The Adsorption and Surface Reaction of SiCl₄ on Si(100)-(2x1)

by


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The adsorption and surface reaction of SiCl₄ on Si(100)-(2x1) have been investigated in the temperature range of 100K-1000K. Adsorption of monolayer SiCl₄ and multilayer SiCl₄ are observed by temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS), and electron stimulated desorption ion angular distribution (ESDIAD). Upon heating to ~200K and above, Si-Cl bond scission in adsorbed SiCl₄ occurs, depositing SiClₓ species. Heating to 673K leaves the surface with only silicon monochloride species, SiCl(a), exhibiting Si-Cl stretching mode, vSiCl, at ~560 cm⁻¹, and a Cl⁺ ESDIAD pattern indicative of inclined Si-Cl bond directions from Cl adsorbed on Si₂ dimer sites. Silicon substrate etching occurs above 800K producing SiCl₂(g) as the desorption product.
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Abstract

The adsorption and surface reaction of \( \text{SiCl}_4 \) on \( \text{Si}(100)-(2\times1) \) have been investigated in the temperature range of 100K-1000K. Adsorption of monolayer \( \text{SiCl}_4 \) and multilayer \( \text{SiCl}_4 \) are observed by temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS), and electron stimulated desorption ion angular distribution (ESDIAD). Upon heating to ~200K and above, Si-Cl bond scission in adsorbed \( \text{SiCl}_4 \) occurs, depositing \( \text{SiCl}_x \) species. Heating to 673K leaves the surface with only silicon monochloride species, \( \text{SiCl}(a) \), exhibiting Si-Cl stretching mode, \( \nu \text{SiCl} \), at \( \sim 560 \text{ cm}^{-1} \), and a Cl\(^+\) ESDIAD pattern indicative of inclined Si-Cl bond directions from Cl adsorbed on \( \text{Si}_2 \) dimer sites. Silicon substrate etching occurs above 800K producing \( \text{SiCl}_2(g) \) as the desorption product.

1. Introduction

Silicon chloride and chlorosilane molecules (\( \text{SiCl}_4 \), \( \text{Si}_2\text{Cl}_6 \), and \( \text{SiH}_2\text{Cl}_2 \), etc.) play an important role in the chemical vapor deposition (CVD) as well as in the dry etching of Si substrates. Silicon chloride and chlorosilane molecules have
been widely used as the source material for the growth of thin films of silicon, silicon nitride, silicon carbide and silicon dioxide [1-7]. These molecules are also the common reaction products in ion [8-9] or photon assisted silicon etching [10-11] processes. Therefore, it is important to understand the chemisorption and surface reaction of these molecules for better control of the CVD and the etching processes, since they are the transport species between the gas phase and the surface in both thin film growth and in etching.

There are a few previous studies of silicon chloride surface chemistry which are limited to the Si(111)-(7x7) substrate. The chemisorption and thermal decomposition of silicon chloride, SiCl₄, on Si(111)-(7x7) have been investigated with laser induced thermal desorption (LITD) and temperature programmed desorption (TPD) techniques [12]. It is observed that the reactive sticking coefficient for SiCl₄ is small (S₀ ~ 0.18 at 160K) and that this coefficient decreases with increasing substrate temperature (S₀ ~ 0.03 at 600K). This is interpreted with a precursor-mediated adsorption model where the first stage of adsorption involves trapping of SiCl₄ in a weakly-bound precursor state. Compared to the SiH₄ surface chemistry, where H₂ is the primary desorption product [13], thermal decomposition of SiCl₄ on Si(111)-(7x7) gives SiCl₂ as the primary desorption product (as opposed to Cl₂) with second-order desorption kinetics (E₂ = 65 ± 5 kcal/mole, ν₂ = 3.2 ± 0.7 cm²/s) [12]. Soft x-ray photoemission spectroscopy (SXPS) combined with thermal desorption studies indicate that upon adsorption at room temperature, SiCl₄ completely dissociates on Si(111)-(7x7) yielding only surface monochloride species, SiCl(a). In contrast, Si₂Cl₆ partially dissociates into SiClₓ (x=1, 2, 3) fragments upon adsorption at room temperature [14]. Dichlorosilane (SiH₂Cl₂) adsorption on Si(111) is also
found to adsorb by a precursor-mediated process yielding H₂, HCl and SiCl₂ as the decomposition products [15].

The surface chemistry of silicon chloride on the more technologically relevant Si(100) substrate, however, has not been studied to our knowledge. On Si(100)-(2x1), core-level spin x-ray photoelectron spectroscopy (SXPS) studies indicate that at temperatures ranging from 298 - 1073K, dichlorosilane chemisorbs dissociatively forming silicon monochloride surface species [16]; higher silicon chloride species are not observed.

In this paper, we report studies of the adsorption and chemical bonding of SiCl₄ on the Si(100)-(2x1) substrate as well as the spectroscopic characterization of the surface reaction intermediates. The fundamental questions addressed are the SiCl₄ bonding states and bonding configurations, the surface species formed from SiCl₄ chemisorption at elevated temperatures, and the surface reaction products which desorb. To answer these questions, a combination of surface probes are employed including temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS), and electron stimulated desorption ion angular distribution (ESDIAD). The Si-Cl bond orientations are monitored by ESDIAD, a measurement technique with a precision of ~ 1° [17a-c]

2. Experimental

Experiments were carried out in two UHV chambers. The first chamber was equipped with a digital ESDIAD/LEED (electron stimulated desorption ion angular distribution/low energy electron diffraction) apparatus, an Auger electron spectrometer (AES), a quadrupole mass spectrometer (QMS) for line-of-sight temperature programmed desorption (TPD), and an additional QMS for ion mass
analysis in ESD. The second UHV chamber housed a high resolution electron energy loss spectrometer (HREELS), LEED, AES and a QMS for TPD. The primary beam energy used for the HREELS study was 4.2 eV and the full width at half maximum (FWHM) of the elastic beam was about 65 cm⁻¹. Flux-calibrated micro capillary-collimated gas dosers [18,19] were used in both chambers for control of the SiCl₄ exposure. SiCl₄ was purchased from Aldrich company with a purity of 99.999%. Before use, it was further purified by several freeze-pump-thaw cycles in the gas line. The Si(100) single crystal was cleaned by Ar⁺ sputtering and subsequent annealing at 1173K. The crystal temperature was measured by a chromel-constantan thermocouple enclosed in a Ta-foil envelope which was inserted into a slot on the crystal edge [18]. The base pressure in both UHV chambers was 1x10⁻¹⁰ mbar or below.

3. Results

3.1 Temperature Programmed Desorption Studies

To characterize the adsorption kinetics and the binding states of SiCl₄ on Si(100)-(2x1), temperature programmed desorption was employed as shown in fig. 1. Here, we employ line-of-sight geometry through a small aperture (diameter is 5 mm) for detecting the desorption from the Si(100)-(2x1) surface. Following the adsorption of SiCl₄ on Si(100)-(2x1) at 125K, the detected desorption products include three SiCl₄ desorption features (monitored by the parent ion SiCl₄⁺, m/e=168 amu) at 132K, 142K and 230K, respectively, and a single SiCl₂(g) desorption feature (monitored with SiCl⁺ m/e=63 amu, the major cracking product of SiCl₂(g) in the ionizer) with a peak temperature at ~860K. No Cl₂(g) desorption was observed as was reported for SiCl₄/Si(111) [14]. The desorption feature at ~132K does not saturate for higher SiCl₄ exposures and is thus
attributed to multilayer SiCl₄ adsorption. SiCl₄ desorption at 230K is observed only above SiCl₄ exposures of 0.7x10¹⁴/cm², below which either there is no population of this adsorption state or the desorption signal is buried in the noise preventing measurement.

The adsorption kinetics for the first adsorbed SiCl₄ layer (142K peak) is shown in the insert of fig. 1. At an exposure of ~1.7x10¹⁴ SiCl₄/cm², a monolayer is completed. We observe, however, that the multilayer desorption feature has appeared (at an exposure of ~1.2x10¹⁴ SiCl₄/cm²) before the full monolayer is completed.

The SiCl₂(g) desorption is shown from SiCl₄ decomposition with a peak temperature of ~860K at 1.7x10¹⁴ SiCl₄/cm² initial exposure. The peak temperature is shifted to lower temperatures for increasing exposure. The SiCl₂(g) desorption feature has been observed for all the SiCl₄ exposures studied here. The amount of Si desorbed in SiCl₂(g) at 1.7x10¹⁴ SiCl₄/cm² exposure is estimated of about 0.04 of a monolayer.

3.2 Low Temperature Adsorption of SiCl₄/Si(100)-(2x1) - HREELS Studies

As shown in fig. 2, adsorption of SiCl₄ at 100K produces a vibrational spectrum similar to that of gas phase SiCl₄ molecules. At a SiCl₄ exposure of 0.67x10¹⁴ molecules/cm², a strong loss peak is observed at 630 cm⁻¹ together with a medium intensity peak at 220 cm⁻¹ (fig. 2a). These two peaks are assigned to the degenerate asymmetric SiCl stretching mode, v₃SiCl₄, and the degenerate umbrella bending mode of the SiCl₃ moiety, δ₃SiCl₃, of the SiCl₄(a) molecules, respectively [20]. Extremely weak peaks at 390 cm⁻¹, 850 cm⁻¹, 1260
cm⁻¹ and 2080 cm⁻¹ are seen as well. It appears that the local point group symmetry of the SiCl₄ molecules is close to Td which would give only two dipole active modes: a degenerate Si-Cl stretching mode, ν₅SiCl₄ (ν₃), and the umbrella bending mode, δ₅(ν₄), of the SiCl₃ moiety. The symmetric stretching mode, νₛSiCl₄ (ν₁), at ~400 cm⁻¹ and the scissors mode, δ₅(ν₂), at ~145 cm⁻¹ [20] are forbidden by the dipole selection rule due to the local Td symmetry. These modes, however, may be excited by the impact scattering mechanism. A weak loss for the symmetric stretching mode at ~390 cm⁻¹ is barely observed and the scissors mode of SiCl₄ (~150 cm⁻¹) is not observed in this study. At an exposure of 1.7x10¹⁴ SiCl₄/cm², nearly the same vibrational features are observed (fig. 2b). The previous 630 cm⁻¹ peak shifts slightly upward to 635 cm⁻¹. At an exposure of 3.4x10¹⁴ SiCl₄/cm², the HREEL spectrum displays an enhancement of the 860 cm⁻¹ and the 1280 cm⁻¹ peaks (fig. 2c). The 860 cm⁻¹ peak may be a combination band of the 220 cm⁻¹ and 640 cm⁻¹ modes. Double loss scattering (with energy losses of 220 cm⁻¹ and 640 cm⁻¹) can also contribute to this peak. The 1280 cm⁻¹ peak is assigned to the overtone of the 640 cm⁻¹ peak. Like the 860 cm⁻¹ peak, a double loss (with energy losses of 640 cm⁻¹ and 640 cm⁻¹) scattering may also contribute. The small probabilities for the double losses and the overtone processes are consistent with the weak intensities of these peaks. For small surface coverages, the bare silicon surface sites are easily attacked by the background water producing a surface hydroxyl group and silicon monohydride. The former has a vibrational feature at 800-900 cm⁻¹ and the latter has the Si-H stretching mode at ~2080 cm⁻¹ [21], and weak features in these regions are also observed.
3.3 Temperature Dependent Behavior of SiCl$_4$/Si(100)-(2x1)

A multilayer initial exposure at 100K results in a HREEL spectrum shown in fig. 3a. The spectrum is identical to fig. 2c. Annealing to 200K removes the multilayer and monolayer SiCl$_4$ and causes shifts of the 640 cm$^{-1}$ peak to 577 cm$^{-1}$, the 220 cm$^{-1}$ peak to 210 cm$^{-1}$, and the 390 cm$^{-1}$ peak to 400 cm$^{-1}$ (fig. 3b). The increase in relative intensity ratios of the 400 cm$^{-1}$ peak to both the 210 cm$^{-1}$ peak and the 577 cm$^{-1}$ peak is observed (fig. 3b) compared to the ratios of the 390 cm$^{-1}$ peak to both the 220 cm$^{-1}$ peak and the 640 cm$^{-1}$ peak (fig. 3a). This is an indication of the breakdown of the local T$_d$ symmetry of the SiCl$_4$ species, probably by partial decomposition. A weak loss peak at 900 cm$^{-1}$ is associated with the vacant sites generated by SiCl$_4$ desorption at 200K and is thus likely to be from the background water adsorption. After 300K annealing, the Si-Cl stretching mode shifts down further to 566 cm$^{-1}$ (fig 3c). The 400 cm$^{-1}$ feature is still observable. Further annealing to 673K leads to the disappearance of both the 200 cm$^{-1}$ peak and the peak at ~800 cm$^{-1}$ (fig. 3d), consistent with the final formation of a surface monochloride species, as previously observed for Cl$_2$ and HCl adsorption on Si(100) [22-23]. The formation of surface monochloride species also leads to the peak intensity enhancement of the Si-Cl stretching mode at 566 cm$^{-1}$ as observed in fig. 3d. A reduction in the peak intensity and a shift of the 566 cm$^{-1}$ peak to 560 cm$^{-1}$ are observed after annealing to 847K (fig. 3e) which is correlated with the depletion of surface chlorine by the thermal desorption of SiCl$_2$(g) (fig. 1).
3.4 ESDIAD Studies of SiCl₄/Si(100)-(2x1)

In the ESDIAD experiment, the surface species containing Cl are subjected to electron beam excitation. The transition of the Si-Cl bond from the ground electronic state to an excited anti-bonding electronic state leads to Cl desorption and ionization (Cl⁺). The trajectories of the Cl⁺ ions are recorded and summed together in ESDIAD which indicate the distribution of the spatial orientation of the Si-Cl chemical bonds. Adsorption of SiCl₄ at 120K to multilayer coverage results in a Cl⁺ ESDIAD pattern shown in fig. 4a. The pattern consists of a strong central beam and a nearly uniform azimuthal intensity distribution. Annealing to 200K results in four shoulder peaks in the <011> and <01T> azimuth, superimposed on a central beam (fig. 4b). Annealing to 300K causes an enhancement of the normal Cl⁺ beam (fig. 4c). An ESDIAD pattern primarily exhibiting four off-normal Cl⁺ beams is observed after annealing the surface to 673K (fig. 4d). These four beams correspond to the orientations of the Si-Cl bonds on the Si₂ dimers in the two orthogonal domains. Similar ESDIAD patterns have been observed for chlorine adsorption on Si(100)-(2x1) at the same annealing temperature [22, 24] and for the HCl adsorption on Si(100)-(2x1) at 120K [23]. Surface monochloride species are responsible for these four off-normal emission beams for the three adsorption systems at this annealing temperature. A decrease of the beam intensities is observed after 847K annealing (fig. 4e). Heating to this temperature leads to the etching of the substrate with SiCl₂(g), causing a decrease of the Cl⁺ ion intensity. The approach to a more random orientation of the Si-Cl bonds for the remaining SiCl(a) species on an etched substrate is indicated by the merging of the four shoulder beams with the broad central beam; similar ESDIAD pattern changes are observed for Cl₂ adsorption onto Si(100) followed by heating to 847K [22].
4. Discussion

4.1 The Bonding of SiCl$_4$ on Si(100)-(2x1) at Low Temperatures

Three SiCl$_4$ desorption states are detected (fig. 1) in the TPD experiments. In order of increasing desorption temperature, they are the multilayer SiCl$_4$(a) ($T_p$~132K), physisorbed SiCl$_4$ within the monolayer range ($T_p$~142K), and a small amount of SiCl$_4$ (≤ 0.01 of the first layer SiCl$_4$(a)) with a peak temperature at ~230K. The monolayer SiCl$_4$ reaches saturation coverage with increasing exposure (Fig. 1 insert) while the multilayer does not show saturation behavior. Both monolayer and multilayer SiCl$_4$(a) display vibrational spectra similar to that of the gas phase molecules, indicative of non-dissociative adsorption (see fig. 2 and the summary of the vibrational mode assignments in Table 1). The lack of a scissors mode peak (~145 cm$^{-1}$) and the extremely weak peak, if any, for the symmetric Si-Cl stretching mode (~390 cm$^{-1}$) (fig. 2a) suggest that the local symmetry of the SiCl$_4$ molecules is nearly the same as for the free SiCl$_4$ molecule (T$_d$). Since the physisorbed monolayer and multilayer molecules are bound to the surface by means of van der Waals forces as opposed to strong directional covalent chemical bonding, a random Si-Cl bond orientation is, therefore, expected. This is confirmed by the nearly uniform azimuthal Cl$^+$ ion intensity distribution in ESDIAD measurements shown in the contour plot (fig. 4a). The angular distribution shows a maximum in the surface normal direction (with polar angle $\Theta$ = 0) due to the lowest neutralization probability for Cl$^+$ ions departing in this direction. According to Hagstrum [25], the rate of Cl$^+$ ion neutralization is exponentially related to the ion-surface separation ($z$):

$$R = A \exp(-\alpha z)$$
where \( z \propto d \cdot \cos \Theta \), \( d \) is the Si-Cl bond length and \( \Theta \) is the polar angle of the Si-Cl bond relative to the surface normal. This leads to a minimized neutralization probability for Cl\(^+\) ions leaving in the direction of surface normal \((\Theta=0)\).

Small amounts \(( \lesssim 0.01 \) of the first layer) of SiCl\(_4\) desorption (\( T_p \approx 230K \)) are clearly observed for SiCl\(_4\) exposures above \( 0.7 \times 10^{14} \) SiCl\(_4\)/cm\(^2\). The following arguments favor recombinative desorption of SiCl\(_x\)(a) + \((4-x)\)Cl(a) \( \rightarrow \) SiCl\(_4\)(g) as the origin of the 230K SiCl\(_4\) desorption state: (1) HREEL spectra show the symmetric Si-Cl stretching mode at \(~ 400 \text{ cm}^{-1}\) with moderate intensity, indicative of a breakdown of the local T\(_d\) symmetry for the SiCl\(_x\) species remaining after desorption of SiCl\(_4\) at 200K (fig. 3b). This can be interpreted as being due to the dissociation of SiCl\(_4\)(a) into SiCl\(_3\)(a); (2) The vibrational features are close to those found for CH\(_3\)SiCl\(_3\) molecules. The asymmetric SiCl stretching mode, \( \nu_a \) at \( 576 \sim 578 \text{ cm}^{-1} \), symmetric SiCl stretching, \( \nu_s \) at \( 450 \sim 458 \text{ cm}^{-1} \), and the bending and rocking modes, \( \delta \) and \( \gamma \), in the range of \( 164 \sim 229 \text{ cm}^{-1} \), for this molecule have been observed \([26a-c]\). These modes correspond well with the HREELS peaks observed at \( 577 \text{ cm}^{-1} \), \( 400 \text{ cm}^{-1} \) and \( 210 \text{ cm}^{-1} \) in fig. 3b; (3) In ESDIAD, annealing to 200K causes the development of the four shoulder peaks along the \( <011> \) and \( <0\overline{1}1> \) directions. These shoulders in the ion angular distribution of Cl\(^+\) are due to the contribution from the surface monochloride species produced from SiCl\(_4\) decomposition with Cl captured on the Si(100) substrate \([22-24]\). An unlikely alternative explanation for the species responsible for the 230K SiCl\(_4\) desorption process is the production of a distorted SiCl\(_4\) species of low coverage on the surface (such as on defect sites).
4.2 The Surface Decomposition of SiCl$_4$ on Si(100)-(2x1)

Beyond a temperature of ~250K, SiCl$_4$ ceases to be a thermal desorption product from the Si(100)-(2x1) surface. Both HREELS and AES measurements show that chlorine remains behind above 250K indicating that SiCl$_4$(a) has decomposed to lower silicon chloride species which are strongly bound. As shown in fig. 3, the $\approx 200$ cm$^{-1}$ $\delta$ bending mode for SiCl$_x$ (a) species remains up to 300K, as does the 400 cm$^{-1}$ symmetric stretching mode for SiCl$_x$(a). It is not possible to discriminate between modes due to SiCl$_3$(a) and SiCl$_2$(a) on the basis of these observed frequencies [26a-d]. At 673K in fig. 3, the vibrational spectrum is closely similar to that found for Cl$_2$ adsorption on Si(100)-(2x1) at the same temperature; the 566 cm$^{-1}$ mode corresponds to the asymmetric stretching mode, $\nu_a$SiCl, at low chlorine coverages. The vibrational frequencies of different silicon chlorides observed in this study and those reported in the literature are summarized in Table 1.

ESDIAD results also indicate that inclined Si-Cl bonds are forming as SiCl$_4$-derived surface species decompose. Fig. 4d, obtained after heating to 673K, is closely similar to the Cl$^+$ ESDIAD pattern produced from Cl$_2$ adsorption on Si(100) at 100K followed by 673K annealing [22,24]. This pattern is dominated by four Cl$^+$ beams lying in the vertical planes parallel to the Si$_2$ dimer bonds in two orthogonal domains on the crystal, and this pattern and the measured Si-Cl bond angle (25$^\circ$$\pm$4$^\circ$) have been extensively discussed previously [22]. Annealing to 847K (fig. 4e) results in a diminished contribution of the four Cl$^+$ beams, coupled to a broad normally oriented Cl$^+$ beam as is also observed for Cl$_2$-derived layers (annealed at 847K) on Si(100)-(2x1). This is due to surface etching with liberation of SiCl$_2$(g), producing randomized Si-Cl bond orientations [22].
SiCl₂ desorption near 800K occurs from a surface containing only SiCl(a) species. Thus SiCl₂(g) must be formed from a recombination process. Assuming second-order kinetics in surface chlorine coverage, we derive an activation energy of 83±7 kcal/mole using the method of Chan et al. [27]. Laser induced thermal desorption studies of SiCl₂ from SiCl₄/Si(111)-(7x7) yield an activation energy of 65±5 kcal/mole for second-order desorption kinetics [12].

A summary of the thermal processes observed in this work, and the temperature employed to observe these processes is given below:

\[
\begin{align*}
\text{SiCl}_4(a) & \text{(multilayer)} \xrightarrow{132K} \text{SiCl}_4(g) \\
\text{SiCl}_4(a) & \text{(monolayer)} \xrightarrow{142K} \text{SiCl}_4(g) \\
\text{SiCl}_4(a) & \text{(monolayer)} \xrightarrow{\geq 200K} \text{SiCl}_x(a) + (4-x) \text{SiCl}(a) \\
\text{SiCl}_x(a) + (4-x) \text{SiCl} & \xrightarrow{230K} \text{SiCl}_4(g) \\
\text{SiCl}_x(a) & (x=2, 3) \xrightarrow{673K} x \text{SiCl}(a) \\
\text{SiCl}(a) + \text{SiCl}(a) \text{ or Cl}(a) & \xrightarrow{\geq 800K} \text{SiCl}_2(g)
\end{align*}
\]

4.3 The Surface Structure Controlled Chemistry

A fundamental question in surface science concerns the role of the detailed surface structure in determining surface chemical processes. It appears that the detailed surface structure does play a role for the SiCl₄ surface dissociation process. With soft x-ray photoemission spectroscopy (SXPS) and thermal desorption studies it is observed that upon adsorption at room temperature, SiCl₄ completely dissociates on Si(111)-(7x7) yielding only surface monochloride
species SiCl(a) [14]. However, from the studies presented here the low temperature adsorption of SiCl$_4$ on Si(100)-(2x1) followed by annealing to 300K does not completely dissociate SiCl$_4$(a). Therefore, in comparison with the Si(111)-(7x7) surface, the Si(100)-(2x1) surface is less reactive for SiCl$_4$ dissociation.

It is well understood that on the Si(111)-(7x7) surface, large backbond strain is present for the adatoms compared to the rest atoms [28-29]. The strained Si-Si backbonds are, from a thermodynamic point of view, active in chemical reactions. This may explain why SiCl$_4$(a) molecules can dissociate completely into surface monochloride species at room temperature on Si(111)-(7x7). On the other hand, only partial dissociation of SiCl$_4$ occurs on the Si(100)-(2x1) surface at 300K, indicative of less bond strain for the Si(100)-(2x1) surface [30]. A similar bond strain effect has been observed for the dissociation of NH$_3$ molecules [31] where on Si(111)-(7x7), NH$_3$ is dissociated into NH(a) at 300-600K while on Si(100)-(2x1), the NH$_2$(a) species is stable up to 600K. In addition, STM studies of hydrogen on Si(111)-(7x7) provide convincing experimental evidence that the strained adatom backbond exhibits a lower reaction barrier toward atomic hydrogen than the unstrained rest atom backbond [32].

4.4 Correlation with Chemical Vapor Deposition of Silicon Films from SiCl$_4$

In the high temperature chemical vapor deposition (CVD) of silicon thin films, mixtures of H$_2$ and SiCl$_4$ gas are admitted to the growth chamber in the temperature range of 1000K-1300K [33-34]. Based on the results of our investigation in this paper, the most likely surface species to be present in this
temperature range is SiCl(a). In the low temperature CVD process, like catalytic CVD (T_{substrate} < 573K) [35], decomposition of SiCl₄ occurs on a hot filament delivering SiClₓ(x=1, 2, 3) species to the surface where also monochloride surface species would likely form. Hydrogenation to produce HCl leaves the silicon film. Current studies of these processes are limited to spectroscopic monitoring of gas phase products [36].

5. Conclusions

The following results are found for the adsorption and decomposition of SiCl₄ on Si(100)-(2x1).

1. Multilayer and monolayer adsorption of SiCl₄ has been observed. Multilayer desorption occurs at 132K; monolayer desorption occurs at 142K.
2. A small quantity (≤ 0.01 of the first layer) of SiCl₄ desorbs at 230K and is postulated to be due to a recombination process between SiClₓ species.
3. Heating in the temperature range 300-673K results in the loss of SiCl₄ species forming Si-Cl bonds which have similar vibrational and directional properties to the Si-Cl bonds formed on Si(100)-(2x1) from Cl₂ in the same surface temperature range.
4. Above ~800K, SiCl₂(g) species desorb with an activation energy of 83±7 kcal/mole assuming second-order kinetics in chlorine coverage.

Acknowledgment

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(c) L. Burnelle and J. Duchesne, J. Chem. Phys. 20 (1952) 1324.


Figure Captions

Fig 1. Temperature programmed desorption of a multilayer SiCl$_4$(a) adsorbed on Si(100)-(2x1) at 125K. The exposure is 1.7x10$^{14}$ SiCl$_4$/cm$^2$. The SiCl$_2$(g) desorption feature from SiCl$_4$ decomposition is displayed for T>800K. Lower temperature SiCl$^+$ signals correspond to the SiCl$_4$(g) cracking in the mass spectrometer. The insert indicates the development of the TPD yield for the monolayer of SiCl$_4$ versus exposure (142K peak).

Fig. 2. HREEL spectra of SiCl$_4$ adsorption on Si(100)-(2x1) at 100K with SiCl$_4$ exposures: (a) 0.67x10$^{14}$/cm$^2$; (b) 1.7x10$^{14}$/cm$^2$; (c) 3.4x10$^{14}$/cm$^2$.

Fig. 3. Thermal development of HREEL spectra for SiCl$_4$/Si(100)-(2x1). The initial SiCl$_4$ exposure is 3.4x10$^{14}$/cm$^2$. (a) 100K adsorption; then annealed
to the following temperatures: (b) 200K; (c) 300K; (d) 673K and (e) 847K. All spectral data are collected at 100K.

Fig. 4. Thermal development of the Cl⁺ ESDIAD pattern produced from SiCl₄ adsorption. Electron beam energy Eₑ = 120V, crystal current Iₑ = 2pA, Vbias (on crystal) = +10V. (a) 120K adsorption of 3.4x10¹⁴ SiCl₄/cm². Then annealed to the following temperatures: (b) 200K; (c) 300K; (d) 673K; and (e) 847K. All data are collected at 120K.
Table 1. Vibrational Frequencies for Silicon Chlorides (cm$^{-1}$)

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<th>$\nu_{dSiCl_4}(v_3)$</th>
<th>$\nu_{gSiCl_4}(v_1)$</th>
<th>$\delta_{dSiCl_3}(v_4)$</th>
<th>$\delta_{dSiCl_2}(v_2)$</th>
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<td>145</td>
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<td>220</td>
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<td>SiCl$_3$(CH$_3$)(g)</td>
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<td>450-458</td>
<td>164-229</td>
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<td>[26a-c]</td>
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<td>[26a]</td>
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<td>SiCl$_2$(CH$_2$)$_3$(g)</td>
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<td>376</td>
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<td>[26d]</td>
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<td>SiCl$_x$(a) (x=2,3)</td>
<td>566-577</td>
<td>400</td>
<td>200-210</td>
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<td>[this work]</td>
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<tr>
<td></td>
<td>$\nu_{aSiCl}$</td>
<td>$\nu_{gSiCl}$</td>
<td>$\delta_{SiCl}$</td>
<td>$\gamma_{SiCl}$</td>
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<tr>
<td>SiCl$_3$(CH$_3$)(g)</td>
<td>576-578</td>
<td>450-458</td>
<td>164-229</td>
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<tr>
<td>SiCl$_2$(CH$_3$)$_2$(g)</td>
<td>533</td>
<td>465</td>
<td>169</td>
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<td>533</td>
<td>376</td>
<td>167-241</td>
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<td>566-577</td>
<td>400</td>
<td>200-210</td>
<td></td>
</tr>
<tr>
<td>[this work]</td>
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<td></td>
<td>$\nu_{SiCl}$</td>
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<td>SiCl(CH$_3$)$_3$(g)</td>
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<td>560-566</td>
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TEMPERATURE PROGRAMMED DESORPTION
FROM SiCl₄/Si(100)-(2x1)

SiCl₄⁺/SiCl₄
m/e=168 amu
dT/dt=4K/sec
1.7x10¹⁴ SiCl₄/cm²

TPD Yield (a. u.)

Adsorption Kinetics of SiCl₄ Monolayer

SiCl⁺/SiCl₂
m/e=63 amu

Gao, et al.,
Figure 1
COVERAGE DEPENDENT HREELS STUDY
OF SiCl₄/Si(100)-(2x1)

Gao, et al.,
Figure 2
HREELS MEASUREMENTS OF THE THERMAL BEHAVIOR OF SiCl$_4$/Si(100)-(2×1)

SiCl$_4$
Exposure
3.4x10$^{14}$/cm$^2$

$T_{\text{anneal}}$

(e) 847K
(d) 673K
(c) 300K
(b) 200K

(a) 100K

Intensity (arb. units)

Energy Loss (cm$^{-1}$)

Gao, et al.,
Figure 3
THERMAL DEVELOPMENT OF CI$^+$ ESDIAD PATTERN - SiCl$_4$/Si(100)-(2×1)

(a) 120K, $3.4 \times 10^{14}$ SiCl$_4$/cm$^2$

(b) 200K anneal

(c) 300K anneal

Gao, et al., Figure 4
THERMAL DEVELOPMENT OF Cl⁺ ESDIAD PATTERN - SiCl₄/Si(100)-(2×1)

(d) 673 K anneal

(e) 847 K anneal

Gao, et al.,
Figure 4
Continued
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