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THE CHEMISORPTION OF CHLOROSILANES AND CHLORINE ON Si(111)7 × 7

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The chemisorption of $SiCl_4$, Si_2Cl_6, and chlorine on Si(111)7 × 7 has been characterized using soft X-ray photoemission with synchrotron radiation, thermal desorption spectroscopy, and Auger electron spectroscopy. $SiCl_4$ dissociatively chemisorbs on room temperature Si(111)7 × 7 with an extremely low sticking coefficient, with only SiCl remaining on the surface. In contrast, Si_2Cl_6 chemisorbs with ~ 500 times greater probability and then partly dissociates into $SiCl_x$ ($x = 1, 2, 3$) fragments. A monolayer of Cl deposited directly also contains SiCl, $SiCl_2$, and $SiCl_3$ surface species, but they are created via reaction with substrate Si atoms and have lower Si 2p core level binding energies. Upon heating the surface all the adsorbed Cl is removed via desorption of silicon chlorides, primarily $SiCl_2$, indicating that $SiCl_4$, Si_2Cl_6, and chlorine will etch Si(111)7 × 7 if an additional reactant is not available to remove the surface Cl. Interestingly, the different reactivities of $SiCl_4$ and Si_2Cl_6 upon adsorption can be explained by the dynamics of different adsorption mechanisms.

1. Introduction

Silane (SiH_4) and dichlorosilane (SiH_2Cl_2) are widely employed in the manufacture of microelectronic devices as sources of Si during film growth via chemical vapor deposition (CVD). Unfortunately these gases are pyrophoric, and therefore constitute a significant safety hazard in the workplace. Motivated by the desire for a safer alternative to these explosive silanes there have been a number of studies investigating the potential of $SiCl_4$ and Si_2Cl_6, relatively stable liquids under ambient conditions, as CVD source materials for silicon, silicon nitride, silicon carbide, and silicon dioxide films [1–5]. Although the studies demonstrate that films can be efficiently deposited with the safer chlorosilanes $SiCl_4$ and Si_2Cl_6, little is known about the basic physics and chemistry of the interaction of these chemicals with semiconductor surfaces. Hence, additional model studies conducted on single crystal surfaces in ultra-high vacuum (UHV) with surface sensitive spectroscopies are needed. In addition to elucidating the CVD process, model studies of $SiCl_4$ and Si_2Cl_6 chemisorption are also of interest as a comparison to studies of the chemisorption of SiH_4 and Si_2H_6 (a surface-active CVD gas-phase reaction product) [6–9].

As reported by Gates [6], SiH_4 dissociatively adsorbs on room temperature Si(111)7 × 7 with a low reactive sticking coefficient, $S_0 \leq 0.001$, and appears to adsorb directly (without a molecular precursor). Very recent measurements indicate that SiH_2 is the stable surface species [9]. Disilane (Si_2H_6), on the other hand, has been found to dissociatively adsorb via a precursor with a much higher $S_0 \approx 0.5$ [6]. A separate study by Imbihl et al. found that at room temperature disilane fragments into SiH, SiH_2, and SiH_3 surface moieties

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[7]. Imbihl et al. also found that when the surface is heated the di- and trihydrides dissociate to monohydride at ~ 400 °C, simultaneously giving rise to a H_2 desorption peak, and that upon further heating the remaining hydrogen desorbs as H_2 over a broad temperature range centered at ~ 550 °C [7]. Similar results have been more recently reported by Uram and Jansson [8].

Based on a study of $SiCl_4$ adsorption on Si(111)7 × 7 using thermal desorption spectroscopy (TDS) and laser induced thermal desorption, Gupta et al. concluded that $SiCl_4$ dissociates on room temperature Si(111)7 × 7 [10]. Although the reactive sticking coefficient of $SiCl_4$ was originally reported to be $S_0 \approx 0.025$ [10], further investigation has lead to a new estimate of $S_0 \approx 0.04$ [11]. Unlike the silane exposed surface where H_2 is the primary desorption product, following adsorption of $SiCl_4$ primarily $SiCl_2$ desorption was observed (as opposed to Cl_2) [10]. We know of no previous model studies of the reaction of Si_2Cl_6 with Si(111)7 × 7.

We have undertaken a study of the chemisorption of $SiCl_4$, Si_2Cl_6, and for comparison, chlorine on single crystal Si and Ge surfaces in UHV employing soft X-ray photoemission spectroscopy (SXPS) with synchrotron radiation, TDS, and Auger electron spectroscopy (AES). In this report we focus on the results for Si(111)7 × 7 surfaces. Our results confirm that $SiCl_4$ adsorbs on Si(111)7 × 7 with a very low sticking coefficient, and reveal that upon adsorption complete dissociation occurs leaving SiCl on the surface. We find that, like Si_2H_6, Si_2Cl_6 adsorbs with a much larger sticking coefficient and only partially decomposes (to a mixture of SiCl, $SiCl_2$, and $SiCl_3$).

2. Experimental

The photoemission measurements were performed in a multi-chamber UHV system at beam line UV-8b on the VUV ring at the National Synchrotron Light Source (NSLS). Spectra shown here were recorded using a 6 m focal length toroidal grating monochromator and an ellipsoidal mirror analyzer with an overall resolution ~ 0.1 eV [12]. The TDS and AES experiments were performed in a different UHV chamber at the National Institute of Standards and Technology (NIST).

The experiments were performed with single crystal Si(111) samples (n-doped, 1 Ω cm, approximately 3 × 8 mm for the SXPS and 5 × 10 mm for the TDS and AES) oriented with a precision of ±0.25 °. For the photoemission experiments the samples were cleaned by heating in vacuo to 1050 °C to remove the native oxide layer and then cooling slowly to room temperature. Photoemission spectra obtained with these surfaces showed the sharp surface states characteristic of a clean, well ordered 7 × 7 reconstructed surface [13]. At NIST the samples were initially cleaned in this way, and subsequently cleaned via sputtering with 500 eV Ar^+ ions (~ 10 $\mu A\ cm^{-2}$) followed by a 10 min anneal at 800 °C. Results obtained with sputter-cleaned surfaces were identical to those obtained with virgin samples. During the photoemission experiments sample temperatures were measured with optical and infrared pyrometers, and controlled manually via resistive heating. Temperatures were measured during TDS and AES with a Chromel–Alumel thermocouple held to the back of the sample by a Ta spring clip, and regulated via computer control of the resistive heating current.

Distilled $SiCl_4$ and Si_2Cl_6 were purified by freeze–pumping at −196 °C (liquid N_2) and −69 °C (dry ice). Exposures were performed by back filling the chamber through a leak valve and are reported in Langmuir units ($1\ L \equiv 1 \times 10^{-6}$ Torr · s) uncorrected for ion gauge sensitivity. Chlorine was deposited using a solid state electrochemical cell [14] in order to avoid exposing the chamber to high ambient pressures of Cl_2 gas. The cell emits a beam composed essentially of Cl_2, although some atomic Cl may also be effused [14]. All exposures were performed with the samples at room temperature.

The chemisorption of $SiCl_4$, Si_2Cl_6, and chlorine on Si(111)7 × 7 was primarily studied by examining the Si 2p core level photoemission. A photon energy of 130 eV was employed to maximize the surface sensitivity of the photoelectrons (kinetic energy ~ 25 eV). In order to observe the surface core level shifts more clearly the Si $2p_{1/2}$

contributions and the secondary-electron backgrounds have been subtracted from the spectra (a spin–orbit splitting of 0.61 eV and ratio of 0.52 was assumed) [15]. The core level binding energies have been determined by fitting the data, following background and Si $2p_{1/2}$ subtraction, to a sum of Gaussian broadened Lorentzians, with the Lorentzian width of all features fixed at 0.12 eV.

Thermal desorption spectra were recorded with a quadrupole mass spectrometer, in line-of-sight with the crystal surface, which was multiplexed to monitor up to ten masses simultaneously ($m/e \leq 200$). During TDS the sample temperature, mass selection, and data acquisition were all controlled by a personal computer. A linear heating rate $\sim 10\,°C\ s^{-1}$ was employed. Auger electron spectra were recorded rapidly (in ≤ 70 s, to minimize electron beam damage) in the derivative mode with an incident electron current of $\sim 1\ \mu A$ at an energy of 1500 eV modulated by 4 eV at 15 kHz. No measurable differences were observed between sequentially recorded spectra, demonstrating that any damage incurred during the brief exposure to the electron beam was minimal.

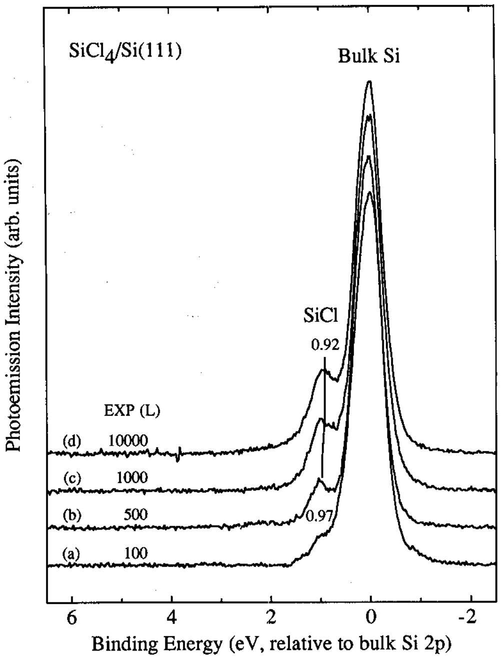

Fig. 1. Photoemission spectra of the Si $2p_{3/2}$ core level after exposure of room temperature Si(111)7×7 to $SiCl_4$: (a) 100, (b) 500, (c) 1000, (d) ≥10000 L (saturation). The core level shifted to higher binding energy, attributed to SiCl with silicon in an oxidation state of +1, is the only additional level observed for all exposures, indicating complete dissociative adsorption. The photon energy was 130 eV. The $2p_{1/2}$ component has been numerically removed following subtraction of the secondary-electron background. The peak positions shown have been determined by fitting the data to a sum of Gaussian broadened Lorentzians.

3. Results and discussion

In fig. 1 Si $2p_{3/2}$ photoemission spectra recorded following increasing $SiCl_4$ exposures on Si(111)7 × 7 are displayed. Following adsorption of $SiCl_4$ a surface core level shifted by ~ 0.97 eV to higher binding energy is observed which shifts ~ 50 meV to lower binding energy with increasing coverage. We attribute this peak to surface SiCl with the Si atoms in an oxidation state of +1 [16,17]. This is the only shifted core level observed for all coverages up to saturation (fig. 1d), indicating that $SiCl_4$ dissociates completely (at least to SiCl) upon adsorption at room temperature. Note that since the dissociation liberates Cl, at least 3/4 of the SiCl must result from reaction with substrate Si. (As will be discussed below, it is not clear whether $SiCl_4$ losses all four or only three of its Cl ligands upon chemisorption). The observation of only SiCl on the surface demonstrates that contrary to the suggestion by Gupta et al. [10], based on their observation of $SiCl_2$ desorption, $SiCl_2$ is not the primary stable chloride. $SiCl_4$ is evidently more reactive than SiH_4 which only dissociates to SiH_2 [9]. The small absolute magnitude of the reactive sticking coefficient necessitates the large exposure (> 100 L) necessary to achieve an observable coverage of SiCl (the SXPS is sensitive to $\sim 1 \times 10^{13}\ cm^{-2}$). Similarly, an extremely large exposure ($\sim 10^4$ L) is necessary to achieve saturation coverage. Note that the reaction we observe cannot be attributed to contamination of the $SiCl_4$ with more reactive Cl_2 or Si_2Cl_6 since, as will be shown below, either of these contaminants would result in a different photoemission spectra following saturation exposure.

The ~ 50 meV downward shift of the SiCl Si 2p binding energy with increasing coverage can be attributed to the different reactivities of the different Si atoms within the unit cell of the Si(111)7 × 7 dimer-adatom-stacking-fault (DAS) [18] surface structure. As observed with scanning tunneling microscopy (STM) by Boland and Villarrubia [19], adsorbed Cl reacts first with surface Si "adatoms" and then with Si "rest" atoms. Since the "rest" atoms are embedded in the surface, in contrast to the "adatoms" which are adsorbed *on* the "rest" atom layer [18], the Si 2p core holes created during photoemission from "rest" atoms should be more efficiently screened by the bulk Si bands then those of the "adatoms"; the additional screening should result in lower core level binding energies for the reacted "rest" atoms [20]. Hence, as the coverage increases and the Cl atoms liberated by $SiCl_4$ dissociative adsorption react first with the "adatoms" and then with the "rest" atoms, the observed binding energy of the SiCl Si 2p core level, which is a convolution of all the surface SiCl Si 2p binding energies, gradually shifts downward.

A progression of spectra for increasing exposures of Si_2Cl_6 on Si(111)7 × 7 is shown in fig. 2. In contrast to $SiCl_4$, three shifted core levels are observed following adsorption of Si_2Cl_6, indicating the presence of surface silicon atoms bonded to (with increasing binding energy) one (oxidation state +1), two (+2), or three (+3) chlorine atoms [16,17]. All three oxidation states appear to be present for all coverages; unlike $SiCl_4$, Si_2Cl_6 does not dissociate to SiCl upon adsorption but, similar to Si_2H_6 [7], fragments into SiCl, $SiCl_2$, and $SiCl_3$. Since there is more SiCl than $SiCl_2$, some of the SiCl must come from the cracking of $SiCl_2$ (which liberates Cl), i.e. the SiCl present is a mixture of adsorbed SiCl molecular fragments and reacted substrate Si.

A comparison of the relative intensities of the shifted core levels and the relative Cl_{LMM}/Si_{LMM} Auger peak height ratios following various exposures of $SiCl_4$ and Si_2Cl_6 allow us to estimate that S_0 for Si_2Cl_6 is ~ 500 times greater than for $SiCl_4$. Gupta et al. recently found $S_0 \approx 0.04$ for $SiCl_4$ [11]. If this were the case, then our measurements imply that the sticking coefficient of Si_2Cl_6 must be > 1 (which is not physically possible). We therefore estimate that, like Si_2H_6 [6], $S_0 \approx 1$ for Si_2Cl_6, and conclude that S_0 for $SiCl_4$ must be ≤ 0.002. (Since the reactive sticking probability of $SiCl_4$ decreases rapidly with coverage [10], our results, based on relatively few exposures, may slightly underestimate S_0 for $SiCl_4$).

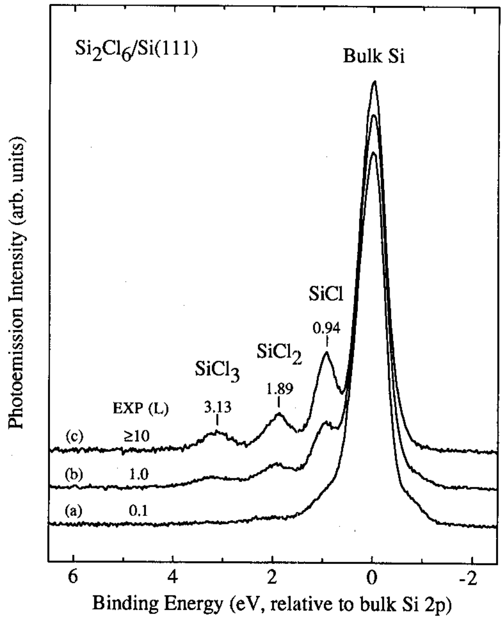

Fig. 2. Photoemission spectra of the Si $2p_{3/2}$ core level after exposure of room temperature Si(111)7×7 to Si_2Cl_6: (a) 0.1, (b) 1, (c) ≥10 L (saturation). The three shifted core levels are attributed to, with increasing binding energy, SiCl (Si in an oxidation state +1), $SiCl_2$ (+2), and $SiCl_3$ (+3), indicating that Si_2Cl_6 only partially dissociates upon chemisorption. The shoulder observed at about −1 eV following the lowest exposure is due to an unquenched surface state.

The vastly different sticking coefficients between $SiCl_4$ and Si_2Cl_6 are similar to those observed for SiH_4 and Si_2H_6 [6]. As proposed by Gates for SiH_4 and Si_2H_6 [6], this difference can be attributed to the relative difficulty of breaking a Si–H (or Si–Cl) bond compared to a Si–Si bond, combined with differing adsorption mechanisms. The presence of a Si–Si bond in the disilane results in a highest occupied molecular orbital (HOMO) lower in energy, and therefore closer in energy to the empty Si surface states, than on the silane, making chemical reaction more likely when the molecule is in the vicinity of the surface [6]. In addition, upon encountering the surface a stronger molecule–surface interaction occurs for the longer

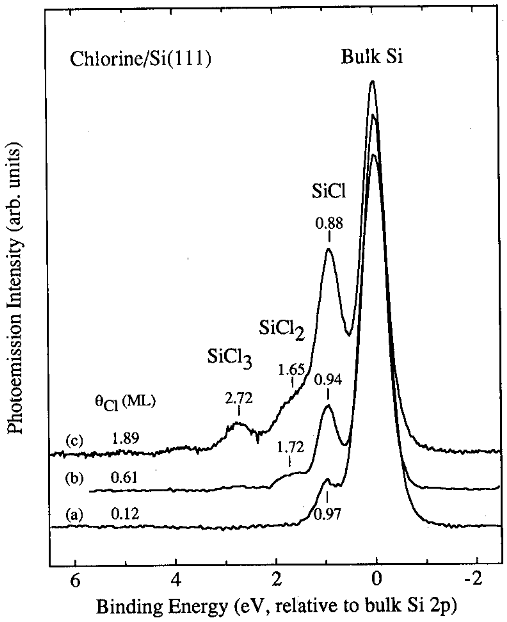

Fig. 3. Photoemission spectra of the Si $2p_{3/2}$ core level after adsorption on room temperature Si(111)7×7 of increasing coverages of Cl from an electrochemical cell: $\theta_{Cl} \approx$ (a) 0.12, (b) 0.61, (c) 1.89 ML. With low coverages only the monochloride is observed, but the higher chlorides appear with increasing Cl coverage. Note that the binding energies are significantly lower as compared with those observed following Si_2Cl_6 exposure. See text for description of θ_{Cl} calibration.

disilanes due to the greater polarizability compared with the relatively spherical silanes. The larger interaction results in the trapping of the disilanes into an adsorption-precursor state, in contrast to the silanes which are more likely to undergo direct scattering from the surface [6]. Similar effects have been reported for the adsorption of the carbon analogues, CH_4 and C_2H_6, on Ni(100); although direct scattering dominates the methane–surface interaction, ethane is more readily trapped on the surface [21].

In order to clarify the structure of the chemisorbed chlorosilanes, chlorine evolved from an electrochemical cell was chemisorbed on Si(111)-7 × 7. As shown in fig. 3a, following adsorption of low coverages only SiCl is observed, nearly identical to that observed following $SiCl_4$ adsorption. Unlike the Si_2Cl_6 case where all three chlorides are observed for all coverages, with chlorine the higher chlorides appear as a function of coverage. The binding energies of all three surface core levels shift slightly lower as a function of coverage (50–70 meV; see figs. 3b and 3c), possibly due to the coverage dependent reactivity of the 7 × 7 surface [19] as discussed above. Annealing the chlorine-saturated surface at 400 °C produces a surface composed solely of SiCl [16,22], which STM has shown to consist of the "rest" atom layer of the DAS surface structure with each Si "rest" atom terminated by a Cl atom [23]. Note that the spectra we observe with saturated surfaces are similar to those observed in a previous photoemission study of chlorine on Si(111)7 × 7 [16].

A close examination of the spectra in figs. 2 and 3 reveals that the silicon di- and trichlorides formed upon chlorine adsorption have significantly lower binding energies than those observed following Si_2Cl_6 adsorption. (Note that the differences are a few times greater than those attribu-

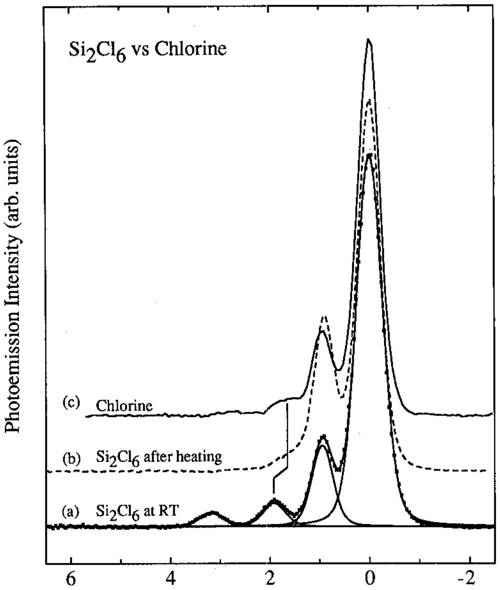

Fig. 4. A comparison of Si $2p_{3/2}$ core levels for (a) a saturation Si_2Cl_6 exposure, (b) the same surface after heating to ~ 300 °C, and (c) a surface with a similar coverage of Cl deposited with the electrochemical cell. After heating, the binding energies of the chlorides resulting from Si_2Cl_6 adsorption are similar to those observed following adsorption of chlorine. A typical fit to the data is shown in (a), where the deconvoluted peaks and the total fit are plotted as solid lines, and the data as symbols. See text for discussion.

Table 1
Summary of the photoemission and AES results for saturation coverages of chlorine (from an electrochemical cell), Si_2Cl_6, and $SiCl_4$ on room temperature Si(111)7×7

Adsorbate	Si 2p energy shift (eV) (normalized peak area)			θ_{Cl} (ML)	Cl_{LMM}/Si_{LMM}
	SiCl	$SiCl_2$	$SiCl_3$		
Chlorine	0.88	1.65	2.72	1.89	0.82
	(0.58)	(0.18)	(0.09)		
Si_2Cl_6	0.94	1.90	3.13	0.84	0.35
	(0.21)	(0.09)	(0.05)		
$SiCl_4$	0.92	–	–	0.35	0.14
	(0.22)	–	–		

The Si 2p binding energy shifts for surface Si in oxidation states of +1 (SiCl), +2 ($SiCl_2$), and +3 ($SiCl_3$) are given with respect to the bulk Si 2p positions. The peak areas are normalized to the areas of the bulk Si 2p peaks. The chlorine coverages, θ_{Cl}, were determined from the normalized peak areas. The AES Cl_{LMM}/Si_{LMM} peak-to-peak height ratios were determined in the derivative mode with an incident electron energy of 1500 eV. See text for descriptions of the fitting procedures and θ_{Cl} calibration.

table to coverage dependent shifts.) This is shown more clearly in fig. 4 where Si $2p_{3/2}$ spectra are displayed for a surface (a) saturated with Si_2Cl_6 and (c) with a similar coverage of Cl from the electrochemical cell. Also shown in fig. 4a is a typical fit of the data to a sum of Gaussian broadened Lorentzians. The binding energies for the shifted core levels are listed in table 1. We attribute the higher binding energies of the silicon chlorides created by the dissociation of Si_2Cl_6 to the presence of $SiCl_2$ and $SiCl_3$ molecules in non-lattice sites as opposed to chlorides formed via Cl reaction with substrate Si atoms. The larger separation of a $SiCl_x$ admolecule from the surface reduces the screening of the Si core hole by the substrate Si bands, thereby increasing the Si 2p binding energy [20]. Note that these binding energy shifts are more drastic than those between the "rest" atoms and "adatoms" discussed above, implying a more significant structural difference between the adsorbed $SiCl_x$ fragments and the reacted substrate atoms.

Following adsorption of a chlorosilane, a similar, albeit, smaller core level binding energy difference should also exist between adsorbed SiCl and that formed via reaction of the liberated Cl with the substrate. However, the difference in binding energies will be obscured by at least two effects. Firstly, any surface with adsorbed SiCl molecular fragments will necessarily have SiCl formed via reaction of the liberated Cl with the substrate as well, so that the observed monochloride photoemission peak will be a convolution of the two similar core levels. (Since no significant broadening of the SiCl Si 2p peak is observed any binding energy difference must be ≤ 0.1 eV). Secondly, even if one core level were dominant the assignment would be ambiguous due to the coverage dependence of the monochloride binding energy. Due to these complications it is not clear whether $SiCl_4$ looses all four or only three of its Cl ligands upon chemisorption on Si(111)7 × 7.

As shown in fig. 4, when a Si_2Cl_6-saturated surface is heated to ~ 300 °C the photoemission intensities of the $SiCl_2$ and $SiCl_3$ Si 2p core levels decrease and the intensity of the SiCl component increases. Furthermore, the binding energies of the adsorbed chlorides shift to approximately the same values as those observed following chlorine adsorption. These results indicate that heating causes the dissociation of the $SiCl_2$ and $SiCl_3$ fragments, with the liberated Cl reacting with the substrate Si, and evidently facilitates the transport of any remaining intact $SiCl_x$ fragments to substrate lattice sites.

Further support for our assertion that Si_2Cl_6 fragments to $SiCl_x$ molecules upon chemisorption on Si(111)7 × 7 comes from our investigation of the chemisorption of chlorosilanes on Ge(111)-2 × 8 [22] where silicon chlorides can only exist on the surface in such a configuration. As shown in fig. 5, a saturation Si_2Cl_6 exposure on Ge(111) results in the appearance of at least two, and possibly three, Si 2p core level binding energy peaks, demonstrating that the Si_2Cl_6 partially dissociates into $SiCl_3$ and $SiCl_2$, and possibly a trace of SiCl. (Less SiCl is expected since there is no additional Si to react with Cl liberated by the dissociation of $SiCl_3$ and $SiCl_2$.) The appearance of the silicon chloride peaks is accompanied by the appearance of a GeCl component in the Ge 3p core level [22]. If the silicon chloride binding energies are referenced to the Si 2p energy ob-

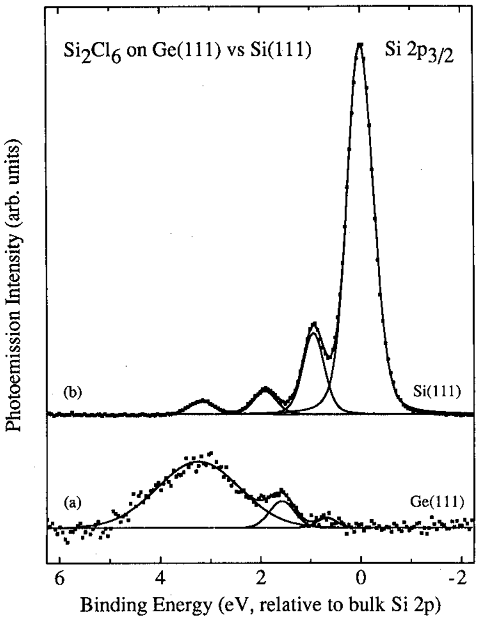

Fig. 5. Comparison of Si $2p_{3/2}$ core levels following adsorption of Si_2Cl_6 on room temperature (a) Ge(111)2 × 8 or (b) Si(111)-7 × 7. Si_2Cl_6 fragments into SiCl, $SiCl_2$, and $SiCl_3$ on both surfaces with similar core level binding energies. On Ge the core levels are referenced to the Si 2p energy observed following an exposure of Ge(111)2 × 8 to Si_2H_6, with a correction for band bending derived from comparison of the Ge core level positions. The fits are plotted as lines and the data as symbols.

served following a saturation Si_2H_6 exposure on Ge(111), with a correction for band bending derived from comparison of the Ge core level positions, we find that the Si 2p binding energy for $SiCl_3$ is approximately the same as that observed following Si_2Cl_6 adsorption on Si(111). The energies for $SiCl_2$ and SiCl, however, are somewhat lower than even those observed with a chlorine-saturated Si(111) surface.

Quantitative analysis of the photoemission and Auger electron spectra combined with recent STM measurements [19,23] allow us to calibrate the relative surface Cl coverages (θ_{Cl}) following adsorption of $SiCl_4$, Si_2Cl_6, or chlorine on room temperature Si(111)7 × 7. Assuming that the photoemission cross sections of the three chemically shifted silicon chloride Si 2p core levels are approximately the same, the photoemission spectra indicate that the relative Cl coverages associated with saturation coverages of chlorine, Si_2Cl_6, and $SiCl_4$ are in the ratio 1 : 0.45 : 0.20. This is consistent with the Cl_{LMM}/Si_{LMM} Auger peak height ratios of 0.82, 0.35, and 0.14 for saturation chlorine, Si_2Cl_6, and $SiCl_4$, respectively (1 : 0.43 : 0.17 scaled to saturation chlorine). If the θ_{Cl} observed after annealing a chlorine-saturated surface to ~ 400 °C, as described above, is taken to be 1 monolayer (ML; $1\ ML \equiv 6.7 \times 10^{14}\ cm^{-2} \equiv$ the density of 7 × 7 *rest* atoms) [18,19,23], then the saturation coverages of chlorine, Si_2Cl_6, and $SiCl_4$ result in $\theta_{Cl} \approx 1.89$, 0.84, and 0.35 ML, respectively. (In terms of the unreacted molecules, the room temperature Si(111)7 × 7 surface saturates following adsorption of 0.14 ML Si_2Cl_6 or 0.09 ML $SiCl_4$.) These results are summarized in table 1. Note that while the relative Cl coverages are known to a precision of approximately 0.02 ML, the absolute coverage scale is accurate to within 20 or 30% at best due to the inhomogeneity of chlorine-saturated-annealed Si(111) surfaces [19,23].

Measurement of the TD spectra following adsorption of $SiCl_4$, Si_2Cl_6, and chlorine on room temperature Si(111)7 × 7 sheds further light on the interaction of these molecules with the surface. As shown in fig. 6a, following a saturation exposure of chlorine from the electrochemical cell desorption peaks are observed near 300 and 700 °C. At 700 °C only $SiCl^+$ ($m/e = 63$) and $SiCl_2^+$ ($m/e = 98$) signals are observed, indicating the desorption of $SiCl_2$. At the lower temperature a $SiCl_3^+$ ($m/e = 133$) signal is also observed. Since we observe $SiCl_4$ to fragment primarily into $SiCl^+$ and $SiCl_3^+$ in our mass spectrometer ionizer (the m/e signals at 63, 98, and 133 have relative magnitudes of 1, 0.06, and 0.24, respectively), and we expect that $SiCl_3$ would give rise to a $SiCl_2^+$ signal much greater than $SiCl_3^+$, we attribute the $SiCl_3^+$ signal to $SiCl_4$ desorption. If the relative intensities of $SiCl_2^+$ and $SiCl^+$ expected from $SiCl_4$ fragmentation are subtracted from the lower temperature peaks, the $SiCl_2^+$ and $SiCl^+$ intensities remaining are in the same ratio as observed during the high temperature desorption of $SiCl_2$, indicating desorption of this species at the lower temperature as well. Hence, we conclude that both $SiCl_4$ and some $SiCl_2$ desorb simultaneously near 300 °C. Note that when $\theta_{Cl} \leq 0.5$ ML only the

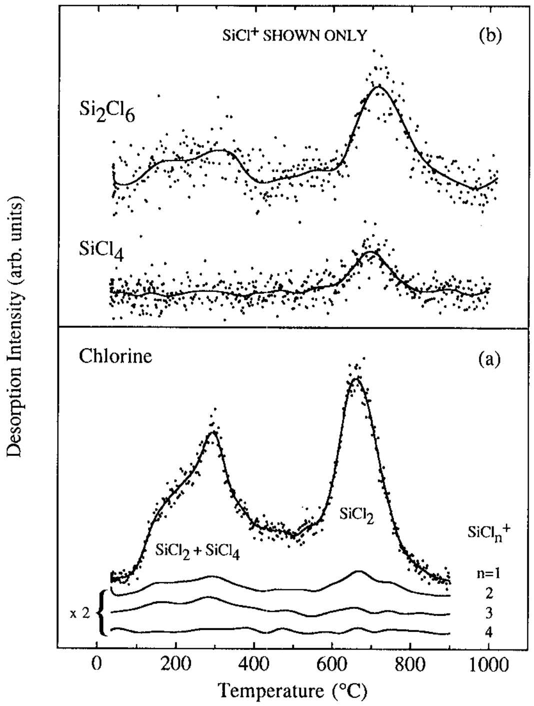

Fig. 6. Thermal desorption spectra recorded with a linear heating rate ~ 10 ° C s^{-1} following saturation exposure of (a) chlorine from an electrochemical cell, or (b) $SiCl_4$ or Si_2Cl_6. Only desorption of $SiCl^+$ (63 amu), $SiCl_2^+$ (98 amu), and $SiCl_3^+$ (133 amu) was detected, indicating the desorption of $SiCl_2$ near 700 ° C, and both $SiCl_2$ and $SiCl_4$ near 300 ° C. In (b) only the $SiCl^+$ signal is shown for simplicity; $SiCl_2^+$ and $SiCl_3^+$ peaks analogous to those shown in (a) were also observed, corresponding to the same desorption products at similar temperatures. See text for further discussion.

high temperature peak associated with the desorption of $SiCl_2$ is observed.

As displayed in fig. 6b, a similar desorption spectrum to that observed from a chlorine-saturated surface is observed following a saturation exposure of Si_2Cl_6. (For simiplicity, only the $SiCl^+$ signal is shown; concomitant $SiCl_2^+$ and $SiCl_3^+$ signals are observed as with the chlorine-dosed surface.) This is consistent with the observation that after heating chlorine- or Si_2Cl_6-saturated surfaces to ~ 400 ° C the only shifted core level observed in the photoemission spectra is that due to SiCl; as the temperature is increased from room temperature some of the adsorbed $SiCl_3$ and $SiCl_2$ must react to form volatile $SiCl_2$ and $SiCl_4$ while the remainder dissociate, leaving SiCl to react and desorb as $SiCl_2$ at higher temperatures. In contrast, following saturation with $SiCl_4$ only the high temperature desorption of $SiCl_2$ is observed, similar to that observed with $\theta_{Cl} \leq 0.5$ ML from the electrochemical cell. This is in accord with the observation of only the monochloride surface core level in the corresponding photoemission spectra. Our conclusion that $SiCl_2$ desorption is not simply direct desorption of an adsorbed species is also in agreement with early modulated beam mass spectrometric studies of Cl_2 reactions with Si(111) reported by Madix and Schwartz [24].

The thermal desorption spectra we observe following adsorption of Cl from either $SiCl_4$, Si_2Cl_6, or the chlorine electrochemical cell are similar to those observed following adsorption of H from SiH_4, Si_2H_6, or a H source [6,7]. As with the chlorosilanes, two desorption peaks may be observed; the lower temperature peak is associated with the simultaneous dissociation and reaction of di- or trihydrides (di- or trichlorides with the chlorosilanes), and the higher temperature peak evolves via reaction of the remaining monohydride (monochloride) species [6,7]. However, there is an extremely important difference between the chlorinated and hydrogenated surfaces. *No appreciable Cl_2 desorption is observed* from the chlorinated surfaces; *$SiCl_2$ is the primary desorption product, resulting in a net loss of Si from the surface*. This is in contrast to the hydrogenated surfaces where *the surface H desorbs as H_2, leaving the adsorbed Si behind*. The different reaction pathways may arise from thermodynamic differences. At least for isolated dimers, it is easier to break a H–Si bond (bond energy 71 kcal mol^{-1}) than a Si–Si bond (75 kcal mol^{-1}), but harder to break a Cl–Si bond (109 kcal mol^{-1}) [25]. Differences in desorption and diffusion kinetics may also contribute. Whatever the reasons, the resulting UHV reaction pathways are consistent with the CVD reports that an excess of H_2 must be added to reactive gas mixtures containing chlorosilanes to achieve good film growth rates [1,3,4]; if there is insufficient H to react with adsorbed Cl (forming gas-phase HCl), $SiCl_4$ and Si_2Cl_6 will *etch* a Si surface.

The different reactivity of $SiCl_4$ versus Si_2Cl_6 upon adsorption is intriguing; one would expect that after a $SiCl_4$ molecule loses a Cl atom, the resulting $SiCl_3$ would have the same reactivity as $SiCl_3$ created by the chemisorption of Si_2Cl_6. An explanation for the different reactivities may lie in the occurrence of different adsorption mechanisms. As discussed above, if the primary interaction of $SiCl_4$ with the surface is via direct inelastic scattering, as is the case for SiH_4 [6], then the extremely low sticking coefficient implies that there is a large activation barrier hindering the rupture of the first Si–Cl bond (which leads to adsorption). Accordingly, those molecules with sufficient energy to adsorb will have a large excess of translational energy which must be dissipated in order for the reaction products, $SiCl_3$ and Cl, to attain thermal equilibrium with the surface. The dissipation of this energy into the remaining Si–Cl bonds would account for the further dissociation of $SiCl_4$ upon adsorption. In contrast, Si_2Cl_6 adsorbed in a precursor state would approach thermal equilibrium with the surface prior to chemisorption, leaving much less energy available to induce subsequent dissociation following the rupture of the Si–Si bond.

Although the above explanation of the different reactivities of $SiCl_4$ and Si_2Cl_6 is consistent with our results and the observed similarities between the silanes and the chlorosilanes, Gupta et al. [10] have found that, unlike SiH_4, S_0 for $SiCl_4$ has a slight inverse temperature dependence. This has been interpreted as an indication that $SiCl_4$ adsorbs via a precursor [10]. However, alternate mechanisms for such a temperature dependence that are consistent with direct activated chemisorption also exist, such as that described by Barker and Auerbach involving the effects of surface substrate atomic motion on the molecule–surface interaction [26]. If further investigation, ideally including molecular beam scattering, demonstrates that $SiCl_4$ and Si_2Cl_6 *both* undergo precursor-mediated adsorption on room temperature Si(111)7 × 7, an alternate explanation must be found for their dramatically different reactivities.

4. Conclusions

$SiCl_4$ dissociatively chemisorbs on room temperature Si(111)7 × 7 with an extremely low sticking coefficient, with only SiCl remaining on the surface. The surface is similar to that resulting from adsorption of very low coverages of Cl. In contrast, Si_2Cl_6 chemisorbs with near unit probability and then partly dissociates into $SiCl_x$ ($x = 1, 2, 3$) fragments. A monolayer of Cl deposited via an electrochemical cell also contains SiCl, $SiCl_2$, and $SiCl_3$, however the Si 2p core level binding energies of these chlorides, created via reaction with substrate Si atoms, are lower than on the Si_2Cl_6-dosed surface due to more efficient screening. Upon heating the chlorinated surfaces to ~ 1000 °C all the Cl is removed via desorption of silicon chlorides, with $SiCl_2$ the primary desorption product; no appreciable Cl_2 desorption is observed, demonstrating that chlorine, $SiCl_4$ and Si_2Cl_6 will etch Si(111)7 × 7 unless an additional reactant is provided to remove the surface Cl.

Interestingly, the different reactivities of $SiCl_4$ and Si_2Cl_6 upon adsorption appear to be determined by the dynamics of the initial adsorption mechanisms. The low sticking coefficient and complete dissociation of $SiCl_4$ can be accounted for if dissociative adsorption (rupture of the first Si–Cl bond) occurs directly, with the excess translational energy dissipated in the remaining Si–Cl bonds. Conversely, precursor-mediated adsorption into a state near equilibrium with the surface would explain the relatively high sticking coefficient (~ 500 times higher) and lower reactivity of Si_2Cl_6. Further investigations with techniques better suited to determining adsorption mechanisms are required. Although we know of no studies directly comparing the efficacy of $SiCl_4$ and Si_2Cl_6 for CVD of Si films, these results suggest that the higher sticking probability of the disilane should make it superior for film growth.

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