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The interaction of methyl chloride and Si(100) 2×1

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Abstract

The interaction of methyl chloride with Si(100) has been studied with electron energy loss spectroscopy (EELS), Auger electron spectroscopy (AES), and temperature programmed desorption (TPD). Dissociative adsorption occurs with near unity sticking probability to form adsorbed CH_3 and Cl at ≤ 300 K. Molecularly adsorbed species are also present at < 100 K. The sticking coefficient is reduced at higher surface temperatures and the possibility of a precursor is discussed. Moderate exposures (100 L) at substrate temperatures above 500 K result in a carbon layer possessing C–C single bonds. In addition, no chlorine is observed on the surface for exposure temperatures ≥ 700 K, making methyl chloride a promising candidate for carbon film growth.

Keywords: Chemical vapor deposition; Electron energy loss spectroscopy; Low index single crystal surfaces; Silicon; Thermal desorption spectroscopy; Vibrations of adsorbed molecules

The interaction of gases with silicon surfaces is important for semiconductor technology, film growth techniques and (methyl)chlorosilane synthesis [1]. Homoepitaxial diamond film growth has been reported in numerous studies using a hot filament immersed in a high pressure of methane and hydrogen producing methyl radicals and dissociated hydrogen. One study showed homoepitaxial film growth to be possible without an activation source through the use of fluorine in place of hydrogen [2]. The success of this chemically driven film growth provided the impetus for the study described in this paper.

Another motivation is the need for *heteroepitaxial* diamond films in order to reduce cost and allow incorporation into electronic materials processing. It is believed that the surface diamond abrasive pre-

growth treatment currently necessary to allow diamond growth is responsible for the polycrystalline films achieved.

Previous studies have determined that saturated hydrocarbons are inert to silicon surfaces while molecules possessing multiple intercarbon bonds react readily [3–5]. Substituting a chlorine for a hydrogen in the simplest saturated hydrocarbon, methane, creates a dipole moment which may increase reactivity. An atmospheric pressure study found significant reaction of CH_3Cl with Si(100) [6] while a low pressure study found methyl chloride reacted with an alkali metal overlayer deposited on Si(100) [7].

In this paper it is shown that methyl chloride (CH_3Cl) dissociatively adsorbs on Si(100) with high probability below room temperature to produce a methyl group and a chlorine. Sustained doses at ≥ 700 K result in no adsorbed chlorine and the formation of intercarbon bonds. The evidence reported suggests that the removal of chlorine is simply due to thermal desorption while the carbon coa-

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lescence is attributed to reactions of adsorbed CH_3 with CH_3Cl in a precursor state.

These experiments were performed in a UHV chamber described in detail elsewhere [8]. The sample was cleaned in a chamber (base pressure = 8×10^{-11} Torr) equipped with an ion gun, Auger spectrometer, and mass spectrometer. The sample can be transferred in vacuo to another chamber (base pressure = 3×10^{-11} Torr) for vibrational analysis with a differentially pumped electron energy loss spectrometer equipped with a multichannel detector. The sample was maintained at 85 K during acquisition of all EEL spectra used in this study. The EELS spectrometer consists of a double-pass cylindrical monochromator and single-pass cylindrical analyzer. Scattering electrons were incident 60° from the surface normal and detected in the specular direction. The incident energy of the electrons was 10 eV. Normal count rates obtained were 16 kHz in the peak channel of a 256-channel resistive anode detector operating with a dispersion of 0.9 meV per channel and a FWHM resolution of 13 meV. An IBM RS6000/520 computer was used for all data acquisition.

The samples used for these experiments were 16 mm in width, 8 mm in height, and 0.4 mm thick. The samples were cleaved from an n-type (phosphorus doped, $3.7 \pm 0.3 \Omega \cdot \text{cm}$) polished Czochralski wafer oriented to less than 0.5° from the Si(100) surface. The samples were tied to a flat piece of 0.1 mm thick rhenium foil. Tantalum spacers were spot-welded to the rhenium at the four corners of the silicon sample to prevent direct contact between the silicon and the rhenium heating foil which would result in differential heating and hazing of the crystal surface. The two ends of the foil were pressed to tantalum rods with homemade tantalum screws, nuts, and tungsten springs. The tantalum rods were brazed to copper feedthroughs which were placed in direct contact with liquid nitrogen for cooling.

The sample was heated radiatively by passing current through the rhenium foil. Temperature readings were made with a chromel–alumel thermocouple junction spot-welded to each of two 75 μm thick tantalum tabs held on the front face of the silicon by 0.25 mm diameter tantalum wire ties. The minimum sample temperature for this study was 85 K. A sample cleaning cycle consists of 5 min of 1 kV Ne^+

bombardment ($4 \mu\text{A}/\text{cm}^2$) incident 45° from the surface normal followed by a 1000 K anneal for 15 min. The substrate was then cooled at 1 K/s to 85 K. While the Auger signal for carbon decreased to below detectable limits after only 4 cleaning cycles, the 100 meV loss peak in EELS attenuated only after 30 cleaning cycles. A low energy electron diffraction (LEED) measurement [9] made with a different apparatus showed that this cleaning procedure results in a sharp 2×1 diffraction pattern. The sample was cleaned with one cleaning cycle prior to each exposure and subsequent measurement.

The methyl chloride used (Matheson, grade 3) was exposed to the sample with a directional micro-capillary array doser (Galileo Electro-Optics) at a distance of 1 cm. Calibration was achieved through comparison with ambient doses.

EEL spectra obtained after 1 L exposures of methyl chloride onto the Si(100) surface held at 85 and 300 K are shown in Fig. 1. The 67 meV energy loss peak present in both cases is due to an adsorbed chlorine atom. The high electronegativity of chlorine is responsible for the strength of this peak relative to the loss peaks at higher energies. Gao et al. reported a Si–Cl EELS loss peak at 69 meV for small coverages of chlorine terminally bonded on Si(100) [10]. The EEL spectrum of the sample dosed at 85 K has a loss peak at 89 meV which is not present after the 300 K exposure. This is explained by the existence of molecularly adsorbed species in addition to adsorbed methyl chloride fragments since methyl chloride has a C–Cl stretch excitation at 91 meV in the gas phase [11]. The molecularly adsorbed methyl chloride after 1 L exposure was found to desorb at 120 K (see inset of Fig. 1). Note that the room temperature exposure, which occurs above the molecular adsorbate desorption temperature, still possesses a small loss peak at 85 meV. This loss peak is assigned to the rocking mode of the Si– CH_3 complex.

The less prominent loss peaks are assigned to an adsorbed CH_3 by comparison with gas phase methyl chloride and a previous EELS study of methyl iodide (CH_3I) adsorption [12,13]. Colaianni et al. determined that the products of the reaction of methyl iodide on Si(100) are adsorbed CH_3 and I. The symmetric deformation or “umbrella” mode of CH_3 adsorbed on a Si(100) substrate was determined to

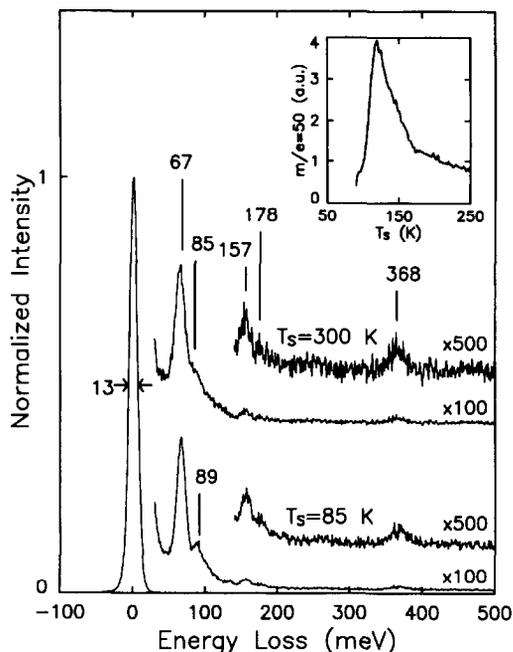


Fig. 1. EEL spectra measured at the specular angle after deposition of 1 L (1×10^{-6} Torr \cdot s) of CH_3Cl on a Si(100) surface at 85 and 300 K. The strong loss feature at 67 meV for both dosing conditions is assigned to the Si–Cl stretch. The loss feature at 89 meV for the 85 K exposure is assigned to the C–Cl stretch of a weakly bound methyl chloride molecule. The small 85 meV peak present after the room temperature exposure is assigned to the Si–(CH_3) stretch. The two loss features at 157 and 178 meV are assigned to the CH_3 symmetric and asymmetric deformation modes, respectively. The loss at 368 meV is due to C–H stretch modes. Inset: TPD spectra of molecular desorption from a sample exposed to 1 L methyl chloride at 85 K. The heating rate was 2 K/s.

occur at 156 meV. In the present study, the corresponding excitation occurred at 157 meV. The asymmetric deformation of CH_3 adsorbed on Si(100)

resulting from methyl iodide (177 meV) and methyl chloride (178 meV) adsorption also agree. The stretching vibrations for the two systems occur at 370 and 368 meV for CH_3 adsorption originating from methyl iodide and methyl chloride, respectively. All the values measured agree very well between the two systems indicating that adsorption of CH_3Cl occurs via cleavage of the carbon–chlorine bond. A summary of vibrational excitation energies found for adsorption of the two methyl halides on Si(100) and of gas phase methyl chloride is provided in Table 1.

Similar EELS studies at higher substrate temperatures provide insight into how CH_3Cl will behave in a chemical vapor deposition (CVD) environment. For all elevated temperature exposures in this study, EEL spectra were obtained after cooling to 85 K at 2 K/s. In contrast to the spectra shown in Fig. 1, the amount of adsorbed chlorine and CH_3 was substantially lower for a substrate held at 500 K and exposed to 1 L of methyl chloride (see Fig. 2). This is inferred from the absence of methyl vibrational loss features and a Si–Cl stretch loss which is reduced by a factor of ~ 10 compared with the low temperature adsorption spectra shown in Fig. 1. AES measurements monitoring the Cl_{LMM} and C_{KLL} peaks after a low temperature exposure showed no thermal desorption until the substrate was raised to 700 K. Desorption of chlorine as SiCl_2 is expected based on the absence of lower mass TPD peaks. Since the reduction in sticking coefficient is occurring at a temperature well below the initial desorption product, it provides evidence for the existence of a precursor to dissociative adsorption. Higher temperatures can reduce the time spent in the precursor potential well and therefore reduce the probability of the molecule finding an adsorption site.

Table 1

Vibrational modes of CH_3Cl adsorbed on Si(100) at 85 K; the subscripts s and a refer to symmetric and asymmetric vibrational modes, respectively

| Normal mode | This work (meV) | $\text{CH}_3/\text{Si}(100)^a$ (meV) | $\text{Cl}/\text{Si}(100)^b$ (meV) | Gas phase CH_3Cl^c (meV) |
|-------------------------------|-----------------|--------------------------------------|------------------------------------|--|
| $\nu(\text{Si}-\text{Cl})$ | 67 | – | 69 | – |
| $\rho(\text{Si}-\text{CH}_3)$ | 85 | 88 | – | – |
| $\nu(\text{C}-\text{Cl})$ | 89 | – | – | 91 |
| $\delta_s(\text{CH}_3)$ | 157 | 156 | – | 168 |
| $\delta_a(\text{CH}_3)$ | 178 | 177 | – | 180 |
| $\nu(\text{C}-\text{H})$ | 368 | 364, 371 | – | 364, 377 |

^a Obtained from Ref. [13]. ^b Ref. [10]. ^c Ref. [11].

Due to the reduced sticking coefficient at 500 K, the study was extended to higher doses. For an exposure of 100 L at 500 K there are two noticeable changes compared with the low temperature adsorption vibrational spectrum. The Si–Cl stretch excitation is shifted from 67 to 74 meV and a peak emerges at 130 meV which is attributed to a $\nu(\text{C–C})$ stretch excitation. The assignment is made based on previous work on polyethylene [14] and a-C:H films [15] which determined that for singly bonded carbon, a C–C excitation occurs at 132 meV. The shift in Si–Cl stretch energy may be due to the interaction with larger adsorbed hydrocarbons. A higher coverage of chlorine shifted the Si–Cl stretch excitation from 69 to 74 meV in a molecular chlorine study [10], which is very similar to the shift observed in this case.

To assist in determining the origin of the new adsorbate, a sample was prepared with a 1000 L exposure at room temperature to create a small surface population of singly bonded carbon. The corresponding EEL spectrum is shown in Fig. 3. The

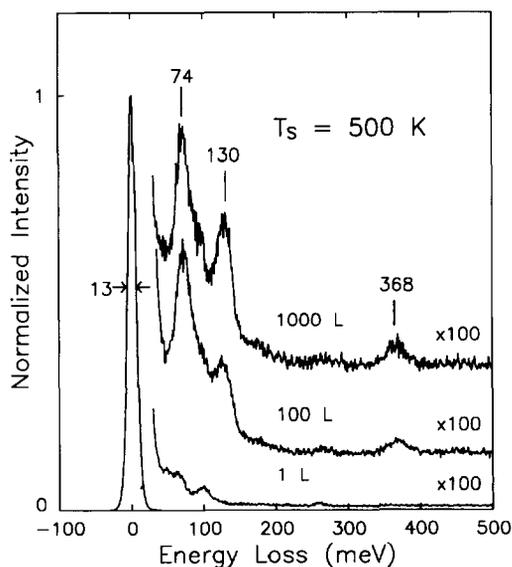


Fig. 2. Specular EEL spectra measured after deposition of 1, 100, and 1000 L of CH_3Cl on a Si(100) surface at 500 K. The sample was cooled after each exposure at 2 K/s to 85 K prior to acquisition of the EEL spectra. Compared to Fig. 1 the Si–Cl is shifted from 67 to 74 meV for both the 100 and 1000 L exposures. A new loss feature appears at 130 meV for the 100 L exposure and more than doubles in size after a 1000 L exposure.

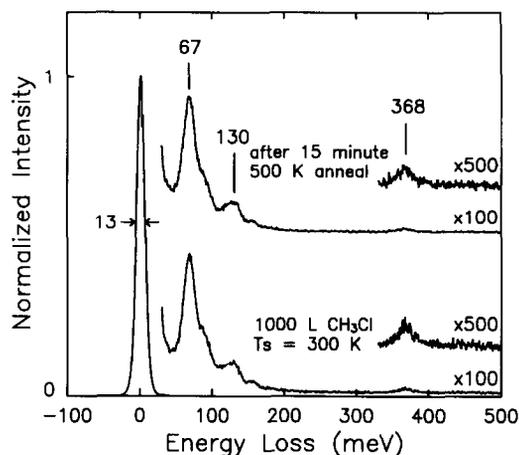


Fig. 3. EEL spectra acquired at the specular angle after 1000 L deposition of CH_3Cl on Si(100) held at room temperature. Also shown is the vibrational spectrum taken after a 15 min anneal to 500 K. In both cases the sample was allowed to cool slowly to 85 K prior to acquiring EEL spectra. The peaks are unshifted and the relative intensities are unchanged after the anneal.

surface was then annealed to 500 K for 15 min, after which another EEL spectrum was taken to determine whether the amount of adsorbed singly bonded carbon would increase. The duration was chosen to be the same as that used to expose the 500 K sample to 1000 L which resulted in the EEL spectrum shown in Fig. 2. The energy loss peak at 130 meV does not increase in height after the anneal nor does the Si–Cl stretch frequency shift to 74 meV. This implies that rather than resulting from adsorption and subsequent thermal desorption or rearrangement, a continued flux of molecules from the gas phase is directly responsible for the observed changes in Fig. 2. The adsorbed Cl and CH_3 at 500 K have higher populations of vibrationally excited states. It is suggested that the vibrationally excited adsorbates have an increased ability to react with methyl chloride resident in the precursor potential well. The reaction can reduce the hydrogen coordination number of the adsorbed CH_3 through a reaction of Cl from the methyl chloride and a hydrogen to form HCl, which desorbs. This process would create reactive sites which could then be filled by the remaining CH_3 left from the methyl chloride thus forming a C–C bond.

The evidence for C–C bond production at 500 K motivated an extension of the study to higher tem-

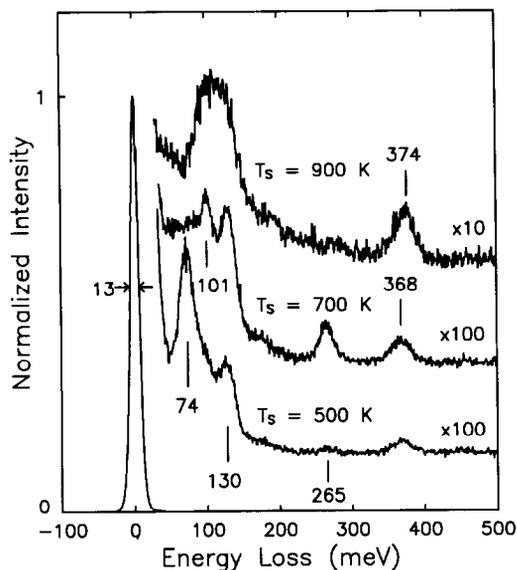


Fig. 4. Specular EEL spectra acquired after deposition of 100 L CH_3Cl on a Si(100) surface at 500, 700, and 900 K. The strong Si–Cl stretch at 74 meV for the 500 K exposure is much smaller for both 700 and 900 K. There are two new loss features for the methyl chloride exposure at 700 K. The peak at 101 meV is assigned to the Si–C stretch mode and the peak at 265 meV is assigned to the Si–H stretch mode. The broad peak near 100 meV for the 900 K exposure is assigned to the Si–C stretch mode and the single carbon bond mode. Also, the C–H stretch frequency has shifted to 374 from 368 meV. The sample was slowly cooled to 85 K prior to acquiring the spectra.

peratures. The vibrational spectra obtained after 100 L exposures of methyl chloride at substrate temperatures of 500, 700, and 900 K are shown in Fig. 4. In addition to the energy loss peaks assigned previously, the spectrum for the substrate temperature of 700 K reveals several new features. The loss peak at 265 meV is assigned to the excitation of the Si–H

stretch mode and indicates that there is hydrogen bonded directly to surface silicon atoms [16] created by the dissociation of CH_3 to form CH_x ($x = 0,1,2$) fragments. Methyl dissociation was observed beginning at 700 K in the vibrational study of methyl iodide adsorption [13]. The peak at 101 meV is assigned to the $\nu(\text{C–Si})$ stretch mode [5].

An exposure of 100 L at 900 K results in a loss of low energy electron reflectivity causing a noticeable reduction in signal-to-noise ratio. It has been shown that this temperature is high enough to allow the formation of silicon carbide alloy layers using other carbon containing precursors [17,18]. The loss peaks at 101 and 130 meV are no longer distinguishable. Only a broad loss feature extending from 100 to 125 meV is observed. The 368 meV loss peak present after lower temperature exposures shifts to 374 meV indicating a slight shift towards graphitic bonding. This conclusion is based on previous EELS studies of amorphous C:H films which found loss peaks at 358, 378, and 412 meV, corresponding to sp^3 , graphitic, and sp^1 bonding, respectively [15]. Due to the lengthy cleaning required after this exposure, it is inferred that a significant portion of the adsorbed carbon had migrated into the bulk. Note the dramatic reduction of the Si–Cl vibrational loss peak at 74 meV for 700 and 900 K exposures indicating a lack of adsorbed chlorine. The absence of chlorine was also established with AES measurements monitoring the Cl_{LMM} peak. In both cases, the chlorine peak was unresolvable ($\text{Cl}_{\text{LMM}}/\text{Si}_{\text{LMM}} \leq 2 \times 10^{-3}$). A summary of the vibrational excitation assignments for high temperature exposures is provided in Table 2.

At sample temperatures ranging from 100 to 900 K, methyl chloride has been found to result readily

Table 2

Vibrational modes of CH_3Cl adsorbed on Si(100) at 500, 700, and 900 K; The sample was cooled at 2 K/s to 85 K after exposure prior to taking EEL spectra; PE denotes polyethylene and the a-C:H film was created with a 160 eV ethane ion beam; NO means not observed

| Normal mode | At 500 K ^a (meV) | At 700 K ^a (meV) | At 900 K ^a (meV) | PE ^b (meV) | a-C:H film ^c (meV) | H/Si(100) ^d (meV) | C/Si(100) ^e (meV) |
|---------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------|----------------------------------|---------------------------------|---------------------------------|
| $\nu(\text{Si–Cl})$ | 74 | NO | NO | – | – | – | – |
| $\nu(\text{Si–C})$ | NO | 101 | 101 | – | – | – | 99 |
| $\nu(\text{C–C})$ | 130 | 130 | 130 | 132 | 132 | – | – |
| $\nu(\text{Si–H})$ | NO | 265 | NO | – | – | 260 | – |
| $\nu(\text{C–H})$ | 368 | 368 | 374 | 360 | 358, 378, 412 | – | – |

^a This work. ^b Ref. [14]. ^c Ref. [15]. ^d Ref. [16]. ^e Refs. [4,5].

in dissociative chemisorption on Si(100) 2×1 . The sticking coefficient is close to unity at ≤ 300 K but decreases at higher temperatures. The adsorbed chlorine resulting from low temperature exposure is found to desorb between 700 and 900 K while the adsorbed carbon does not desorb but begins to migrate into the bulk at 900 K. A reduced sticking coefficient at 500 K provides evidence for a precursor to dissociative chemisorption. Exposures at substrate temperatures below 100 K result in adsorbed molecular species which desorb at 120 K and may be molecules trapped in the precursor well. Moderate doses (100 L) at ≥ 500 K result in adsorbed carbon structures which consist of C–C single bonds. Thermal desorption is responsible for the absence of chlorine in hydrogenated carbon films created with exposures at ≥ 700 K. On the other hand, the production of adsorbed single bonded carbon pairs appears to be a direct consequence of the prolonged exposure to methyl chloride. The higher reactivity of methyl chloride relative to methane despite the structural similarity, makes it an interesting candidate for diamond and silicon carbide film growth.

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