

β -hydride elimination processes on silicon

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The adsorption and decomposition of ethylbromide on the Si(100) and Si(111) surfaces is investigated. Ethylbromide adsorbs molecularly on Si at surface temperatures below 110 K. Warming the ethylbromide-covered surface above 200 K results in the cleavage of the carbon–bromine bond with the formation of surface ethyl groups and coadsorbed bromine atoms. Further heating of the surface leads to the decomposition of surface ethyl groups which desorb as ethylene leaving hydrogen at the Si surface. The hydrogen atoms recombine at higher surface temperatures (near 800 K) and desorb as molecular hydrogen. Isotopic labeling of the hydrogen within the ethyl group provides greater insight into the mechanism for ethylene formation. A branching reaction is observed between β - and α -hydride elimination within the ethyl group to form ethylene. The ratio of the amount of ethylene produced by β -hydride to α -hydride elimination can be varied by the position of the deuterium label within the ethyl group. The reaction rate for ethylene production is measured and how this rate is influenced by the isotopic substitution is discussed. © 1996 American Vacuum Society.

I. INTRODUCTION

The growth of III–V and II–VI semiconductors in a self-limiting layer-by-layer process using alternating cycles of precursor gases is known as atomic layer epitaxy (ALE).^{1,2} Control of film thickness and uniformity over a large area has been achieved. Recently, film growth and surface chemistry studies have begun to consider the deposition of group IV materials by ALE.^{3–8} Diethylsilane and diethylgermane are two precursors that show some promise for the ALE of Si and Ge, respectively. In surface chemistry studies^{9–21} of these two molecules, ethyl groups are deposited onto the surface by decomposition of the parent molecule and desorb at higher temperatures as ethylene. The proposed mechanistic step for the decomposition of surface ethyl groups to form ethylene is β -hydride elimination.

The results of these previous studies are consistent with a β -hydride elimination reaction, however, no direct evidence for this mechanism was obtained. Another possible reaction is α elimination of hydrogen, followed by a hydrogen shift to yield ethylene. This latter mechanism was used to explain experimental results for the gas phase decomposition of ethylsilanes. However, the gas phase studies have not unambiguously determined the decomposition mechanism.^{22,23} Francisco and Schlegel have also proposed, based on their *ab initio* calculations for the photodissociation of gas phase monoethylsilane, that the 1,1-hydrogen elimination of H₂ to form C₂H₅SiH followed by β -hydride elimination of C₂H₄, was the lowest energy pathway to yield ethylene.²⁴

β -hydride and β -alkyl elimination surface reactions and their role in chemical vapor deposition were first directly observed by Bent and co-workers.^{25,26} They examined the thermal decomposition of trisisobutylaluminum (TIBA) on Al(111) and Al(100). This molecule was an effective precursor for the deposition of Al with the evolution of isobutylene

and hydrogen. The formation of isobutylene was possible only through a β -hydride reaction. However, when the same molecule is decomposed on Si(111) or Si(100), reversible desorption was observed at low surface temperatures.²⁶ If the Si surface temperature is increased above 750 K during the TIBA exposure, some nucleation of Al is observed with a significant amount of carbon incorporation. This observation suggests that TIBA decomposes differently on Si than on Al and makes the comparison with diethylgermane and diethylsilane studies difficult.

In this study, ethylbromide (EtBr) is used as a precursor to deposit ethyl groups onto Si(100) and Si(111). A recent study has shown that EtBr is an excellent precursor for ethyl group deposition onto Si(100).²⁷ Deuterium labeling of the α - or β -carbon within the ethyl group is used to help distinguish the decomposition mechanism of surface ethyl groups to form ethylene. The surface processes are followed by ultraviolet photoelectron spectroscopy (UPS) and temperature programmed desorption (TPD).

II. EXPERIMENT

The experiments are carried out in a stainless steel ultra-high vacuum chamber. The chamber is equipped with a double-pass cylindrical mirror analyzer (CMA) for Auger electron and photoelectron spectroscopies, a differentially pumped ultraviolet discharge lamp, a twin x-ray source, an ion gun, and a quadrupole mass spectrometer for both TPD and secondary ion mass spectrometry. The base pressure of the system is 8×10^{-11} Torr with a typical working pressure of 1×10^{-10} Torr.

The samples are cleaved into $10 \times 25 \times 0.4$ mm rectangles from *n*-type Si(100) and Si(111) wafers [Virginia Semiconductor, $\pm 0.25^\circ$ of the (100) or (111) plane, Sb doped, 5–10 m Ω cm resistivity] and mounted to a liquid nitrogen cooled manipulator. The sample is held by molybdenum clamps for resistive heating. The sample temperature is monitored by a

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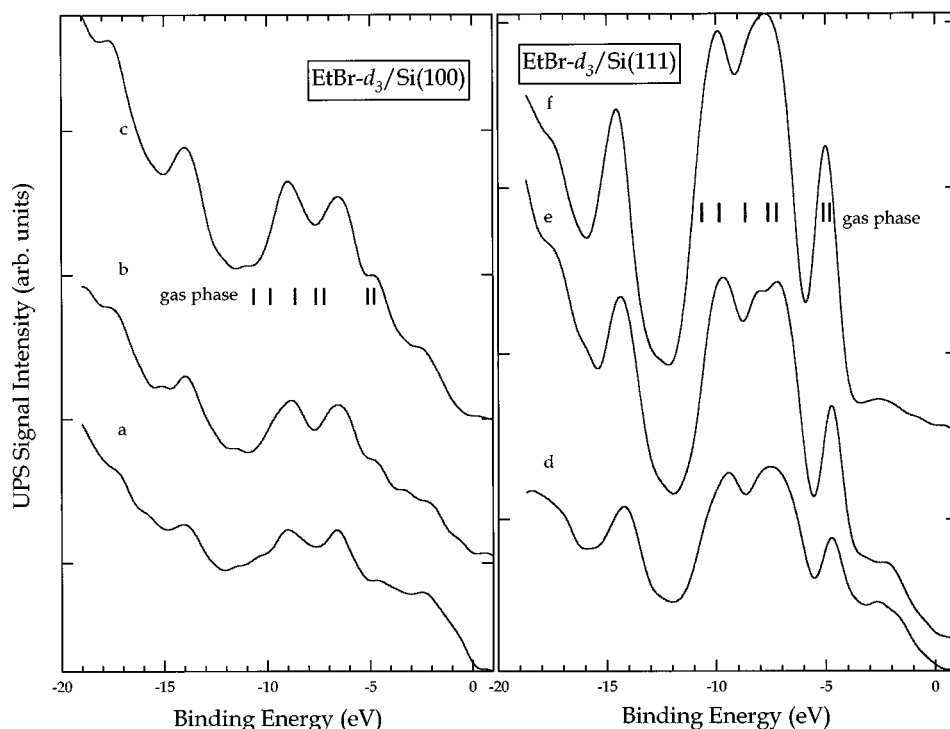


FIG. 1. Left-hand panel: He II UPS spectra for various exposures of EtBr- d_3 to Si(100) at 90 K. The EtBr- d_3 coverages shown are (a) 0.10, (b) 0.14, and (c) 0.40 ML. The bar graph under curves (c) and (f) is for the gas-phase photoelectron spectrum of EtBr. Right-hand panel: He II UPS spectra for various exposures of EtBr- d_3 to Si(111) at 90 K. The EtBr- d_3 coverages shown are (d) 0.13, (e) 0.24, and (f) 0.45 ML.

pair of Chromel–Alumel thermocouples attached to the back of the sample with Aremco 516 ceramic adhesive.

Surface cleanliness is followed by Auger electron and ultraviolet photoelectron spectroscopies. A clean surface is generated by the removal of the native oxide by repeated heating to 1213 K in vacuum followed by slow cooling to room temperature. The sample is cleaned, as needed, by 2 keV Ar⁺ sputtering, followed by annealing to 1213 K. The number of defects induced by sputtering can be reduced by exposing the Si sample to an apparent pressure of 5×10^{-8} Torr Si₂H₆ (Voltaix, ultrahigh purity grade, minimum purity 99.999%) while the surface temperature is maintained at 850 K for about 5 min. The Si₂H₆ gas flow is then turned off and the sample is annealed at 1213 K before cooling.

Bromoethane (Aldrich, 99+% purity), 1,1-bromoethane- d_2 (C/D/N Isotopes, Inc., 98.7 at. % D), 2,2,2-bromoethane- d_3 (C/D/N Isotopes, Inc., 98.7 at. % D), and bromoethane- d_5 (C/D/N Isotopes, Inc., 98.7 at. % D) are further purified by several freeze–pump–thaw degassing cycles and the purity of the gases is checked *in situ* by mass spectrometry. The gas is admitted to the chamber through an effusive doser and directed onto the front face of the crystal at an apparent pressure of 3×10^{-10} Torr above the base pressure for various periods of time. The surface coverages are measured by either x-ray photoelectron spectroscopy or H₂ thermal desorption.

X-ray photoemission spectra are taken with Al $K\alpha$ radiation (1486.6 eV) with the anode operating at 435 W of power. The CMA is operated at a fixed pass energy of 25 eV.

The Si(2*p*) transition for the clean Si surface is measured at 99.4 ± 0.1 eV binding energy.

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

Temperature programmed experiments are conducted with a linear temperature ramp of 6 K s⁻¹ with the crystal in line of sight of the quadrupole mass spectrometer (nondifferentially pumped). The absolute coverage at saturation for hydrogen on Si(100) near room temperature has been determined using nuclear microanalysis by Lu and co-workers²⁸ as 2 monolayers (ML) (1 ML = 6.8×10^{14} Si atoms cm⁻²). The TPD area from a saturation coverage of H atoms is then used as an internal standard for H₂ thermal desorption.

III. RESULTS AND DISCUSSION

A. Ultraviolet photoelectron spectroscopy

The low-temperature adsorption of ethylbromide is examined by ultraviolet photoelectron spectroscopy (UPS). Figure 1 presents the He II UPS spectra for several coverages of EtBr- d_3 (CD₃CH₂Br) adsorbed on Si(100) and Si(111) at 90 K. The left-hand side of Fig. 1 shows the data obtained on the Si(100) surface. At the highest coverage shown [Fig. 1(c)], five peaks are observed. These five features are observed at the lowest coverages and increase in intensity as the coverage of EtBr- d_3 is increased. The measured positions

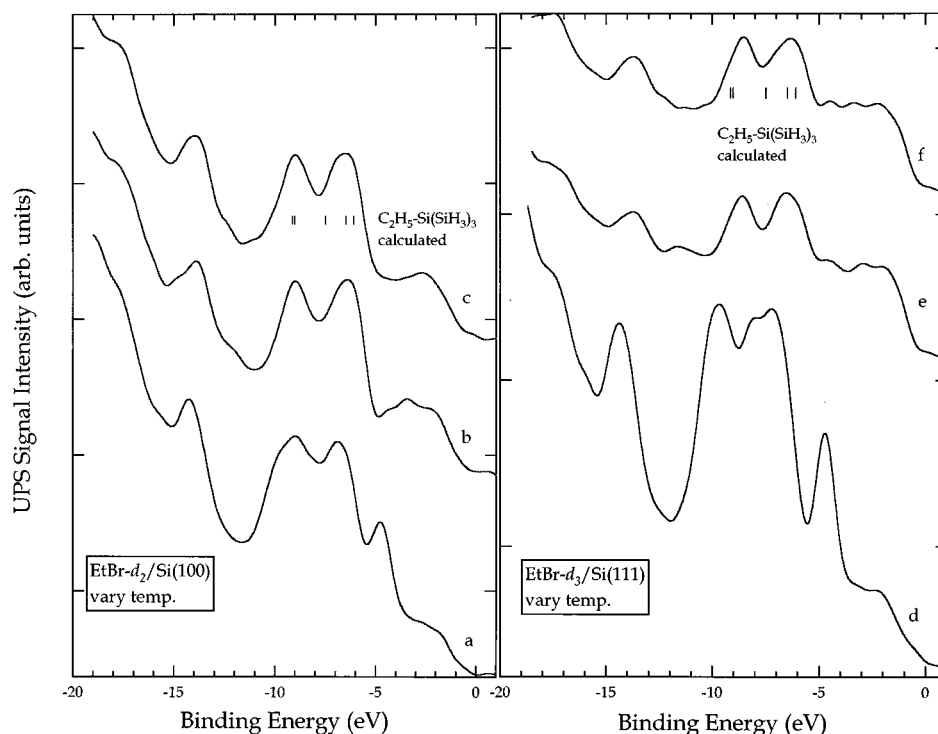


FIG. 2. Left-hand panel: He II UPS spectra for an initial coverage of 0.40 ML of EtBr- d_2 adsorbed on Si(100) at a surface temperature of 110 K and annealed to several different temperatures. The temperatures shown are (a) 110, (b) 200, and (c) 400 K. The bar graph under curves (c) and (f) is for the calculated gas-phase photoelectron spectrum of $C_2H_5Si(SiH_3)_3$. Right-hand panel: He II UPS spectra for an initial coverage of 0.45 ML of EtBr- d_3 adsorbed on Si(111) at a surface temperature of 90 K and annealed to several different temperatures. The temperatures shown are (d) 90, (e) 200, and (f) 400 K.

of the peaks in Fig. 1(c) are 4.7, 6.5, 9.0, 13.9, and 17.6 eV binding energy. The small peak centered near 2 eV binding energy is due to the valence band of the Si substrate. The bar graph under Fig. 1(c) indicates the energies for the gas phase photoelectron spectrum of EtBr.²⁹ The energy of the highest occupied molecular orbital for gas phase EtBr is aligned with the feature at 4.7 eV in Fig. 1(c). The agreement between the gas phase energies and the measured photoelectron spectrum [Fig. 1(c)] is interpreted as due to molecular adsorption of EtBr- d_3 . The features in Fig. 1(c) are assigned (using the symmetry notation of Jorgensen and Salem)³⁰ as follows: $\sigma(CBr)$, 4.7 eV; $\pi(CH_3)$, 6.5 eV; $\pi'(CH_3)$, 9.0 eV; $\sigma(CH_3, CC)$, 13.9 eV; and $C(2s)$, 17.6 eV. The peaks energies agree well with the previously published energies for EtBr adsorbed on Si(100) at 110 K.²⁷

The right-hand side of Fig. 1 shows the data obtained on the Si(111) surface. As observed with the Si(100) surface, there are distinct photoemission peaks that can be assigned to molecularly adsorbed EtBr- d_3 . For the highest coverage shown [Fig. 1(f)], the position of the peaks are 5.0, 7.7, 9.9, 14.5, and 17.4 eV binding energy. On both Si surfaces there are small shifts in the position of these features with increasing coverage without appreciable differential splitting of the peaks. The small shifts are most likely due to final state relaxation effects.

Additional UPS experiments are performed as a function of surface annealing temperature. These results are summarized in Fig. 2 for the Si(100) and Si(111) surfaces. The

left-hand side of Fig. 2 shows the He II UPS spectra for EtBr- d_2 (CH_3CD_2Br) with an initial coverage of 0.40 ML as a function of temperature on the Si(100) surface. Figure 2(a) is the result obtained after adsorbing EtBr- d_2 onto the Si(100) at a surface temperature of 110 K. Warming the EtBr- d_2 covered Si(100) surface to 200 K, cooling to 110 K, and recording the He II photoelectron spectrum is shown in Fig. 2(b). The peak at 4.7 eV is removed by the anneal to 200 K, while the remainder of the spectrum is relatively unchanged. Heating the surface to 400 K [Fig. 2(c)] does not produce any significant changes in the spectrum when compared to spectrum 2(b).

The bar graph underneath Fig. 2(c) indicates the calculated molecular orbital energies²⁷ for gas phase $C_2H_5Si(SiH_3)_3$ assuming that Koopmans's theorem³¹ is obeyed in the photoelectron experiment. This substituted silane is a model molecule used to represent an ethyl group adsorbed on a silicon surface. There is reasonable agreement between the measured photoelectron spectrum [Fig. 2(c)] and the calculated gas phase spectrum for the ethyl group. The calculated spectrum is shifted in energy by the same amount as the measured gas phase spectrum for EtBr. This shift in energy results in the calculated molecular orbital at 7.7 eV binding energy to fall at a valley compared to the measured spectrum in Fig. 2(c). The calculated energy levels, however, are within 0.5 eV of the measured energy levels. Based on this agreement and the lack of the molecular orbital at 4.7 eV, we assign the photoelectron spectra shown in Figs.

2(b) and 2(c) as adsorbed ethyl groups. The disappearance of the peak at 4.7 eV is then due to cleavage of the C–Br bond. High resolution electron energy loss spectroscopy studies of EtBr and EtBr- d_2 covered Si(100) surfaces²⁷ also confirm the assignment of these features to surface ethyl groups above room temperature.

The right-hand side of Fig. 2 shows the same type of annealing experiments performed on the Si(111) surface. Figure 2(d) shows the He II UPS spectrum for EtBr- d_3 adsorbed on the Si(111) surface with an initial coverage of 0.45 ML. Warming the EtBr- d_3 covered Si(111) surface to 200 K, cooling to 90 K, and recording the He II photoelectron spectrum is shown as Fig. 2(e). The peak at 5.0 eV is removed by the anneal to 200 K in a similar manner to what was observed on the Si(100) surface. Heating the Si(111) surface to 400 K [Fig. 2(f)] does not produce any significant changes and this result is interpreted as due to the formation of stable surface ethyl groups.

B. Temperature programmed desorption studies

The decomposition of EtBr on the silicon surfaces is followed by TPD. The only desorption products observed by TPD at all coverages are hydrogen, ethylene, and bromine atoms. In general, the ethylene is produced by the decomposition of the surface ethyl groups. The hydrogen gas is formed by the recombinative desorption of hydrogen atoms that are generated by ethyl group decomposition. Auger electron spectroscopy results after the temperature ramp did not reveal any carbon deposition.

Figure 3 shows a typical set of TPD data obtained for the Si(100) surface exposed to various amounts of EtBr- d_3 at an initial surface temperature of 90 K. The lower portion of Fig. 3 shows the ethylene desorption intensity. The $m/z=30$ intensity is shown. This signal can be a combination of the $C_2D_3^+$ and $C_2D_2H_2^+$ ions. The desorption of ethylene is centered near 640 K at the lowest coverage. As the EtBr- d_3 coverage is increased the ethylene desorption intensity increases and the maximum peak temperature shifts to lower temperatures. The hydrogen desorption is shown in the upper portion of Fig. 3. The desorption curves shown are for hydrogen desorbing as HD. The hydrogen thermal desorption exhibits a peak near 800 K. As the EtBr- d_3 coverage is increased, this peak increases in intensity and the maximum peak temperature does not shift within experimental reproducibility. This peak is attributed to desorption of hydrogen from the monohydride phase on Si(100) as previously observed by Schulze and Henzler.³² The presence of HD is evidence of both α - and β -hydride elimination steps leading to ethylene formation. D_2 and H_2 are also detected, but are not included in Fig. 3 for clarity. The desorption temperature of D_2 and H_2 is the same as that for HD. Quantitation of the hydrogen isotopes enables one to determine the amount of ethylene produced and how it is produced (either α - and β -hydride elimination in the ethyl group, discussed below).

Figure 4 presents a set of TPD results for the decomposition of EtBr- d_3 on the Si(111) surface. The desorption of hydrogen ($m/z=3$ and $m/z=4$) is similar to that observed on

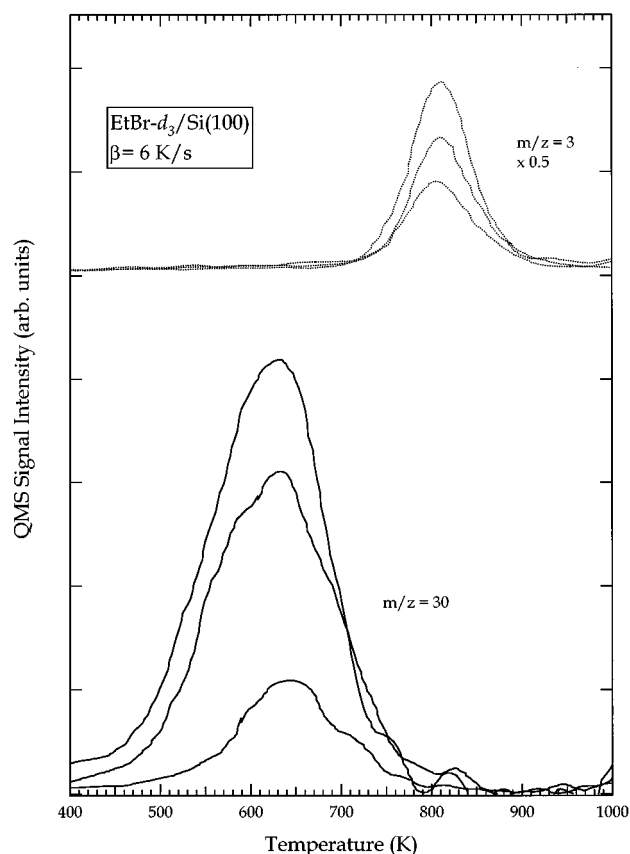


Fig. 3. Upper portion: HD TPD spectra for several EtBr- d_3 coverages from the Si(100) surface. The HD intensities have been multiplied by a factor of 0.5. The temperature ramp rate was 6 K s^{-1} and the adsorption temperature was 90 K. The EtBr- d_3 coverages shown (from smallest to largest area) are 0.09, 0.19, and 0.30 ML. Lower portion: Ethylene TPD spectra ($C_2D_3^+$) for the same EtBr- d_3 coverages shown in the upper portion.

the Si(100) surface. H_2 desorption is also observed but not included in the figure for clarity. On Si(111) the maximum peak temperature for ethylene is higher compared to Si(100). The peak temperature is measured at 670 K and does not shift within experimental reproducibility.

The kinetic parameters for ethylene desorption are also determined and these results are summarized in Table I. The first column of Table I lists the ethyl group generated from ethylbromide on Si(100) and Si(111) with the appropriate deuterium label. The second column indicates the type of hydrogen atom transferred to the surface if β -hydride elimination occurs. The last two columns summarize the kinetic parameters for the reaction rate of ethylene. The desorption of ethylene was found to be first order. The kinetic parameters are determined by fitting the ethylene TPD spectra with the desorption rate equation. These values are determined for each of the detected ethylene molecules whether produced by α - or β -hydride elimination. This procedure was adopted because the reaction rates did not exhibit a coverage dependence or an isotope effect that was measurable within experimental error.

The major difference between the two silicon surfaces is that the preexponential factor and activation energy for de-

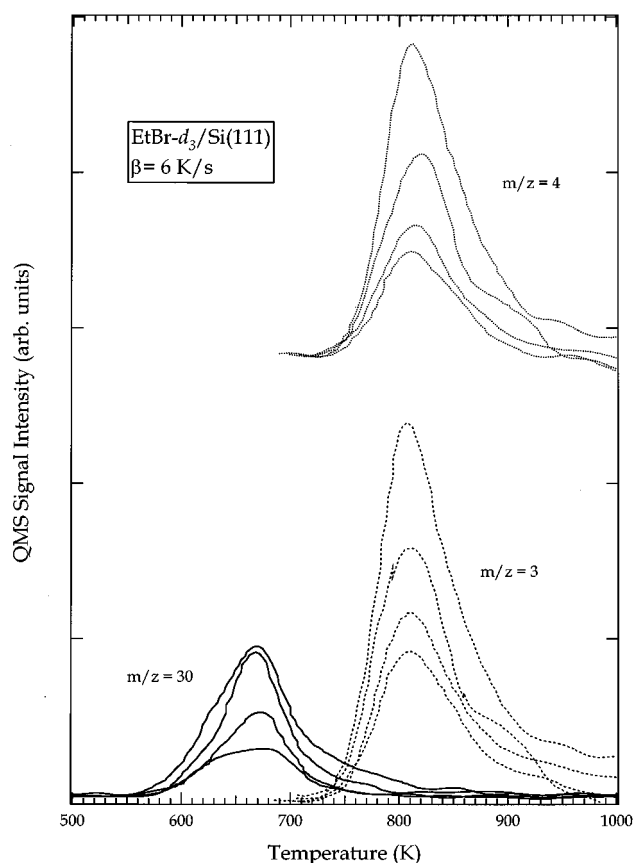


FIG. 4. Upper portion: D_2 TPD spectra for several $EtBr-d_3$ coverages from the Si(111) surface. The temperature ramp rate was 6 K s^{-1} and the adsorption temperature was 90 K. The $EtBr-d_3$ coverages shown (from smallest to largest area) are 0.07, 0.09, 0.13, and 0.19 ML. Lower portion: Ethylene ($C_2D_3^+$) and HD TPD spectra for the same $EtBr-d_3$ coverages shown in the upper portion.

sorption on the Si(111) surface are higher. This difference can be most easily seen by the higher peak desorption temperature on Si(111) for ethylene.

Since the β -carbon in the surface ethyl group is labeled with deuterium when $EtBr-d_3$ is the precursor, insight as to how ethylene is formed can be gained. If β -hydride elimination occurs in the production of ethylene, then a deuterium atom is left behind at the surface (no hydrogen desorption is observed concurrent with the ethylene). Two deuterium at-

TABLE I. Kinetic parameters for the desorption of ethylene from the decomposition of deuterium labeled ethyl groups on Si(100) and Si(111).

Species	Transferred	ν (s^{-1})	E_a (kcal mol^{-1})
$CH_3CH_2/Si(100)$	H	$8 \times 10^{6 \pm 1}$	20.1 ± 2
$CH_3CD_2/Si(100)$	H	$1 \times 10^{6 \pm 1}$	20.5 ± 2
$CD_3CH_2/Si(100)$	D	$1 \times 10^{7 \pm 1}$	21.6 ± 2
$CD_3CD_2/Si(100)$	D	$9 \times 10^{7 \pm 1}$	25.3 ± 2
$CD_3CH_2/Si(111)$	D	$2 \times 10^{9 \pm 1}$	27.1 ± 2
$CD_3CD_2/Si(111)$	D	$5 \times 10^{9 \pm 1}$	31.0 ± 2

oms can then recombine at higher surface temperatures to form D_2 . H atoms can also be deposited onto the surface by α -hydride elimination and these atoms can combine to form H_2 . However, as shown in Figs. 3 and 4, a substantial amount of HD is produced. This means that both α - and β -hydride elimination processes are leading to the formation of ethylene.

A branching ratio of the amount of ethylene produced by β -hydride to α -hydride elimination can be calculated by determination of the amounts and types of hydrogen produced. In the case of $EtBr-d_3$ as the ethyl group precursor, this ratio is shown as

$$\frac{\beta}{\alpha} = \frac{\theta_{D_2} + \frac{1}{2}\theta_{HD}}{\theta_{H_2} + \frac{1}{2}\theta_{HD}} \quad (1)$$

In Eq. (1), θ is the coverage of the appropriate type of hydrogen in monolayers. The branching ratio as a function of surface coverage for $EtBr-d_3$ on the Si(100) surface is shown in Fig. 5 (open triangles). The line through the data points is to aid in the viewing of the data. The branching ratio is a weak function of coverage and the ratio is less than unity for $EtBr-d_3$. This result means that α -hydride elimination is slightly preferred to β -hydride elimination in the decomposition of the ethyl group when the deuterium label is attached to the β -carbon. The solid squares show the same branching ratio (β/α) with $EtBr-d_2$ as the ethyl group precursor. With $EtBr-d_2$ there is a strong coverage dependence in the branching ratio. At low coverages, α -hydride elimination dominates (ratio < 1) and for coverages greater than about 0.25 ML, β -hydride elimination is strongly favored. Again it should be pointed out that this ratio is based on a mass balance and is not a branching ratio based on reaction rates.

The reaction rates of ethylene formation on Si(100) are, within experimental uncertainty, independent of ethyl source. However, the position of the deuterium atoms within the ethyl group plays a role in how much ethylene is formed by α -hydride or β -hydride elimination. When the deuterium atoms are attached to the β -carbon it is easier to transfer a H atom from the α -carbon to the Si surface. Mass differences between H and D obviously play a role in this mechanistic step. The other main point is the surface coverage. At low ethyl group surface coverages, there are a number of open Si sites. The number of open nearby sites could also influence how ethylene is formed as evidenced by the coverage dependence for $EtBr-d_2$ in Fig. 5. With $EtBr-d_2$ as the ethyl source at low coverages, D atom transfer from the α position becomes a competitive reaction channel even with the difference in hydrogen masses.

IV. SUMMARY

The adsorption and decomposition of ethylbromide to form ethyl groups on Si(100) and Si(111) has been examined. At surface temperatures less than 110 K, molecular adsorption of the molecule occurs. The carbon-bromine bond is broken by annealing the surface above 200 K and this results in the formation of surface ethyl groups. A

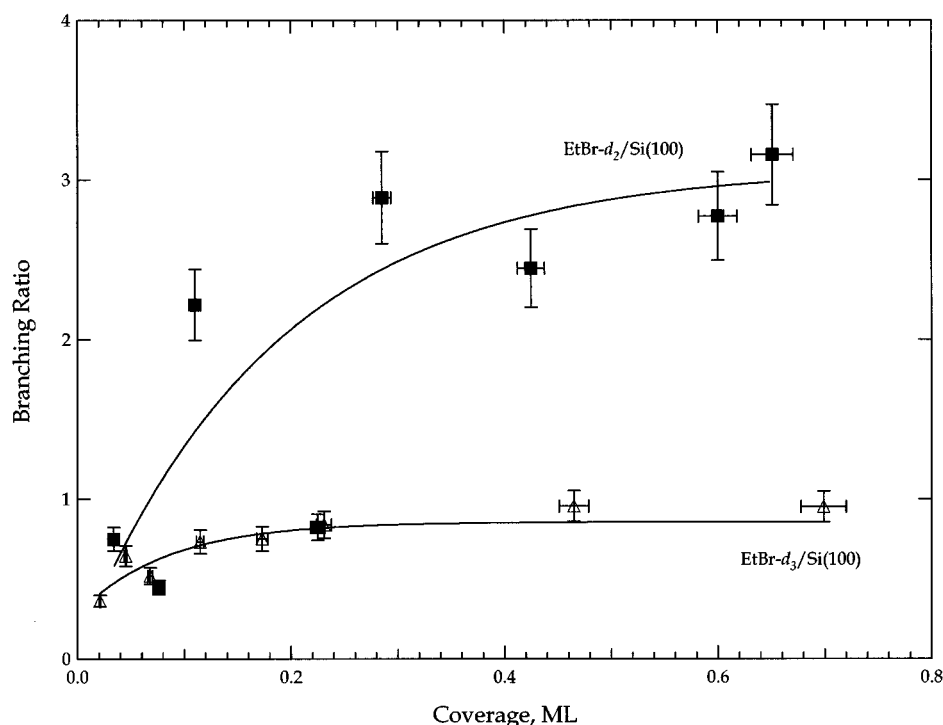


FIG. 5. Branching ratio as a function of ethyl group surface coverage on Si(100) with EtBr- d_3 (open triangles) and EtBr- d_2 (solid squares) as the ethyl group precursor.

branching pathway between α -hydride and β -hydride elimination to produce ethylene is observed. The ethylene reaction rates do not exhibit, within experimental uncertainty, an isotope effect when deuterium labeled EtBr is used. However, the amount of ethylene produced by α -hydride and β -hydride elimination is influenced by isotopic substitution. When deuterium is in the α -position (CH_3CD_2), β -hydride elimination is the dominant pathway for ethylene formation.

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