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The Adsorption and Surface Reaction of SiCl_4 on $\text{Si}(100)-(2 \times 1)$

by

Q. Gao, Z. Dohnalek, C.C. Cheng, W.J. Choyke and J.T. Yates, Jr.

Submitted To

Surface Science

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May 26, 1993

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The Adsorption and Surface Reaction of SiCl_4 on $\text{Si}(100)\text{-(}2\times 1\text{)}$

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Abstract

The adsorption and surface reaction of SiCl_4 on $\text{Si}(100)\text{-(}2\times 1\text{)}$ have been investigated in the temperature range of 100K-1000K. Adsorption of monolayer SiCl_4 and multilayer 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 $\sim 200\text{K}$ and above, Si-Cl bond scission in adsorbed SiCl_4 occurs, depositing SiCl_x species. Heating to 673K leaves the surface with only silicon monochloride species, SiCl(a) , exhibiting Si-Cl stretching mode, νSiCl , at $\sim 560\text{ cm}^{-1}$, and a Cl^+ ESDIAD pattern indicative of inclined Si-Cl bond directions from Cl adsorbed on Si_2 dimer sites. Silicon substrate etching occurs above 800K producing $\text{SiCl}_2\text{(g)}$ as the desorption product.

1. Introduction

Silicon chloride and chlorosilane molecules (SiCl_4 , Si_2Cl_6 , and SiH_2Cl_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, SiCl_4 , 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 SiCl_4 is small ($S_0 \sim 0.18$ at 160K) and that this coefficient decreases with increasing substrate temperature ($S_0 \sim 0.03$ at 600K). This is interpreted with a precursor-mediated adsorption model where the first stage of adsorption involves trapping of SiCl_4 in a weakly-bound precursor state. Compared to the SiH_4 surface chemistry, where H_2 is the primary desorption product [13], thermal decomposition of SiCl_4 on Si(111)-(7x7) gives SiCl_2 as the primary desorption product (as opposed to Cl_2) with second-order desorption kinetics ($E_d = 65 \pm 5$ kcal/mole, $\nu_d = 3.2 \pm 0.7$ cm²/s) [12]. Soft x-ray photoemission spectroscopy (SXPS) combined with thermal desorption studies indicate that upon adsorption at room temperature, SiCl_4 completely dissociates on Si(111)-(7x7) yielding only surface monochloride species, $\text{SiCl}(a)$. In contrast, Si_2Cl_6 partially dissociates into SiCl_x ($x=1, 2, 3$) fragments upon adsorption at room temperature [14]. Dichlorosilane (SiH_2Cl_2) adsorption on Si(111) is also

found to adsorb by a precursor-mediated process yielding H_2 , HCl and $SiCl_2$ 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 $Si(100)-(2\times1)$, core-level soft 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 $SiCl_4$ on the $Si(100)-(2\times1)$ substrate as well as the spectroscopic characterization of the surface reaction intermediates. The fundamental questions addressed are the $SiCl_4$ bonding states and bonding configurations, the surface species formed from $SiCl_4$ 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 $\sim 1^\circ$ [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 SiCl_4 exposure. SiCl_4 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 1×10^{-10} mbar or below.

3. Results

3.1 Temperature Programmed Desorption Studies

To characterize the adsorption kinetics and the binding states of SiCl_4 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 SiCl_4 on Si(100)-(2x1) at 125K, the detected desorption products include three SiCl_4 desorption features (monitored by the parent ion SiCl_4^+ , $m/e=168$ amu) at 132K, 142K and 230K, respectively, and a single $\text{SiCl}_2(\text{g})$ desorption feature (monitored with SiCl^+ $m/e=63$ amu, the major cracking product of $\text{SiCl}_2(\text{g})$ in the ionizer) with a peak temperature at $\sim 860\text{K}$. No $\text{Cl}_2(\text{g})$ desorption was observed as was reported for $\text{SiCl}_4/\text{Si}(111)$ [14]. The desorption feature at $\sim 132\text{K}$ does not saturate for higher SiCl_4 exposures and is thus

attributed to multilayer SiCl_4 adsorption. SiCl_4 desorption at 230K is observed only above SiCl_4 exposures of $0.7 \times 10^{14}/\text{cm}^2$, 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 SiCl_4 layer (142K peak) is shown in the insert of fig. 1. At an exposure of $\sim 1.7 \times 10^{14} \text{ SiCl}_4/\text{cm}^2$, a monolayer is completed. We observe, however, that the multilayer desorption feature has appeared (at an exposure of $\sim 1.2 \times 10^{14} \text{ SiCl}_4/\text{cm}^2$) before the full monolayer is completed.

The $\text{SiCl}_2(\text{g})$ desorption is shown from SiCl_4 decomposition with a peak temperature of $\sim 860\text{K}$ at $1.7 \times 10^{14} \text{ SiCl}_4/\text{cm}^2$ initial exposure. The peak temperature is shifted to lower temperatures for increasing exposure. The $\text{SiCl}_2(\text{g})$ desorption feature has been observed for all the SiCl_4 exposures studied here. The amount of Si desorbed in $\text{SiCl}_2(\text{g})$ at $1.7 \times 10^{14} \text{ SiCl}_4/\text{cm}^2$ exposure is estimated of about 0.04 of a monolayer.

3.2 Low Temperature Adsorption of $\text{SiCl}_4/\text{Si}(100)-(2 \times 1)$ - HREELS Studies

As shown in fig. 2, adsorption of SiCl_4 at 100K produces a vibrational spectrum similar to that of gas phase SiCl_4 molecules. At a SiCl_4 exposure of $0.67 \times 10^{14} \text{ molecules}/\text{cm}^2$, 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, $\nu_d\text{SiCl}_4 (\nu_3)$, and the degenerate umbrella bending mode of the SiCl_3 moiety, $\delta_d (\nu_4)$, of the $\text{SiCl}_4(\text{a})$ 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 SiCl_4 molecules is close to T_d which would give only two dipole active modes: a degenerate Si-Cl stretching mode, $\nu_d \text{SiCl}_4 (\nu_3)$, and the umbrella bending mode, $\delta_d (\nu_4)$, of the SiCl_3 moiety. The symmetric stretching mode, $\nu_s \text{SiCl}_4 (\nu_1)$, at $\sim 400 \text{ cm}^{-1}$ and the scissors mode, $\delta_d (\nu_2)$, at $\sim 145 \text{ cm}^{-1}$ [20] are forbidden by the dipole selection rule due to the local T_d symmetry. These modes, however, may be excited by the impact scattering mechanism. A weak loss for the symmetric stretching mode at $\sim 390 \text{ cm}^{-1}$ is barely observed and the scissors mode of SiCl_4 ($\sim 150 \text{ cm}^{-1}$) is not observed in this study. At an exposure of $1.7 \times 10^{14} \text{ SiCl}_4/\text{cm}^2$, 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 $3.4 \times 10^{14} \text{ SiCl}_4/\text{cm}^2$, 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 $800\text{-}900 \text{ cm}^{-1}$ and the latter has the Si-H stretching mode at $\sim 2080 \text{ cm}^{-1}$ [21], and weak features in these regions are also observed.

3.3 Temperature Dependent Behavior of $\text{SiCl}_4/\text{Si}(100)\text{-(2x1)}$

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 $\sim 800\text{ cm}^{-1}$ (fig. 3d), consistent with the final formation of a surface monochloride species, as previously observed for Cl_2 and HCl adsorption on $\text{Si}(100)$ [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 $\text{SiCl}_2(\text{g})$ (fig. 1).

3.4 ESDIAD Studies of $\text{SiCl}_4/\text{Si}(100)\text{-(}2\times 1\text{)}$

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 SiCl_4 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 $\langle 011 \rangle$ and $\langle 0\bar{1}\bar{1} \rangle$ 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 Si_2 dimers in the two orthogonal domains. Similar ESDIAD patterns have been observed for chlorine adsorption on $\text{Si}(100)\text{-(}2\times 1\text{)}$ at the same annealing temperature [22, 24] and for the HCl adsorption on $\text{Si}(100)\text{-(}2\times 1\text{)}$ 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 $\text{SiCl}_2(\text{g})$, causing a decrease of the Cl^+ ion intensity. The approach to a more random orientation of the Si-Cl bonds for the remaining $\text{SiCl}(\text{a})$ 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 Cl_2 adsorption onto $\text{Si}(100)$ followed by heating to 847K [22].

4. Discussion

4.1 The Bonding of SiCl₄ on Si(100)-(2x1) at Low Temperatures

Three SiCl₄ desorption states are detected (fig. 1) in the TPD experiments. In order of increasing desorption temperature, they are the multilayer SiCl₄(a) ($T_p \sim 132K$), physisorbed SiCl₄ within the monolayer range ($T_p \sim 142K$), and a small amount of SiCl₄ (≤ 0.01 of the first layer SiCl₄(a)) with a peak temperature at $\sim 230K$. The monolayer SiCl₄ reaches saturation coverage with increasing exposure (Fig. 1 insert) while the multilayer does not show saturation behavior. Both monolayer and multilayer SiCl₄(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 ($\sim 145 \text{ cm}^{-1}$) and the extremely weak peak, if any, for the symmetric Si-Cl stretching mode ($\sim 390 \text{ cm}^{-1}$) (fig. 2a) suggest that the local symmetry of the SiCl₄ molecules is nearly the same as for the free SiCl₄ 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):

$$R = A \exp(-a z)$$

where $z \propto d \cdot \cos\Theta$, d is the Si-Cl bond length and Θ 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 (≤ 0.01 of the first layer) of SiCl_4 desorption ($T_p \sim 230\text{K}$) are clearly observed for SiCl_4 exposures above $0.7 \times 10^{14} \text{ SiCl}_4/\text{cm}^2$. The following arguments favor recombinative desorption of $\text{SiCl}_x(\text{a}) + (4-x)\text{Cl}(\text{a}) \rightarrow \text{SiCl}_4(\text{g})$ as the origin of the 230K SiCl_4 desorption state: (1) HREEL spectra show the symmetric Si-Cl stretching mode at $\sim 400 \text{ cm}^{-1}$ 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 $\text{SiCl}_4(\text{a})$ into $\text{SiCl}_3(\text{a})$; (2) The vibrational features are close to those found for CH_3SiCl_3 molecules. The asymmetric SiCl stretching mode, ν_a at $576 \sim 578 \text{ cm}^{-1}$, symmetric SiCl stretching, ν_s at $450 \sim 458 \text{ cm}^{-1}$, and the bending and rocking modes, δ and γ , 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 cm^{-1} , 400 cm^{-1} and 210 cm^{-1} in fig. 3b; (3) In ESDIAD, annealing to 200K causes the development of the four shoulder peaks along the $\langle 011 \rangle$ and $\langle 0\bar{1}\bar{1} \rangle$ 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).

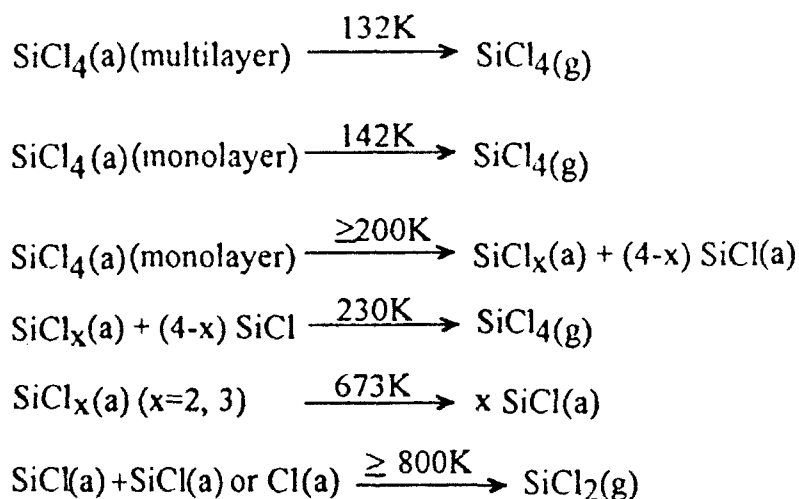
4.2 The Surface Decomposition of SiCl_4 on $\text{Si}(100)\text{-(}2\times 1\text{)}$

Beyond a temperature of $\sim 250\text{K}$, SiCl_4 ceases to be a thermal desorption product from the $\text{Si}(100)\text{-(}2\times 1\text{)}$ surface. Both HREELS and AES measurements show that chlorine remains behind above 250K indicating that $\text{SiCl}_4(\text{a})$ has decomposed to lower silicon chloride species which are strongly bound. As shown in fig. 3, the $\sim 200\text{ cm}^{-1}$ δ bending mode for $\text{SiCl}_x(\text{a})$ species remains up to 300K , as does the 400 cm^{-1} symmetric stretching mode for $\text{SiCl}_x(\text{a})$. It is not possible to discriminate between modes due to $\text{SiCl}_3(\text{a})$ and $\text{SiCl}_2(\text{a})$ 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 $\text{Si}(100)\text{-(}2\times 1\text{)}$ at the same temperature; the 566 cm^{-1} mode corresponds to the asymmetric stretching mode, $\nu_{\text{a}}\text{SiCl}$, 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 $\text{Si}(100)$ 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 $\text{Si}(100)\text{-(}2\times 1\text{)}$. This is due to surface etching with liberation of $\text{SiCl}_2(\text{g})$, 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:



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 SiCl₄ on Si(100)-(2x1) followed by annealing to 300K does not completely dissociate SiCl₄(a). Therefore, in comparison with the Si(111)-(7x7) surface, the Si(100)-(2x1) surface is less reactive for SiCl₄ 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 SiCl₄(a) molecules can dissociate completely into surface monochloride species at room temperature on Si(111)-(7x7). On the other hand, only partial dissociation of SiCl₄ 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 NH₃ molecules [31] where on Si(111)-(7x7), NH₃ is dissociated into NH(a) at 300-600K while on Si(100)-(2x1), the NH₂(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 SiCl₄

In the high temperature chemical vapor deposition (CVD) of silicon thin films, mixtures of H₂ and SiCl₄ 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 ($T_{\text{substrate}} < 573\text{K}$) [35], decomposition of SiCl₄ occurs on a hot filament delivering SiCl_x ($x=1, 2, 3$) 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 SiCl_x 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.

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References

1. P. van der Putte, L. J. Giling and J. Bloem, *J. Cryst. Growth* 31 (1975)299.
2. S. Motojima, M. Iwamori and T. Hattori, *J. Mater. Sci.* 21 (1986) 3836.
3. R. C. Taylor, B. A. Scott, S. T. Lin, F. LeGouse and J. C. Tsang, *MRS Symp. Proc.* 77 (1987) 709.
4. R. C. Taylor and B. A. Scott, *MRS Symp. Proc.* 105 (1988) 319.
5. R. C. Taylor and B. A. Scott, *J. Electrochem. Soc.* 136 (1989) 2382.
6. C. W. Pearce, in *VLSI Technology*, 2nd ed., S. M. Sze ed. Chap. 2, McGraw-Hill, New York, 1988.
7. S. K. Ghandhi, *VLSI Fabrication Principles*, Chap. 5, Wiley, New York, 1983.
8. M. C. Chuang and J. E. Coburn, *J. Vac. Sci. Technol.* A8 (1990) 1969.
9. J. O. Chinn and J. E. Coburn, *J. Vac. Sci. Technol.* B3 (1985) 410.
10. R. B. Jackman, H. Ebert and J. S. Foord, *Surf. Sci.* 176 (1986) 183.
11. W. Sesselman and T. J. Chuang, *J. Vac. Sci. Technol.* B3 (1985) 1507.
12. P. Gupta, P. A. Coon, B. G. Koehler and S. M. George, *J. Chem. Phys.* 93(4) (1990) 2827.
13. R. Imbihl, J. E. Demuth, S. M. Gates and B. A. Scott, *Phys. Rev.* B39 (1989) 5222.
14. L. J. Whitman, S. A. Joyce, J. A. Yarmoff, F. R. McFeely and L. J. Terminello, *Surf. Sci.* 232 (1990) 297.
15. P. A. Coon, P. Gupta, M. L. Wise and S. M. George, *J. Vac. Sci. Technol.* A(10) (1992) 324.
16. J. A. Yarmoff, D. K. Shuh, T. D. Durbin and C. W. Lo, D. A. Lapiano-Smith, F. R. McFeely and F. J. Himpsel, *J. Vac. Sci. Technol.* A10 (1992)2303.
17. (a) R. D. Ramsier and J. T. Yates, Jr., *Surf. Sci. Reports*, 12 (1991) 243.

- (b) J. T. Yates, Jr., M. D. Alvey, M. J. Dresser, M. A. Henderson, M. Kiskinova, R. D. Ramsier and A. Szabo, *Science*, 225 (1992) 1397.
- (c) T. E. Madey, *Science*, 234 (1986) 316.
18. M. J. Bozack, L. Muehlhoff, J. N. Russell, Jr., W. J. Choyke, and J. T. Yates, Jr., *J. Vac. Sci. Technol. A* 5, (1987), 1.
19. A. Winkler and J. T. Yates, Jr., *J. Vac. Sci. and Technol. A* 6 (5) (1988) 2929.
20. K. Nakamoto, in *Infrared Spectra of Inorganic and Coordination Compounds*, 4th ed, p. 132, New York, John Wiley and Sons, Inc., 1986, and references therein.
21. H. Ibach, H. Wagner and D. Bruchmann, *Solid State Commun.* 42 (1982) 457.
22. Q. Gao, C.C. Cheng, P. J. Chen, W. J. Choyke and J. T. Yates, Jr., *J. Chem. Phys.*, in print, and references therein.
23. Q. Gao, C. C. Cheng, P. J. Chen, W. J. Choyke and J. T. Yates, Jr., *Thin Solid Films*, 225 (1993) 140, and references therein.
24. C.C. Cheng, Q. Gao, W. J. Choyke and J. T. Yates, Jr. *Phys. Rev. B* 46 (1992) 12810.
25. H. D. Hagstrum, *Phys. Rev.* 123 (1961) 758.
26. (a) M. C. Tobin, *J. Am. Chem. Soc.* 75 (1953) 1788 and references therein.
- (b) K. Shimizu and H. Murata, *Bull. Chem. Soc. Japan* 32 (1959) 46 and references therein.
- (c) L. Burnelle and J. Duchesne, *J. Chem. Phys.* 20 (1952) 1324.
- (d) J. Laane, *Spectrochimica Acta*, 26A (1970) 517.
27. C.-M. Chan, R. Aris and W. H. Weinberg, *Appl. Surf. Sci.* 1 (1978) 360.
28. I. K. Robinson, W. K. Waskiewicz, P. H. Fuoss and L. J. Norton, *Phys. Rev. B* 37 (1988) 4325.
29. R. D. Meade and D. Vanderbilt, *Phys. Rev. B* 40 (1989) 3905.

30. A general review is available in: The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis, Vol. 5, Eds. D. A. King and D. P. Woodruff, Elsevier, Amsterdam, 1988, Chap. 2 by M. Schluter, p.37, and references therein.
31. P. J. Chen, M. L. Colaiaanni and J. T. Yates, Jr. Surf. Sci. Lett. 274 (1992) L605.
32. J. J. Boland, Surf. Sci. 244 (1991)1.
33. V. S. Ban, J. Electrochem. Soc. 122 (1975) 1389.
34. T. Aoyama, Y. Inoue, and T. Suzuki, J. Electrochem. Soc. 130 (1983) 203.
35. H. Matsumura and H. Ihara, J. Appl. Phys. 64 (1988) 6505.
36. J. Nishizawa and H. Sakuraba, Surf. Sci. Rep. 15 (1992) 137.

Figure Captions

Fig 1. Temperature programmed desorption of a multilayer $\text{SiCl}_4(\text{a})$ adsorbed on $\text{Si}(100)-(2 \times 1)$ at 125K. The exposure is $1.7 \times 10^{14} \text{ SiCl}_4/\text{cm}^2$. The $\text{SiCl}_2(\text{g})$ desorption feature from SiCl_4 decomposition is displayed for $T > 800\text{K}$. Lower temperature SiCl^+ signals correspond to the $\text{SiCl}_4(\text{g})$ 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 $\text{Si}(100)-(2 \times 1)$ at 100K with SiCl_4 exposures: (a) $0.67 \times 10^{14}/\text{cm}^2$; (b) $1.7 \times 10^{14}/\text{cm}^2$; (c) $3.4 \times 10^{14}/\text{cm}^2$.

Fig. 3. Thermal development of HREEL spectra for $\text{SiCl}_4/\text{Si}(100)-(2 \times 1)$. The initial SiCl_4 exposure is $3.4 \times 10^{14}/\text{cm}^2$. (a) 100K adsorption; then annealed

to the following temperatures: (b) 200K; (c) 300K; (d) 673K and (e) 847K.

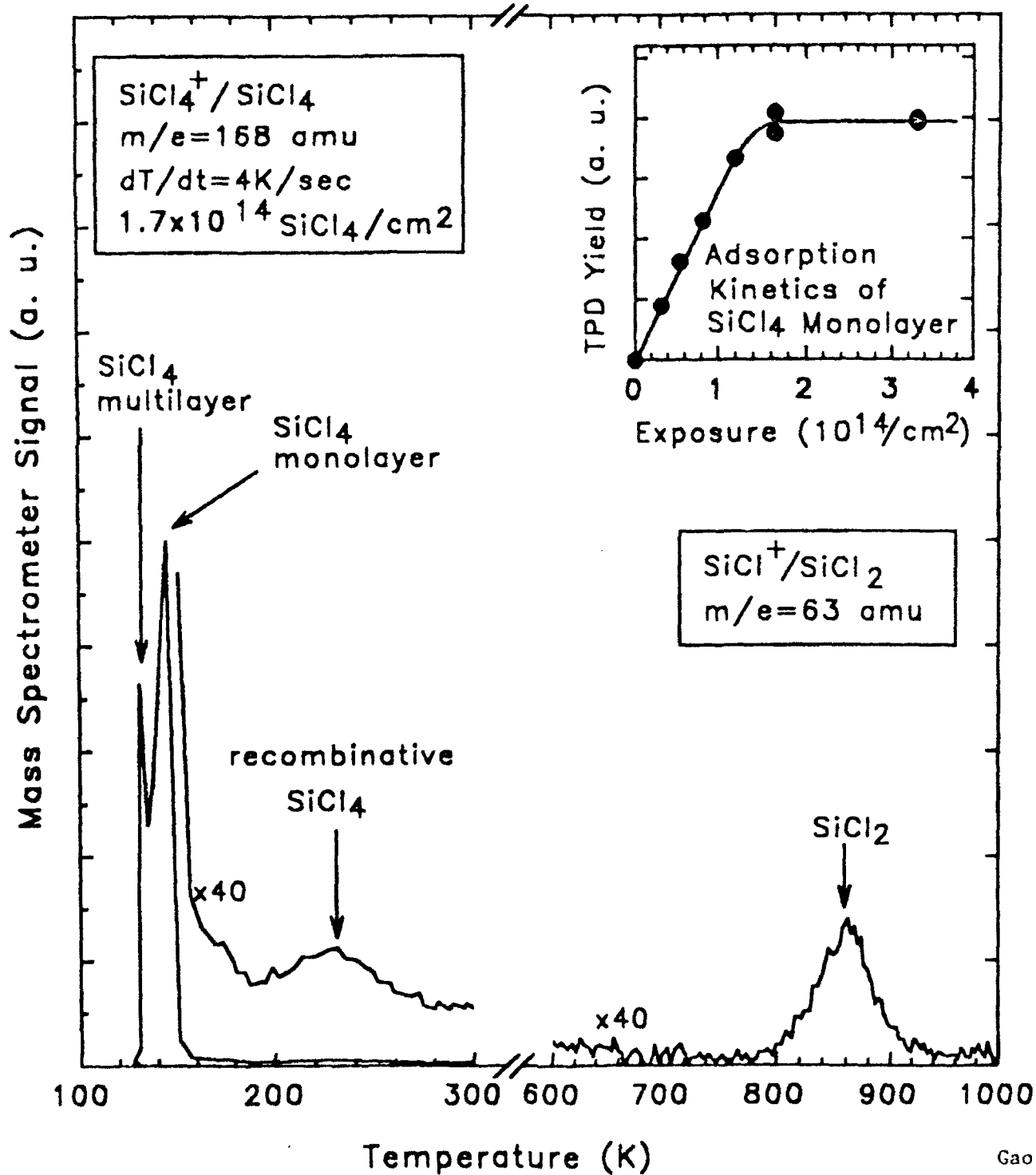
All spectral data are collected at 100K.

Fig.4. Thermal development of the Cl^+ ESDIAD pattern produced from SiCl_4 adsorption. Electron beam energy $E_e = 120\text{V}$, crystal current $I_e = 2\text{pA}$, V_{bias} (on crystal) = $+10\text{V}$. (a) 120K adsorption of $3.4 \times 10^{14} \text{ SiCl}_4/\text{cm}^2$. 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})

	$\nu_{\text{dSiCl}_4}(\nu_3)$	$\nu_{\text{SiCl}_4}(\nu_1)$	$\delta_{\text{dSiCl}_3}(\nu_4)$	$\delta_{\text{dSiCl}_2}(\nu_2)$
SiCl ₄ (g) [20]	616.5	423	220	145
SiCl ₄ (a) [this work]	630-640	390	220	
	ν_{aSiCl}	ν_{SiCl}	δ_{SiCl}	γ_{SiCl}
SiCl ₃ (CH ₃)(g) [26a-c]	576-578	450-458	164-229	229
SiCl ₂ (CH ₃) ₂ (g) [26a]	533	465	169	
SiCl ₂ (CH ₂) ₃ (g) [26d]	533	376	167-241	
SiCl _x (a) (x=2,3) [this work]	566-577	400	200-210	
	ν_{SiCl}			
SiCl(CH ₃) ₃ (g) [26a]	467			
SiCl(a) [23]	553-600			
SiCl(a) [this work]	560-566			

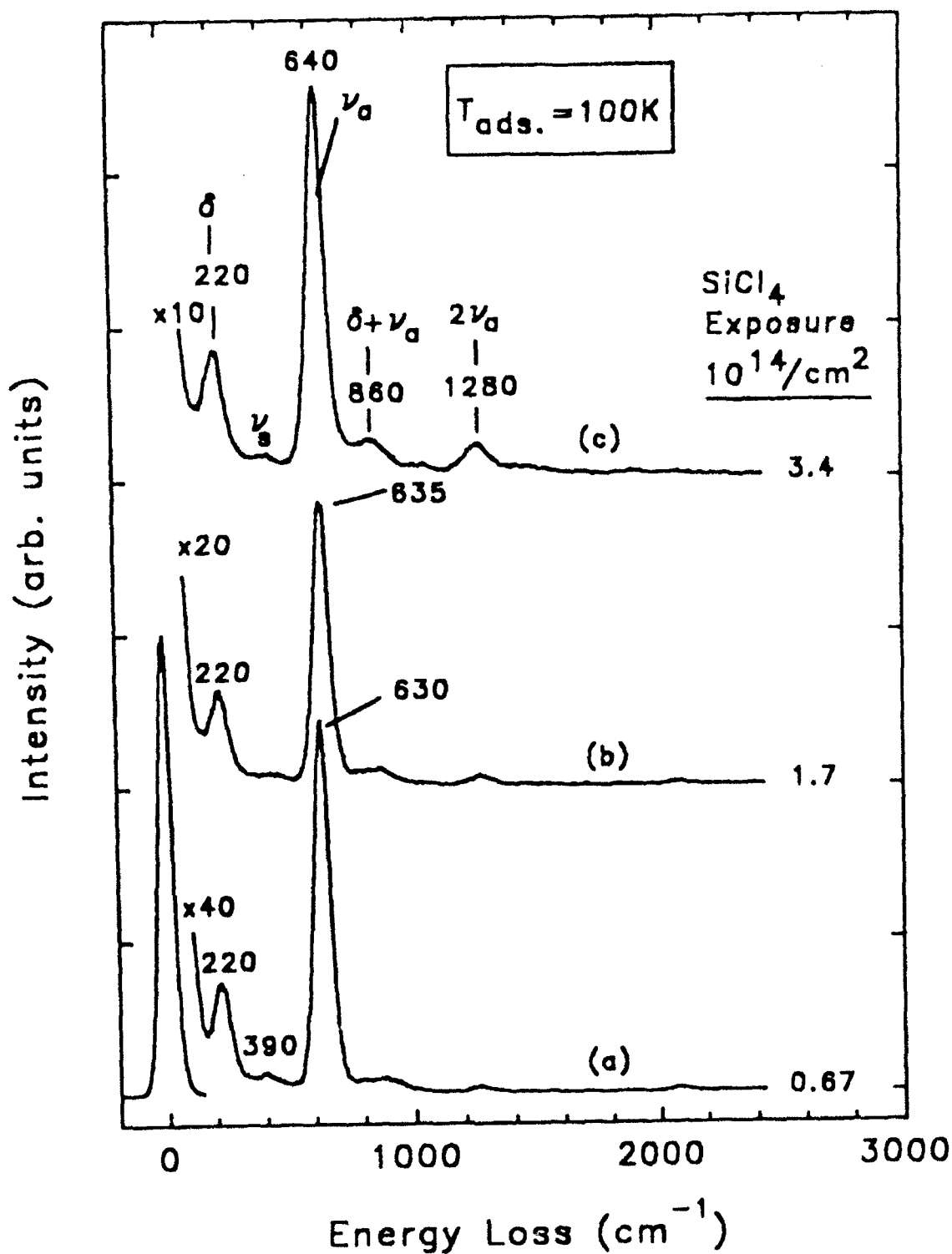
TEMPERATURE PROGRAMMED DESORPTION
FROM $\text{SiCl}_4/\text{Si}(100)-(2\times 1)$



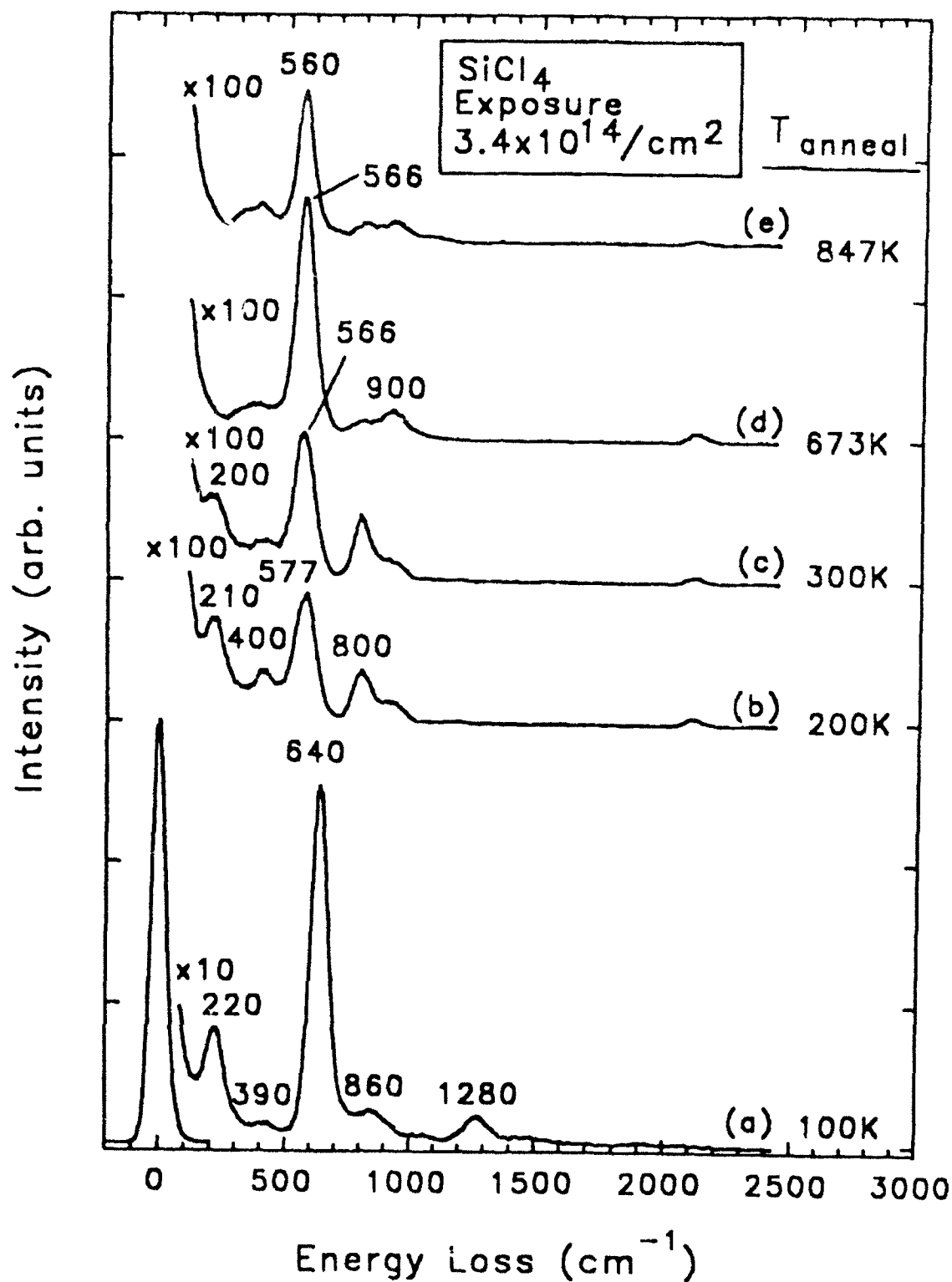
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Figure 1

COVERAGE DEPENDENT HREELS STUDY OF $\text{SiCl}_4/\text{Si}(100)-(2 \times 1)$

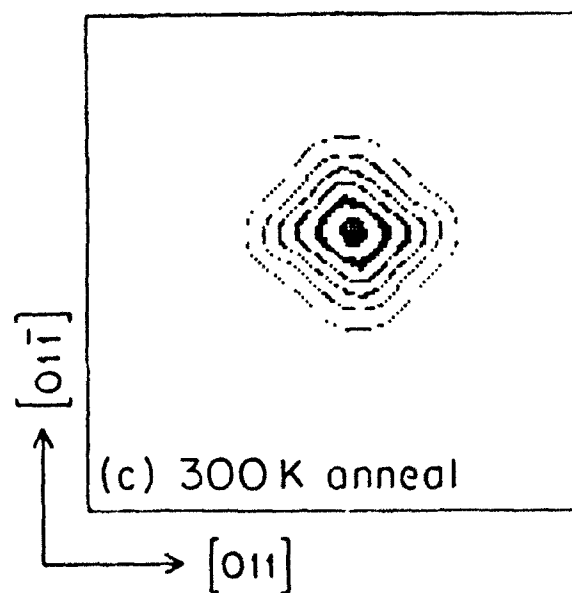
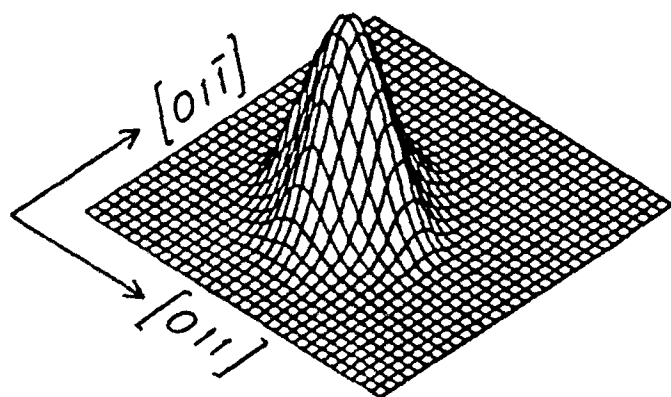
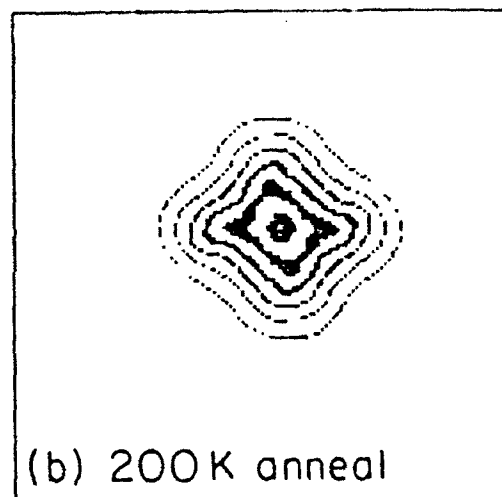
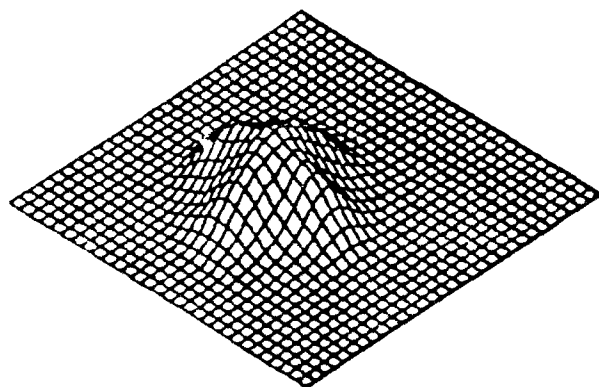
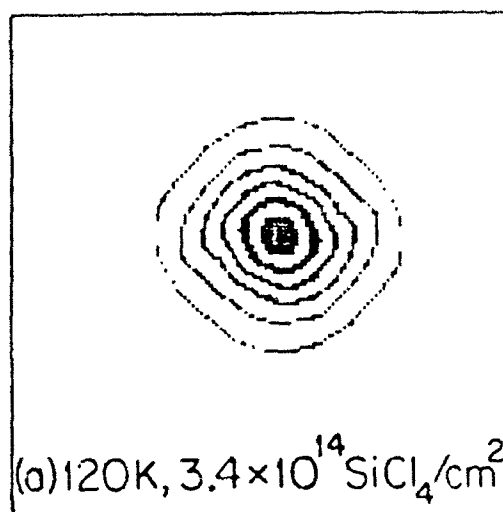
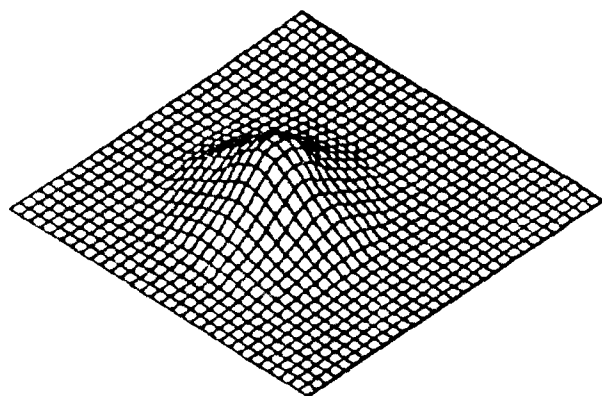


HREELS MEASUREMENTS OF THE THERMAL BEHAVIOR OF $\text{SiCl}_4/\text{Si}(100)-(2\times 1)$

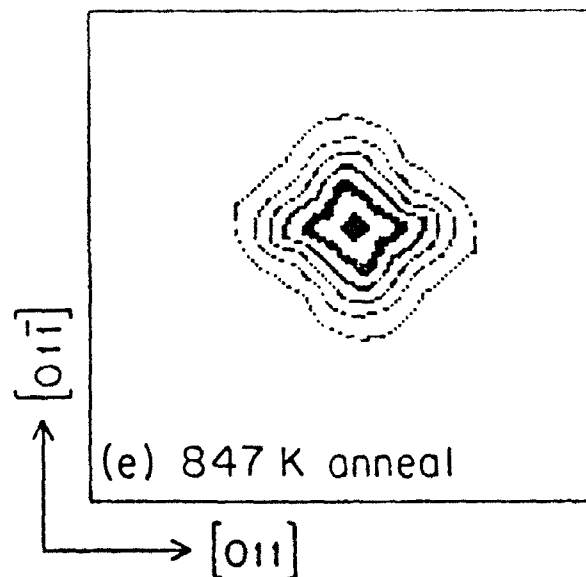
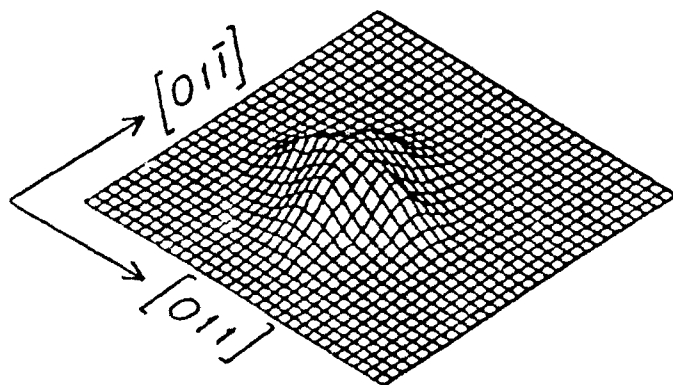
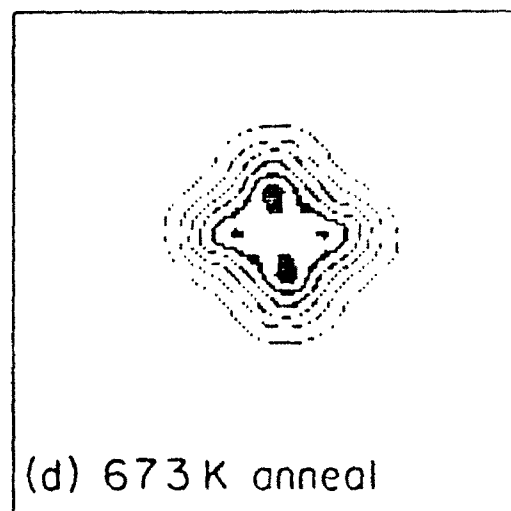
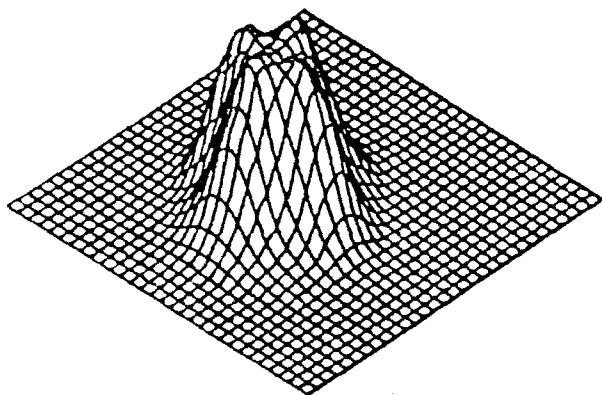


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Figure 3

THERMAL DEVELOPMENT OF Cl^+ ESDIAD
PATTERN - $\text{SiCl}_4/\text{Si}(100)-(2 \times 1)$



THERMAL DEVELOPMENT OF Cl^+ ESDIAD
PATTERN - $\text{SiCl}_4/\text{Si}(100)-(2 \times 1)$



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