ and $S_{0,\text{HBr}/\text{HBr}} = 0.200 \pm 0.012$, giving an initial sticking probability for HBr adsorption at 273 K of 0.772 ± 0.059.

The remaining high-temperature product, GeBr$_2$, was detected as the GeBr cracking fraction, as explained earlier. A series of desorption-versus-coverage scans at $T_{\text{dose}} = 273$ K are shown in Fig. 3.5.6, indicating second-order desorption at $T_p = 710$ K. Coverage-versus-exposure data are given in Fig. 3.5.7, scaled to $\theta_{\text{GeBr}_2/\text{HBr, sat}} = 0.297$, and result in $S_{0,\text{GeBr}_2/\text{HBr}} = 0.428 \pm 0.027$, in fair agreement with $S_{0,\text{H}_2/\text{HBr}}$.

When the dosing temperature was raised to 373 K, sticking probabilities fell, as shown in Figs. 3.5.8 ($\text{H}_2/\text{HBr}$) and 3.5.9 ($\text{HBr}/\text{HBr}$), to $S_{0,\text{H}_2/\text{HBr}} = 0.418 \pm 0.010$ and $S_{0,\text{HBr}/\text{HBr}} = 0.134 \pm 0.008$. Adding these two apparent initial sticking probabilities results in an actual initial sticking probability for HBr adsorption = 0.552 ± 0.013, a drop of ~ 30% from 273 K. An attempt—not shown here—was made to determine the fate of $S_0$
Fig. 3.5.5. HBr desorption from Ge(100) as a function of HBr exposure for $T_{\text{dose}} = 273$ K. Initial sticking probability, obtained from a least-squared fit, is $0.200 \pm 0.012$.

<table>
<thead>
<tr>
<th>Trace</th>
<th>Coverage (monolayers)</th>
<th>$T_p$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.30</td>
<td>708</td>
</tr>
<tr>
<td>b</td>
<td>0.24</td>
<td>720</td>
</tr>
<tr>
<td>c</td>
<td>0.14</td>
<td>732</td>
</tr>
<tr>
<td>d</td>
<td>0.11</td>
<td>744</td>
</tr>
<tr>
<td>e</td>
<td>0.03</td>
<td>767</td>
</tr>
</tbody>
</table>

Fig. 3.5.6. GeBr/HBr/Ge(100) desorption at various initial coverages of GeBr$_2$ from HBr ($T_{\text{dose}} = 273$ K).
Fig. 3.5.7. GeBr$_2$ coverage on Ge(100) as a function of HBr exposure for a $T_{\text{dose}}$ of 273 K. $\theta_{\text{sat,GeBr}_2}$ is scaled to 0.297 ML by stoichiometric comparison to $\theta_{\text{sat,H}_2}$. $S_0$ obtained from a least-squares fit is 0.428 ± 0.027.

Fig. 3.5.8. H$_2$ coverage on Ge(100) as a function of HBr exposure for a $T_{\text{dose}}$ of 373 K. $\theta_{\text{sat}}$ is scaled to 0.277 ML by comparison to $\theta_{\text{sat,H}_2/H_2S}$. $S_0$ obtained from a least-squares fit is 0.418 ± 0.010.
Fig. 3.5.9. HBr coverage on Ge(100) as a function of HBr exposure for a dosing temperature of 373 K. $\theta_{\text{sat}}$ is scaled to 0.223 ML by comparison to $\theta_{\text{sat,H}_2/\text{HBr}}$. The initial sticking probability obtained from a least-squares fit is $0.134 \pm 0.008$.

at a still higher temperature (448 K). Although significant desorption of H$_2$ from H$_2$S made calibration of the H$_2$/HBr peak unfeasible, it seems probable that $S_0$ may be as low as 0.05.
4. Results and Discussion

4.1. Ge(100) Dimer as Doubly-Bonded Species

4.1.1. Structure of Digermenes

Disilenes (compounds containing Si=Si bonds) and digermenes (compounds containing Ge=Ge bonds) have been known for over a decade. The first report of a disilene was published by West and coworkers in 1981, and involved photolysis of a trisilane into a sterically-hindered disilene. Numerous other substituted disilenes have followed. Likewise, synthesis of a digermene was achieved by Masamune and coworkers in 1982, and other substituted digermenes have been reported since (Fig. 4.1.1). While the double-bond character of Group 14 compounds decreases as one moves down the column, considerable π-bond character remains even with Sn=Sn bonds.

Lendvay recently has calculated the bond order for Si=Si as 1.76 and Ge=Ge as 1.61. It is therefore prudent to consider the Ge(100) surface, usually regarded as an extended array of dimers with dangling bonds, instead as an array of Ge=Ge species. A “dangling bond”

![Diagram of digerme analogs](image)

**Fig. 4.1.1.1. Several molecular digermene analogs of a Ge(100) dimer.**
model suggests almost no overlap between neighboring electronic wavefunctions, yet the chemistry of molecular compounds with singly-occupied orbitals on adjacent Si or Ge atoms is much better described by the existence of a π-bond.

Table 4.1.1.1. Structural data for several disilenes and digermmes (RR'M=MR'R).

<table>
<thead>
<tr>
<th>M</th>
<th>Substituent</th>
<th>M=M bond length (Å)</th>
<th>folding angle θ (deg)</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>mesityl</td>
<td>2.160 ± 0.001</td>
<td>18</td>
<td>66f, g</td>
</tr>
<tr>
<td>Si</td>
<td>2,6-Et₂Φ</td>
<td>2.133 ± 0.003</td>
<td>0</td>
<td>66c</td>
</tr>
<tr>
<td>Si</td>
<td>R = mesityl (trans isomer) R' = t-Bu</td>
<td>2.140 ± 0.003</td>
<td>0</td>
<td>66g, h</td>
</tr>
<tr>
<td>Ge</td>
<td>(Me₃Si)₂CH</td>
<td>2.347 ± 0.002</td>
<td>32</td>
<td>68a</td>
</tr>
<tr>
<td>Ge</td>
<td>2,6-Et₂Φ</td>
<td>2.213 ± 0.003</td>
<td>15</td>
<td>67</td>
</tr>
<tr>
<td>Ge</td>
<td>R = 2,6-iPr₂Φ (Z isomer) R' = mesityl</td>
<td>2.301 ± 0.001</td>
<td>36</td>
<td>68b</td>
</tr>
</tbody>
</table>

Calculations by Trinquier and Malrieu⁷⁰ as well as by Liang and Allen⁷¹ indicate that the molecular Ge=Ge bond is trans-bent by 32–39° (the folding angle θ), with a Ge=Ge bond length of 2.21–2.30 Å [Fig. 4.1.1.2 (a)]. Structural determinations of known digermmes (Table 4.1.1.1) indicate a trans-bent structure with a folding angle of 15–36°, and a Ge=Ge bond length of 2.21–2.35 Å. A Ge(100) surface dimer, however, is cis-bent with its Ge=Ge bond elongated to roughly 2.41 Å (2.34 ± 0.04 Å parallel to the surface, according to x-ray diffraction data reported by Grey, et al.⁷², combined with a tilt⁷⁸a,⁷³ calculated to be about 14° with respect to the surface¹³ε [Fig. 4.1.1.2 (b)]). A π-bond in surface dimers thus will be weaker and more reactive than that in analogous disilenes and digermmes because lattice strain increases the dimer bond length and reduces
the orbital overlap. Isomerization measurements\textsuperscript{68b} and theoretical computations\textsuperscript{74} indicate a $\pi$-bond strength of approximately 88–110 kJ mol$^{-1}$ for both disilenes and digermenes.

4.1.2. Chemistry of Disilenes and Digermenes

There are a number of reviews concerning the chemistry of doubly-bonded Group 14 elements.\textsuperscript{66d,75} Due to the longer $\sigma$-bond distances of Si–Si and Ge–Ge, $p_\pi - p_\pi$ overlap is poor, so weaker $\pi$-bonds compared to ethene derivatives are formed. These Si=Si and Ge=Ge systems are more reactive than C=C bonds, so must be sterically protected, but nevertheless undergo olefinic reactions. Addition to the double bond is well-known, including water, alcohols, halogens, and HCl to form R$_2$HM–M(OH)R$_2$, R$_2$HM–M(OR)$_2$, R$_2$XM–MXR$_2$, and R$_2$HM–MClR$_2$. Cycloaddition also has been reported, both for carbonyls and ethynes to form compounds a and b.\textsuperscript{65,66d,76} Further similarity to alkenes is indicated by reaction of disilenes with diazomethane to give disilacyclop propane [Eq. 4.1.2.1 (a)] and with phenylazide to produce disilaziridine\textsuperscript{66d} [Eq. 4.1.2.1 (b)].
As one moves down the Group 14 column, increasing preference for the MII oxidation state exists and so digermenes are much less stable than disilenes, hence tend to retain the monomeric form :GeR₂ in solution.²⁸a,²⁶a Few addition reactions to trap digermenes are known, but do include methanol addition across the double bond.²⁷

Synthesis of disilenes is accomplished by photolysis²⁶d, or elimination of halogens from 1,2-dihalotetraorganodisilanes:

\[
\text{(a)} \quad R_2\text{Si}=\text{SiR}_2 + \text{CH}_2\text{N}_2 \rightarrow R_2\text{Si}=\text{SiR}_2 + \text{N}_2
\]

\[
\text{(b)} \quad R_2\text{Si}=\text{SiR}_2 + \phi \text{N}_3 \rightarrow R_2\text{Si}=\text{SiR}_2 + \phi \text{N}_3 \rightarrow R_2\text{Si}=\text{SiR}_2 + \text{N}_2 \quad (4.1.2.1)
\]

In the case of digermenes, reductive cyclizations are performed, followed by photolysis as with disilenes²⁷:

\[
\text{(a)} \quad R_2\text{Si} \xrightarrow{\text{hv} = 254 \text{ nm}, -60^\circ} R_2\text{Si}=\text{SiR}_2 \quad (4.1.2.2)
\]

\[
\text{(b)} \quad R_2\text{Si}=\text{SiR}_2 \xrightarrow{\text{alkali metal}} 2\text{M}X + R_2\text{Si}=\text{SiR}_2
\]

\[
R_2\text{GeCl}_2 \xrightarrow{\text{LiC}_10\text{H}_8} \xrightarrow{\text{hv}} R_2\text{Ge}=\text{GeR}_2 \quad (4.1.2.3)
\]

4.1.3. Adsorption as a Type of Digermene Addition

The link between (100) surface dimers and molecular dimetallenes now becomes clear: if the dimers are essentially highly strained dimetallenes, then they ought to undergo dimetallene chemistry. With the π-bond picture in mind, dissociative adsorption on semiconductor (100) surfaces ought to be viewed as an addition reaction, analogous to similar additions to disilenes and digermenes, discussed in the previous section. Hydride
desorption should likewise be viewed as an elimination reaction, analogous to eliminations known or calculated for disilanes and digermanes.66a,66d,77

A high sticking probability implies a very small activation energy for addition, which, in turn, suggests a four-center transition state, in which new adsorbate-dimer bonds are formed at the same time that intra-adsorbate bonds are being broken, as illustrated in Eq. 4.1.2.1:

\[
\begin{align*}
\text{H—B} & \quad \xrightarrow{\text{Ge=Ge}} \quad \text{[H····B] } \\
\text{Ge=Ge} & \quad \xrightarrow{\text{Ge=Ge}} \quad \text{HGe—Ge} \quad \xrightarrow{\text{Ge=Ge}} \quad \text{H—B}
\end{align*}
\]

(4.1.2.1)

Four-center transition states for molecular reactions are well-known and have been proposed for silicon compounds since the early 1960s.78 They also have been predicted for addition of water to disilene and germaethene (H₂Ge=CH₂) by ab initio calculations of Nagase and coworkers.79 It is suggested that similar transition states occur for adsorbates on semiconductor surface dimers.

For the case of H₂ adsorption, however, a symmetric four-center transition state is symmetry-forbidden,80 and would not be expected to occur. If, though, as seems likely, the Si(100) and Ge(100) dimers are asymmetric, the strict applicability of orbital-symmetry as delineated by Woodward and Hoffmann is called into question, and four-center transition states thus may be possible for adsorption of H₂. It is well known, however, that the sticking probability for molecular hydrogen on these dimers is extremely small,7a for significant hydrogen adsorption must be effected by dissociation of H₂ into atomic H. This observation may be explained through arguments that bond-length mismatch between the short H—H bond and the very much longer Ge—Ge or Si—Si bond result in extremely poor orbital interactions as well as from symmetry-induced unfavorable energetics.
4.2. Precursor Model

Explanation of the decrease in the sticking probability, generally seen for molecules that dissociatively adsorb on silicon and germanium surfaces, is readily explained qualitatively by a precursor model.\textsuperscript{36d,81} As first envisioned by Lennard-Jones,\textsuperscript{82} molecules colliding with a surface initially feel a weak physisorptive attraction, and then a stronger, chemisorptive well (Fig. 4.2.1). Shown schematically in Fig. 4.2.2, some

![Diagram of potential-energy curves and trajectories](image)

**Fig. 4.2.1.** Potential-energy curves for a hydride HB near a surface, invoking a precursor model.

**Fig. 4.2.2.** Possible trajectories for an incoming hydride HB.
fraction of molecules colliding with the surface become trapped in a physisorption well and may undergo numerous bounces against the surface layer of atoms, before ultimately desorbing or dissociatively adsorbing. Two crucial factors are the magnitude of the activation energy for dissociation and the depth of the physisorption well: if there is a low activation energy for dissociation or there also is a deep physisorption well—permitting more “attempts” at dissociation—then dissociative chemisorption is favored.

The size of the barrier to dissociation may also affect the ease with which an impinging molecule can stick to a surface. If the barrier is small, then the adsorbate’s initial sticking probability $S_0$ will be independent of the substrate temperature. If the barrier is large, however, then there will be a temperature effect on $S_0$. Another factor with which to contend is the trapping probability $\alpha$ for becoming trapped in the physisorption well rather than scattering off of the surface.

4.3. Thermochemistry of Hydride Adsorption

Accurate values of the enthalpy for dissociative adsorption $\Delta H_{\text{ads}}$ of the hydrides H$_2$S, H$_2$O, and NH$_3$ are not attainable due to lack of high-quality thermochemical data for germanium compounds, but rough estimates are given in Table 4.3.1. Using bond energies can help rationalize the observed trends. Adsorption of HB (B = SH, OH, NH$_2$, Cl, or Br) results in breaking the H—B bond and the Ge—Ge dimer $\pi$ bond and in the formation of Ge—H and Ge—B bonds. From Table 4.3.1, we see that the enthalpy of adsorption for H$_2$O greatly exceeds that of adsorption for NH$_3$ (the difference is 152 ± 33 kJ mol$^{-1}$). Because activation energies tend to be smaller for more exothermic reactions,$^{83}$ the large difference in $\Delta H_{\text{ads}}$ for H$_2$O and NH$_3$ is consistent with the observed greater reactivity ($S_0$) for H$_2$O, as well as suggesting that dissociative adsorption of NH$_3$ on Ge(100) has an activation barrier. Of course, the large $\Delta H_{\text{ads}}$ for both HCl and HBr on Ge(100) causes the substantial sticking probabilities (0.3 ~ 0.8) for both admolecules.
Table 4.3.1. Calculation$^{84}$ of $\Delta H_{ads}$ for M dimer + HB(g) $\rightarrow$ H(a) + B(a), compared to the desorption barrier $E_d$ calculated with Eq. 1.3.7.

<table>
<thead>
<tr>
<th>M</th>
<th>HB</th>
<th>$\Delta H_{ads}$/kJ mol$^{-1}$</th>
<th>$E_d$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>H$_2$</td>
<td>$-202 \pm 12$</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>NH$_3$</td>
<td>$-273 \pm 17$</td>
<td>190$^{62}$</td>
</tr>
<tr>
<td>Si</td>
<td>H$_2$O</td>
<td>$-386 \pm 12$</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>H$_2$S</td>
<td>$-256 \pm 10$</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>HCl</td>
<td>$-260 \pm 9$</td>
<td>220$^{85}$</td>
</tr>
<tr>
<td>Si</td>
<td>HBr</td>
<td>$-331 \pm 9$</td>
<td>220$^{85}$</td>
</tr>
<tr>
<td>Ge</td>
<td>H$_2$</td>
<td>$-146 \pm 23$</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>NH$_3$</td>
<td>$-116 \pm 28$</td>
<td>...</td>
</tr>
<tr>
<td>Ge</td>
<td>H$_2$O</td>
<td>$-268 \pm 17$</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>H$_2$S</td>
<td>$-201 \pm 20^{86}$</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>HCl</td>
<td>$-336 \pm 17$</td>
<td>155$^{87}$</td>
</tr>
<tr>
<td>Ge</td>
<td>HBr</td>
<td>$-302 \pm 17$</td>
<td>155$^{85}$</td>
</tr>
</tbody>
</table>

To resolve the apparent paradox of the high reactivity of H$_2$S on Ge despite its smaller $\Delta H_{ads}$ compared to H$_2$O, the HS—H bond length (1.34 Å) is considerably longer than HO—H (0.958 Å),$^{84}$ suggesting that addition of H$_2$S may be geometrically more favorable on the long Ge=Ge bond. The generally longer bond lengths with sulfur, a third-row element, imply a larger, more extended transition state, suggesting a shallower and more easily accessible “channel” for the physisorbed H$_2$S to enter, causing a larger value for $S_0$. The much smaller decrease in $S_0$ with temperature for H$_2$S than for H$_2$O is consistent both with a smaller dissociative activation barrier and a smaller heat of physisorption, when employing a precursor model.
With the precursor model, one can also investigate the relationship of \( S_0 \) for \( \text{H}_2\text{O} \) to adsorption temperature, 

\[
S_0(T) = \frac{\alpha}{1 + \frac{k_d}{k_c}}
\]

(4.3.1)

where \( \alpha \) = the trapping probability of a molecule into a physisorbed precursor state, and \( k_d/k_c \) is the ratio of rate constants for desorption and chemisorption of the precursor. We can write an Arrhenius expression for the rate constants, \( k_d/k_c = (\nu_d/\nu_c) \exp(-\Delta E/RT) \), in which \( \nu_d/\nu_c \) is the ratio of pre-exponential factors for desorption and chemisorption, and \( \Delta E \) is the difference between the energy barriers for desorption and chemisorption of the precursor state. Substituting the Arrhenius expression for \( k_d/k_c \) in Eq. 4.3.1, we obtain Eq. 4.3.2:

\[
S_0(T) = \frac{\alpha}{1 + \frac{\nu_d}{\nu_c} \exp \left( \frac{-\Delta E}{RT} \right)}
\]

(4.3.2)

Assuming \( \alpha = 1 \), a two-parameter fit (Fig. 4.3.1) was performed on the data for \( S_0(T) \) of \( \text{H}_2\text{O}/\text{Ge}(100) \), resulting in the values \( \nu_d/\nu_c = 14 \, 400 \pm 12 \, 200 \) and \( \Delta E = 12.1 \pm 1.1 \) kJ mol\(^{-1}\). Extrapolating Eq. 4.3.2 to \( T = 0 \), we expect \( S_0 \) to rise to unity, for as \( T \) decreases, \( \exp(-\Delta E/RT) \to 0 \), hence \( S_0 \to \alpha \).

An estimate of \( E_d \), the barrier from the physisorbed precursor state to desorption, was obtained by comparing it to known values of \( E_d \) of monolayer desorption of \( \text{H}_2\text{O} \) from metals. TPD studies\(^{88}\) show a peak attributed to monolayer desorption of water from metals typically in the temperature range 160–190 K. Using Redhead’s equation\(^{38}\) to calculate \( E_d \) based on the peak temperature,

\[
\frac{E_d}{RT_p} = \ln \left( \frac{\nu T_p}{\beta} \right) - 3.64,
\]

(4.3.3)

where \( R \) = the gas constant, \( \nu \) = reaction rate constant (for first-order reactions, assumed to
Fig. 4.3.1. Dependence of H$_2$O initial sticking probability on Ge temperature. The solid curve is a two-parameter fit ($\alpha$ is assumed to be 1).

be $10^{13}$ s$^{-1}$ and $\beta = 10$ K s$^{-1}$, with $T_p = 175 \pm 15$ K, then $E_d = 42 \pm 4$ kJ mol$^{-1}$. From the definition $\Delta E \equiv E_d - E_c$, the energy for H$_2$O chemisorption on Ge(100) from the precursor state was calculated, $E_c = 29 \pm 4$ kJ mol$^{-1}$, which is comparable to the calculated barrier for addition of water to germaethene ($\sim 47$ kJ mol$^{-1}$), silaethene ($\sim 44$ kJ mol$^{-1}$), and disilene ($\sim 35$ kJ mol$^{-1}$).$^{78c,79}$

4.4. Desorption of H$_2$

Both experiment$^{21,89b,89c}$ and theory$^{20}$ suggest that approximately first-order desorption of H$_2$ from the Si(100) surface is a consequence of preferential pairing of H atoms on dimers. Given the first-order kinetics for H$_2$ desorbing from Ge(100) at 570 K in Figs. 3.1.2 and 3.2.2, it is evident that similar considerations apply to Ge(100). An
interesting result is that co-adsorbed S, O, Cl, or Br hardly affects the kinetics, for $T_p$ is essentially identical for desorption from adsorbed H, H + O, H + S, H + Cl, and H + Br on Ge(100). Assuming a pre-exponential factor of $10^{13}$ s$^{-1}$, the observed peak desorption temperature of 570 K and Eq. 4.3.3 give an estimate of 150 kJ mol$^{-1}$ for the activation energy for desorption of H$_2$.

4.5. Desorption of GeY (Y = S or O)

After dosing the Ge(100) surface with H$_2$S or H$_2$O, and then heating above $\sim$ 570 K, the desorption temperature of H$_2$, only adsorbed S or O remains. From previous studies information on the structure of O(a) is available. Both an EELS study of O/Ge(100) and infrared spectroscopy of acid-etched Ge observed a Ge–O vibrational mode at 810–860 cm$^{-1}$. This frequency range indicates that the stable form of O(a) on Ge(100) is a bridge-bonded species, as on Si(100). A germanone-like terminally-bonded oxygen moiety, which is not observed, would have exhibited a Ge–O stretching frequency near 970 cm$^{-1}$, as seen in germanone (H$_2$Ge=O) and germanic acid ((HO)$_2$Ge=O).

The observation, however, that GeO and GeS desorb at the same temperature, 660 K, suggests that the rate-limiting step in desorption involves bond breakage between Ge atoms, and not between Ge and O or S. A plausible mechanism, therefore, is that bridge-bonded Y (Y = S or O) rearranges to form a germanone- or germathione-like species (R$_2$Ge=Y) prior to desorption, as proposed in Eq. 4.5.1.

$$
\begin{array}{c}
  \text{Ge} \\
  \text{Y} \\
  \downarrow \\
  \text{Ge=Ge} \\
\end{array} \xrightleftharpoons{K} \begin{array}{c}
  \text{Y} \\
  \downarrow \\
  \text{Ge} \\
\end{array} \xrightarrow{K} \begin{array}{c}
  \text{Ge} \\
  \text{Y} \\
\end{array}
$$

(4.5.1)

Though Green, in 1963, discounted the possibility of a germanone-like stable moiety to describe O/Ge(100) on the basis of lack of known molecular compounds for comparison, germanones and germathiones later were postulated as intermediates and have been
isolated and characterized spectroscopically in low-temperature matrices.\textsuperscript{91,94} Three-membered Ge rings exist in molecular cyclotrimeranes and hexagermanaprismanes (Fig. 4.5.1), the former being useful as digermene precursors.\textsuperscript{67,68,95} The mechanism then supposes that the surface germathione or germanone decomposes near 660 K through a three-center transition state, common in pyrolytic organic reactions.

![Cyclotrimerane](image1)

![Hexagermanaprismane](image2)

**Fig. 4.5.1.** Known molecular analogs of the proposed cyclotrimeranium surface intermediate.

If interconversion of Y(a) and GeY(a) is fast compared to desorption of GeY, one may assume a quasiequilibrium, so that the effective rate constant for desorption will be $k_{\text{eff}} = k K$. Assuming a pre-exponential factor of $10^{16} \text{ s}^{-1}$, which is larger than the typical value of $10^{13} \text{ s}^{-1}$, but similar to that observed for GeO desorption by Madix and colleagues\textsuperscript{22c} ($7 \times 10^{15} \text{ s}^{-1}$) and Surnev and Tikhov\textsuperscript{22f} ($10^{16} \pm 0.5 \text{ s}^{-1}$), the observed $T_p$ of 660 K provides an estimate of $\sim 213 \text{ kJ mol}^{-1}$ for the desorption activation energy of GeY. Such a value is in agreement with those reported by Madix and coworkers (230 ± 21 kJ mol\textsuperscript{-1}) and by Surnev and Tikhov (226 ± 8 kJ mol\textsuperscript{-1}) for GeO desorption. The anomalously large pre-exponential factor may result from the measured rate constant $k_{\text{eff}}$ being a composite quantity.
4.6. Behavior of HX (X = Cl or Br)

The behavior of HX (X = Cl or Br) shows strong similarities to the previously discussed hydrides, including strongly negative $\Delta H_{\text{ads}}$ for adding HX to the Ge=Ge dimer as calculated in Table 4.3.1 ($\Delta H_{\text{ads}} = -336$ kJ mol$^{-1}$ for HCl, and $\Delta H_{\text{ads}} = -302$ kJ mol$^{-1}$ for HBr). An additional complication, though, arises as to the branching ratio between desorption of HX and H$_2$, that is, what are the relative proportions of the desorption products at $T_p = 570$–$580$ K, and why. From the TPD data of HX/Ge(100) presented in §§ 3.4 and 3.5 we may be able to deduce some kinetic and mechanistic information.

4.6.1. Product Yields

As outlined in § 3.4, absolute coverages of H$_2$ and HX were calibrated against saturation coverages of H$_2$S. Branching ratios (product yields) are listed in Table 4.6.1.

**Table 4.6.1.** Product yields (H$_2$:HX) for HX/Ge(100) at various coverages and temperatures.

<table>
<thead>
<tr>
<th>HX</th>
<th>Dosing $T/K$</th>
<th>initial coverage</th>
<th>saturated coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>273</td>
<td>0.904</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>0.833</td>
<td>0.773</td>
</tr>
<tr>
<td>HBr</td>
<td>273</td>
<td>2.86</td>
<td>1.46</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>3.12</td>
<td>1.24</td>
</tr>
</tbody>
</table>

For HCl, the amounts of H$_2$ and HCl produced were quite similar, independent of coverage and adsorption temperature, easily explainable by postulating nearly random adsorption sites of H and Cl on the Ge(100) surface. Invoking the doubly-occupied dimer model$^{20}$ for adsorption, however, leads to the conclusion that HCl molecules adsorb across the Ge dimers, and thereafter exchange of adsorbed H or Cl with neighboring dimers is
facile. Another way of stating this is that $\Delta H$ is nearly zero for the HCl exchange reaction between two dimers, i.e.,

\[
\begin{align*}
\text{Ge-Ge} & \quad \Delta H = 0 \quad \text{Ge-Ge} \\
\begin{array}{c}
\text{Ge-Ge} \\ \text{Ge-Ge}
\end{array} & \quad \begin{array}{c}
\text{Ge-Ge} \\ \text{Ge-Ge}
\end{array}
\end{align*}
\]

(4.6.1.1)

For HBr adsorption, however, about three times as much H$_2$ exists on the surface as HBr initially, which we attribute to the large size of Br (van der Waals radius = 1.95 Å$^{96}$). In this case, $\Delta H$ for pairing Br with another adsorbate on a Ge(100) dimer may be positive by a few kJ mol$^{-1}$, so that adsorbed Br tends to prefer singly-occupied dimers marginally.

When the surface is saturated with HBr, the weak Br(a) repulsion is overcome somewhat.

### 4.6.2. Kinetics of adsorbed HX

The doubly-occupied dimer model$^{20}$ once again seems to be the obvious answer to explain the observed first-order kinetics for the desorption of HX. Using Redhead’s equation with $T_p = 580$ K, an activation energy for HX desorption is found to be $\sim 155$ kJ mol$^{-1}$, assuming $v = 10^{13}$ s$^{-1}$ for first-order desorption.

The similarity between desorption kinetics of H$_2$ and HX is seductive, because the peak temperatures (570 K versus 580 K) and thus the desorption energies (150 kJ mol$^{-1}$ versus 155 kJ mol$^{-1}$) are so close in value. The relative reactivities for HCl ($S_0 = 0.1-0.3$) and HBr ($S_0 = 0.5-0.8$) are orders-of-magnitude larger than that for H$_2$ on Ge(100) ($S_0 = 1 \times 10^{-6}$)$^{7a}$, and so the activation energy for adsorption is nearly 0 for HX but quite large for H$_2$. A resolution to this paradox probably lies in differences in bond length (relatively short for H$_2$ while long for HX); other factors may include differences in orbital symmetry or desorption channels.
4.6.3. Desorption of GeX₂

Above the desorption temperature of HX and H₂, i.e., 580 K, the adsorbed halogen not desorbing as HX remains, until it, too, desorbs, as GeX₂ at \( T_p = 680-710 \) K. Given our new proposal describing the desorption of GeO and GeS, a hypothetical mechanism for germanium dihalide desorption becomes clear at once. At lower substrate temperatures the adsorbed X forms the monohalide (one X per Ge surface atom), but then rearranges to form the dihalide GeX₂, which then desorbs above 680 K, as delineated in Eq. 4.6.3.1.

\[
\begin{align*}
&\text{Ge} + \text{Ge} + X + X \xrightarrow{K_p} \text{Ge} \leftrightarrow \text{Ge} \rightarrow \text{Ge} + \text{Ge} + X + X \xrightarrow{K} \text{Ge} + \text{Ge} + X + X \xrightarrow{k_d} \text{Ge} + \text{Ge} + X + X \\
&\text{(4.6.3.1)}
\end{align*}
\]

The second-order kinetics are an indication of the mobility of the X(a) species across singly-occupied dimers prior to desorption.

Although no previous studies have been performed investigating the adsorption of HX/Ge(100), it is useful to consider the behavior of the nearest analogs, Cl₂ and Br₂, on Ge(100).⁵² For the high-temperature (600 K ≤ \( T \) ≤ 1000 K) reaction of Cl₂ with Ge(100), Madix and Schwarz determined the pre-exponential factor for first-order desorption of GeCl₂, \( v = 6 \times 10^7 \) s⁻¹, as well as the activation energy for desorption, \( E_d = 107 \) kJ mol⁻¹. They also calculated an initial sticking probability for Cl₂/Ge(100), \( S_0 \sim 0.3 \), and reported no other germanium halides as desorption products. Desorption of GeCl₂ was found to dramatically increase above 700 K. Using Madix and Schwarz’s Arrhenius parameters, a peak temperature for desorption is predicted at 645 K, in fair agreement with the observed value of 680-720 K. It is worthwhile to note that the pre-exponential is orders-of-magnitude lower than usual, possibly because \( k_{eff} \) is a composite quantity, just as for GeO (§ 4.5). A proper second-order Redhead analysis, using Eq. 1.3.8 and assuming a typical
Arrhenius pre-exponential factor \( (ν_2 = 10^{13} \text{ monolayer}^{-1} \text{ s}^{-1}) \), provides an estimate of \( E_d \approx 167 \text{ kJ mol}^{-1} \).

For \( \text{Br}_2/\text{Ge}(100) \), Madix and Susu performed similar high-temperature studies, and observed both germanium dibromide and tetrabromide products, attributing the \( \text{GeBr}_2 \) as being a precursor state for \( \text{GeBr}_4 \). The calculated first-order Arrhenius parameters were \( E_d = 84 \text{ kJ mol}^{-1} \) and \( ν_1 = 10^7 \text{ s}^{-1} \), but they reported deviations from first-order desorption below 900 K. Substituting Madix and Susu’s parameters into the Redhead equation gives an estimate of 560 K for the TPD peak temperature, which agrees poorly with the observed value of 710–760 K. A second-order Arrhenius analysis, using the peak temperatures tabulated in Fig. 3.5.6 and \( ν_2 = 10^{13} \text{ monolayer}^{-1} \text{ s}^{-1} \), gives \( E_d = 184 \text{ kJ mol}^{-1} \).

A rationalization for the difference in desorption energies for \( \text{GeCl}_2 \) and \( \text{GeBr}_2 \) may be ascribed to the greater electronegativity of Cl, which withdraws electron density from the Ge adatom backbonds to the Ge surface, thus weakening the backbonds, making Ge—Ge bond scission more favorable and causing a lower \( \text{GeCl}_2 \) desorption temperature. Such a model gains support from Bell and coworkers’ theoretical calculations of Si—Si dissociation energies for the series of Cl-substituted disilanes,\(^97\) which find a weakening of the Si—Si bond when Cl is substituted for H: for \( \text{H}_3\text{Si}—\text{SiH}_3 \), \( D(\text{Si}—\text{Si}) = 331 \text{ kJ mol}^{-1} \), while for \( \text{Cl}_3\text{Si}—\text{SiCl}_3 \), \( D(\text{Si}—\text{Si}) = 326 \text{ kJ mol}^{-1} \).

### 4.7. Comparison of Reactivity of Hydrides on Ge(100) and Si(100)

A summary of results comparing adsorption on germanium in this work to previous studies on silicon is presented in Tables 4.7.1 and 4.7.2, and a detailed discussion follows.

#### 4.7.1. Hydrogen Sulfide/Ge(100)

As was shown in § 3.1 and this chapter, \( \text{H}_2\text{S} \) has an initial sticking probability of about 0.2 with little dependence upon substrate temperature, i.e., with little or no activation barrier. By the time the Ge(100) surface is heated to 570 K, \( \text{H}_2\text{S} \) has dissociated into H(a)
Table 4.7.1. Comparative sticking probabilities of adsorbates on Ge(100) and Si(100).

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>$S_0$ on Si(100)</th>
<th>$S_0$ on Ge(100) [This work]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>$\sim 1 , @ , 350 , K$</td>
<td>0.28 $, @ , 173 , K$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\leq 0.02 , @ , 273 , K$</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>$\sim 1 , @ , 150 , K$</td>
<td>$\sim 0.23 , @ , 173-373 , K$</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>$\sim 1 , @ , 120 , K$</td>
<td>$\leq 6 \times 10^{-5}$</td>
</tr>
<tr>
<td>HCl</td>
<td>?</td>
<td>0.30 $, @ , 273 , K$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.066 $, @ , 373 , K$</td>
</tr>
<tr>
<td>HBr</td>
<td>?</td>
<td>0.77 $, @ , 273 , K$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.55 $, @ , 373 , K$</td>
</tr>
</tbody>
</table>

Table 4.7.2. Comparative TPD peak temperatures of molecules from Ge(100) and Si(100).

<table>
<thead>
<tr>
<th>Product</th>
<th>$T_p$ on Si(100)/K</th>
<th>$T_p$ on Ge(100)/K [This work]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$</td>
<td>650$^{62f,g}$</td>
<td>...</td>
</tr>
<tr>
<td>H$_2$</td>
<td>$\beta_2$ 795$^{98}$</td>
<td>570</td>
</tr>
<tr>
<td></td>
<td>$\beta_1$ 680</td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>835$^{85}$</td>
<td>580</td>
</tr>
<tr>
<td>HBr</td>
<td>835$^{85}$</td>
<td>580</td>
</tr>
<tr>
<td>oxide</td>
<td>980$^{99}$</td>
<td>660</td>
</tr>
<tr>
<td>sulfide</td>
<td>$&gt; 550^{55g}$</td>
<td>660</td>
</tr>
<tr>
<td>dichloride</td>
<td>900$^{57b}$</td>
<td>680-720</td>
</tr>
<tr>
<td>dibromide</td>
<td>920$^{85}$</td>
<td>710-770</td>
</tr>
</tbody>
</table>
and SH(a) across the Ge=Ge dimer, and then desorption of H₂ commences, leaving only bridge-bonded S(a) on the surface. At 660 K, the remaining sulfur desorbs as GeS, possibly through a mechanism involving a germathione intermediate.

The behavior of H₂S on Si(100) is quite similar to that on Ge(100). Schröder-Bergen and Ranke’s work⁵⁵ using photoelectron spectroscopy on cylindrically-shaped Si(100) samples (thus including a wide variety of vicinal planes) indicates that H₂S has an initial sticking probability of about 1 at 150 K, with a saturation coverage of 0.5 monolayer. At 90 K, evidence suggests molecular adsorption, while at 150 K complete dissociation of H₂S into H(a) + SH(a) on Si(100) is indicated. By the time substrate temperature reaches 550 K, the photoelectron spectra show evidence of complete dissociation of H₂S into S(a) + 2H(a).

While the present work does not study adsorption of H₂S on Ge(100) at 90 K, the behavior of H₂S on Ge(100) at higher temperatures is similar to that seen by Schröder-Bergen and Ranke on Si(100). The slightly smaller value of S₀ for H₂S/Ge(100) compared to H₂S/Si(100) may be explained by the generally weaker bonding to Ge, as shown in Table 4.3.1.

4.7.2. Water/Ge(100)

In this work, water has been shown to readily stick (S₀ = 0.2) to Ge(100) at low temperatures, but the initial sticking probability rapidly falls as the temperature rises above 173 K, an indication of a substantial activation barrier. Just as for H₂S, the adsorbed water dissociates (before H₂ desorption at 570 K) into H(a) + OH(a) across the Ge=Ge dimer. After desorption of hydrogen, the remaining O(a) is probably bridge-bonded until it desorbs—perhaps through a three-centered germanone intermediate—as GeO at 660 K.

Like H₂S, H₂O behaves qualitatively similar on Si(100) and Ge(100). In contrast to the H₂S/Ge(100) system, however, water has been extensively studied on Si(100). From various sorts of measurements, including infrared spectroscopy,⁵⁵d photoelectron
spectroscopy,\textsuperscript{55g,h} and electron-stimulated desorption ion-angular distribution (ESDIAD),\textsuperscript{55i} it is clear that water dissociates into H(a) + OH(a) across the Si=Si dimer within a large range of temperatures (80–500 K). Saturation coverage is 0.5 monolayer, and the initial sticking probability has been reported to be nearly unity at 350 K by Schröder-Bergen and Ranke\textsuperscript{55g}.

The major difference between adsorption of H$_2$O on Si(100) and on Ge(100) seems to be a strong variation in reactivity with temperature in the case of Ge but no variation for Si ($S_0 \sim 1$). Evidently the activation barrier to chemisorption is minimal for water on Si(100), whereas, in this work, is calculated to be roughly 29 kJ mol$^{-1}$ on Ge(100). As with H$_2$S/Ge(100), generally weaker bonding to Ge results in lower $S_0$ and reactivity compared to Si.

4.7.3. Ammonia/Ge(100)

No measurable reaction was found between NH$_3$ and the Ge(100), which gives perhaps the starkest contrast with the NH$_3$/Si(100) system. Ammonia readily adsorbs on Si(100), and most workers generally agree that it dissociates into H(a) + NH$_2$(a) across the Si=Si dimer at 90 K < $T$ < 700 K.\textsuperscript{62} Extensive kinetic and structural studies were performed by Yates and coworkers,\textsuperscript{62f,g} who showed that saturation coverage = 0.5 monolayer, with $S_0 = 1$ up to 0.43 ML at $T = 120$ K, followed by slower adsorption. A small amount of recombinatively-desorbed NH$_3$ was observed at $T_p = 650$ K (first-order), giving $E_d = 190$ kJ mol$^{-1}$ using Redhead's equation (4.3.3). H$_2$ was seen to desorb at $T_p = 680$ K (first order, 200 kJ mol$^{-1}$), and silicon nitride was formed from the remaining N(a). Although the temperature dependence of the initial sticking coefficient has not been reported, the barrier to chemisorption of ammonia on Si(100) must be negligible, whereas on Ge(100) it is large enough to prevent sticking altogether at the temperatures studied, when combined with substantially weaker bonding than on Si.
A glance at Table 4.3.1 shows a large discrepancy between Yates and colleagues’ reported desorption barrier of 190 kJ mol⁻¹ and our calculation of the heat of adsorption for NH₃ on Si(100), −273 kJ mol⁻¹. Ideally the two values ought to be equal and opposite. Part of the problem in determining thermodynamic values from bond-additivity calculations is the inherent uncertainty of many tabulated bond energies. The Si—H and H—NH₂ bond energies are well-known, and the Si(100) dimer π-bond is uncertain but small, but the Si—N bond strength is less clear. Accordingly, we attribute the difference in values to a weakening in the Si—N bond strength for highly-substituted silicon compounds (or surfaces).

4.7.4. Hydrogen Halides/Ge(100)

HCl readily adsorbs dissociatively at \( T = 273 \text{ K} \) \( (S_0 = 0.299 \pm 0.098 \text{ at } 273 \text{ K}) \) on Ge(100) to form H(a) + Cl(a) on the same dimer, with facile exchange of H or Cl between dimers. When the substrate temperature is raised to 373 K, the initial sticking probability drops by a factor of five to 0.066 ± 0.002. The desorption products are HCl at a peak temperature of 580 K, and H₂ at peak temperature of 570 K, with nearly equal amounts of each. Residual adsorbed chlorine etches the germanium surface, producing GeCl₂ at \( T_p = 680-720 \text{ K} \), varying with coverage. The reaction for HBr is qualitatively similar except that the initial sticking probability is somewhat higher at 273 K \( (S_0 = 0.772 \pm 0.059) \), dropping only slightly to 0.549 ± 0.013 at 373 K, and the GeBr₂ etch product desorbs at 710–760 K.

While halogens, especially SiCl₄ and HF, are extensively employed in the semiconductor-processing industry, little work has been done concerning HCl and HBr adsorption on Si(100). Very recent work by Cheng and coworkers,¹⁸⁵ investigating extraction of halogens from Si(100) using atomic hydrogen doses, shows that HCl, HBr, and HI all desorb at \( T_p \sim 835 \text{ K} \), slightly above the H₂ desorption temperature. Using their
heating rate ($\beta = 4 \text{ K s}^{-1}$) and assuming a typical first-order pre-exponential factor ($v_1 = 10^{13} \text{ s}^{-1}$) provides an estimate of $E_d = 220 \text{ kJ mol}^{-1}$.

As for NH$_3$, differences are found between our calculated $\Delta H_{\text{ads}}$ for HX/Ge(100) or Si(100) and $E_d$ values computed from TPD data (Table 4.3.1), although the problem is least severe for HCl/Si(100). In the same manner as was done for NH$_3$, the difference between the calculated $\Delta H_{\text{ads}}$ and measured $E_d$ is attributed to weakening of the X–M bond strength when M is highly substituted. The Si–Cl bond energy is fairly well-known (hence better agreement between the values), and the Si–Br is somewhat less-understood, but the effects of substituents on the bond energy between the central Ge atom and a halogen is hardly known at all. It is clear that further thermochemical research needs to be done on germanium compounds.

To supplement the meager amount of data for halogens on semiconductors, a comparison is invoked again between HX and X$_2$. Christman and coworkers, and Vvedensky, et al. have studied the bonding site for Cl on Si(100) using UV photoemission, EXAFS, and NEXAFS, and concluded that it is quite similar to that for H/Si(100), namely, one Cl per dimer atom, tilted slightly from the surface normal.$^{57a}$ Jackman and colleagues used TPD to explore Cl$_2$ interactions with Si(100), and deduced a fairly complicated reaction and etching scheme involving two adsorption states.$^{57b}$ The $\alpha$ (low-temperature desorption, 450 K) state evolved mostly SiCl$_4$ ($E_d = 115 \text{ kJ mol}^{-1}$) while the $\beta$ (high-temperature desorption, 900 K) state created a mixture of SiCl$_4$ and SiCl$_2$ ($E_d = 235 \text{ kJ mol}^{-1}$). The combined ($\alpha + \beta$) $S_0$ at 300 K was found to be $\geq 0.5$. Surprisingly, Müller-Markgraf and Rossi, however, reported that ground-state ($^2\text{P}_{3/2}$) and spin-orbit excited ($^2\text{P}_{1/2}$) atomic Cl stuck only weakly ($S_0 \leq 5 \times 10^{-5}$ and $S_0^* = 4.6 \times 10^{-4}$, respectively) to Si(100).$^{100}$ Given the high reactivity of closed-shell molecules such as Cl$_2$ as well as radicals such as atomic H, one would have expected atomic Cl to have $S_0$ of nearly unity.
Comparison of HCl and HBr also ought to be made to HF and F₂. Madey, et al. used ESDIAD to investigate the structure of adsorbed HF on Si(100), and concluded that HF dissociates across the Si=Si dimer à la H₂O and NH₃, with the Si—F bond 29° from the surface normal.¹⁰¹ Craig and Smith employed theoretical calculations (SLAB-MINDO) recently to study adsorbed HF and F₂, confirming the dissociative behavior of HF, but predicted that F₂ prefers to remain an undissociated unit, bonded primarily to one of the two dimer atoms.¹⁰² Engel and colleagues, however, published an extensive study of F₂/Si(100), reporting that F₂ dissociatively adsorbs readily (S₀ = 0.46 ± 0.02) on Si(100) within the temperature range 120–600 K, to θₘ = 1.5 ML. TPD of fluorinated Si(100) surfaces displayed complicated kinetic behavior, and was interpreted as evidence of spatially inhomogeneous reactivity (i.e., preferred at defects or steps).⁵⁷c
5. **Conclusions**

All the hydrides studied (H₂S, H₂O, HCl, HBr) by temperature-programmed desorption except NH₃ have been found to chemisorb readily on Ge(100), dissociating across the Ge(100) dimers. In the case of H₂S, the initial sticking probability is ~ 0.2 and is relatively insensitive to temperature within the range 173 K ≤ T ≤ 373 K, whereas for H₂O, the initial sticking probability is ~ 0.2 but drops off by an order of magnitude as the temperature is raised from 173 K to 273 K. For the hydrogen halide HCl, S₀ = 0.3 at 273 K, but falls by a factor of five at 373 K, whereas for HBr, S₀ seems to be more constant with temperature: S₀ = 0.8 at 273 K, dropping to 0.5 at 373 K. The upper bound for the initial sticking probability of NH₃ on Ge(100) was shown to be ≤ 6 × 10⁻⁵.

The behavior of these adsorbates can be explained by treating semiconductor dimers as containing π-bonds. Adsorption of molecules across these π-bonded dimers is thus analogous to molecular addition reactions, and desorption is likewise similar to molecular elimination reactions. Variation in reactivity can be rationalized by simple thermochemical analysis of bonding between the atoms, as well as invoking a precursor model for adsorption and desorption. Clearly it is not enough to extrapolate from silicon: experimental evidence must be taken into account.

Still unconfirmed is the nature of the adsorbed species below the desorption temperature. One technique available to help answer this question is infrared spectroscopy. Using the germanium sample as an internal reflection element can “amplify” the absorption signal by the number of bounces the infrared light suffers off of the adsorbate-covered surface. Though at elevated substrate temperatures (> ~ 200 °C) free carrier absorption precludes use of the internal-reflection technique,¹⁰³ at dosing temperatures used in this study (≤ 100 °C) infrared spectroscopy is feasible. The range of wavelengths for which Ge is reasonably transparent (20–30% transmittance) to infrared radiation is 700–4000 cm⁻¹.¹⁰⁴ In Table 5.1, a list of potentially-detectable adsorbate structures is given.
Table 5.1. Adsorbates potentially detectable on the Ge(100) surface using infrared spectroscopy.

<table>
<thead>
<tr>
<th>Species</th>
<th>Predicted vibrational frequency/cm(^{-1})</th>
<th>Detectable on Ge(100) using internal-reflection?</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge—SH</td>
<td>(\nu, 410-430)</td>
<td>N</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>(\delta, 780)</td>
<td>Y</td>
<td>105</td>
</tr>
<tr>
<td>S—H</td>
<td>(\nu, 2590)</td>
<td>Y</td>
<td>105</td>
</tr>
<tr>
<td>Ge—OH</td>
<td>(\nu, 660-730)</td>
<td>?</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>(\delta, 885-925)</td>
<td>Y</td>
<td>92</td>
</tr>
<tr>
<td>O—H</td>
<td>(\nu, 3630-3690)</td>
<td>Y</td>
<td>92, 105</td>
</tr>
<tr>
<td>Ge—H</td>
<td>(\nu, 1980-1990)</td>
<td>Y</td>
<td>106</td>
</tr>
<tr>
<td>Ge—Cl</td>
<td>(\nu, 465)</td>
<td>N</td>
<td>105</td>
</tr>
<tr>
<td>Ge—Br</td>
<td>(\nu, 260-310)</td>
<td>N</td>
<td>107</td>
</tr>
<tr>
<td>Ge=S</td>
<td>(\nu, 600)</td>
<td>N</td>
<td>95</td>
</tr>
<tr>
<td>Ge=O</td>
<td>(\nu, 970)</td>
<td>Y</td>
<td>92</td>
</tr>
<tr>
<td>Ge—O—Ge</td>
<td>(\nu, 810-860)</td>
<td>Y</td>
<td>22b, d, 33a</td>
</tr>
<tr>
<td>Ge—S—Ge</td>
<td>(\nu, 380-420)</td>
<td>N</td>
<td>108</td>
</tr>
</tbody>
</table>

*In situ* infrared studies might reveal directly what adsorbed groups exist on the germanium surfaces, and even any reactions at temperatures intermediate between dosing and desorption. It is obvious from Table 5.1, though, that the lower-frequency modes will be invisible, and some other detection method will have to be employed in order to directly detect these adsorbates, such as x-ray photoelectron spectroscopy or electron-energy-loss spectroscopy.

A number of details of the proposed reactions and mechanisms need to be clarified. While it is clear that the lower-temperature desorption features (570–580 K) are first-order
reactions, the higher-temperature peaks (660 K) have not been confirmed as second-order for GeO and GeS. The initial sticking probabilities for water needs to be more precisely determined, especially in light of the relationship between $S_0$ and substrate temperature in H$_2$O. Measurements of the variation of initial sticking probability over a wider temperature range ought to be performed on HCl and HBr. From better values of $S_0$, the energy barriers between chemisorption and physisorption can be more precisely calculated.

A natural question, finally, is whether the findings in this research apply to other hydrides, e.g., AsH$_3$, PH$_3$, H$_2$Se, HI, and HF, on both Ge(100) and Si(100) surfaces.
References


49. V.T. Smith, L.M. Ulvick, and M.P. D’Evelyn, to be published.


84. Bond strengths used were \( D(\text{H–SH}) = 381 \pm 4 \text{ kJ mol}^{-1} \), \( D(\text{H–H}) = 436.0 \pm 1.4 \text{ kJ mol}^{-1} \), \( D(\text{H–NH}_2) = 435 \pm 8 \text{ kJ mol}^{-1} \), \( D(\text{H–OH}) = 458.8 \pm 1.4 \text{ kJ mol}^{-1} \), \( D(\text{H–Cl}) = 428.0 \pm 0.42 \text{ kJ mol}^{-1} \), \( D(\text{H–Br}) = 366.1 \pm 0.4 \text{ kJ mol}^{-1} \), B. deB. Darwent, NSRDS–NBS 31 (1970); \( \text{Si(100)} \) dimer \( \pi \)-bond strength = \( 24 \pm 5 \text{ kJ mol}^{-1} \), ref. 20; \( \text{Ge(100)} \) dimer \( \pi \)-bond strength = \( 24 \pm 5 \text{ kJ mol}^{-1} \), by analogy to \( \text{Si(100)} \) and ref. 20; \( D(\text{H–Si(Me}_3\text{Si)} = 331 \pm 8 \text{ kJ mol}^{-1} \), J.M. Kanabus-Kaminska, J.A. Hawari, D. Griller, and C. Chatgilialoglu, \textit{J. Am. Chem. Soc.} \textbf{109} (1987), 5267; \( D(\text{Si–S}) = 330 \text{ kJ mol}^{-1} \), S. Pawlenko, \textit{Organosilicon Chemistry} (Berlin, DeGruyter, 1986); \( D(\text{Si–OH}) = 538 \pm 8 \text{ kJ mol}^{-1} \), \( D(\text{Si–NH}) = 401 \pm 11 \text{ kJ mol}^{-1} \), see ref. 17(f); \( D(\text{Ge–O}) = 448 \text{ kJ mol}^{-1} \), \( D(\text{Ge–Cl}) = 485 \text{ kJ mol}^{-1} \), \( D(\text{Ge–Br}) = 435 \text{ kJ mol}^{-1} \), \( D(\text{Si–Br}) = 390 \text{ kJ mol}^{-1} \), R.A. Jackson, \textit{J. Organomet. Chem.} \textbf{166} (1979), 17; \( D(\text{Ge–N}) = 272 \pm 21 \text{ kJ mol}^{-1} \), G. Wilkinson, F.G.A. Stone, and E.W. Abel, eds., \textit{Comprehensive Organometallic Chemistry}, vol. 2 (Oxford, Pergamon Press, 1982); \( D(\text{Si–Cl}) = 381 \text{ kJ mol}^{-1} \), Ch. Elschenbroich and A. Salzer, \textit{op. cit.} \( D(\text{Ge–H}) \) was calculated by correcting for Ge–H bond weakening when attached to highly substituted germanes, cf. \( D(\text{H}_3\text{Si–H}) = 378 \text{ kJ mol}^{-1} \) but \( D(\text{H–Si(Me}_3\text{Si)} = 331 \pm 8 \text{ kJ mol}^{-1} \), only 0.875 ± 0.022 of silane [J.M. Kanabus-Kaminska, \textit{et al.}, \textit{op. cit.}]. Thus \( D_{\text{germane}}(\text{Ge–H}) = 346 \pm 10 \text{ kJ mol}^{-1} \) [P.N. Noble and R. Walsh, \textit{Int. J. Chem. Kin.} \textbf{15} (1983), 547], multiplied by a weakening correction factor of 0.875 ± 0.022, gives \( D(\text{Ge–H}) = 303 \pm 16 \text{ kJ mol}^{-1} \) for a highly-substituted germane.

85. (a) C.C. Cheng, S.R. Lucas, H. Gutleben, W.J. Choyke, and J.T. Yates, Jr., \textit{J. Am. Chem. Soc.} (in press); (b) C.C. Cheng, private communication. \( E_d \) calculated from a reported \( T_p = 835 \text{ K} \) for HCl and HBr/Si(100), \( \beta = 4 \text{ K s}^{-1} \), and assuming \( \nu_1 = 10^{13} \text{ s}^{-1} \).

86. \( D(\text{Ge–S}) \) is calculated using Pauling’s electronegativity values, \( x_{\text{Ge}} = 2.01 \) and \( x_S = 2.58 \) [J. Huheey, \textit{Inorganic Chemistry}, 2nd ed., (New York, Harper & Row, 1978), pp. 162–4], \( D(\text{Ge–Ge}) = 142–188 \text{ kJ mol}^{-1} \) [including both \( D(\text{H}_3\text{Ge–GeH}_3) \) and \( D(\text{elemental Ge}) \)], Huheey, \textit{op cit.}, and Darwent, \textit{op. cit.}, and \( D(\text{S–S}) = 225 \text{ kJ mol}^{-1} \). The equation for computing the Ge–S bond dissociation energy is

\[
D(\text{Ge–S}) = \frac{D(\text{Ge–Ge}) + D(\text{S–S})}{2} + 96 \left( x_{\text{Ge}} - x_S \right)^2
\]

calculations for the other hydrides adsorbed on Ge(100) have an average error $\Delta = 79$ kJ mol$^{-1}$ too low, so a revised estimate for $D(\text{Ge-S}) = D_{\text{raw}}(\text{Ge-S}) + \Delta = 293-314$ kJ mol$^{-1}$.

87. $T_p = 580$ K, $\beta = 2$ K s$^{-1}$, and $v_1$ is assumed to be $10^{13}$ s$^{-1}$.


