Comparison of Cl₂ and HCl Adsorption on Si(100)-(2x1)

by


Submitted to:

2nd International Symposium
on Atomic Layer, Epitaxy
Session E-12

Surface Science Center
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260

June 1, 1992

Reproduction in whole or in part is permitted for any
purpose of the United States Government

This document had been approved for public release and sale;
it distribution is unlimited
The chemisorption and reaction of Cl\(_2\) and HCl on Si(100)-(2x1) have been studied using a variety of measurement methods. At 100K, both Cl\(_2\) and HCl dissociatively chemisorb on the dangling bonds of Si(100). At saturation coverage, the surface concentration of Cl is about one Cl atom per Si atom while HCl can produce a Cl coverage only one fourth of that achieved with Cl\(_2\). This is the first report of a self-site-blocking effect in adsorption on a semiconductor surface. HREEL spectra indicate that both Cl\(_2\) and HCl adsorption at 100K give a monochloride surface species with a Si-Cl stretching frequency of -550-600 cm\(^{-1}\). Digital EDXRF measurements reveal that the Si-Cl bond angle for the monochloride from both Cl\(_2\) and HCl adsorption is oriented on the vertical plane containing the Si-Si dimer bond and is inclined from the surface normal. The etching products of Si(100) by Cl\(_2\) at elevated temperatures are SiCl\(_2\) at -800K and a small amount of SiCl\(_4\) at -500K. For HCl, the only observed etching product is SiCl\(_2\).
Comparison of Cl₂ and HCl Adsorption on Si(100)-(2×1)


Surface Science Center
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260
412-624-8320
Comparison of Cl$_2$ and HCl Adsorption on Si(100)-(2x1)


Surface Science Center
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260

and

*Department of Physics
University of Pittsburgh
Pittsburgh, PA 15260.

Abstract

The chemisorption and reaction of Cl$_2$ and HCl on Si(100)-(2x1) have been studied using a variety of measurement methods. At 100K, both Cl$_2$ and HCl dissociatively chemisorb on the dangling bonds of Si(100). At saturation coverage, the surface concentration of Cl is about one Cl atom per Si atom while HCl can produce a Cl coverage only one fourth of that achieved with Cl$_2$. This is the first report of a self-site-blocking effect in adsorption on a semiconductor surface. HREEL spectra indicate that both Cl$_2$ and HCl adsorption at 100K give a monochloride surface species with a Si-Cl stretching frequency of ~550-600 cm$^{-1}$. Digital ESDIAD measurements reveal that the Si-Cl bond angle for the monochloride from both Cl$_2$ and HCl adsorption is oriented on the vertical plane containing the Si-Si dimer bond and is inclined from
the surface normal. The etching products of Si(100) by Cl₂ at elevated temperatures are SiCl₂ at ~ 800K and a small amount of SiCl₄ at ~ 500K. For HCl, the only observed etching product is SiCl₂.
1. Introduction

It is important to understand the basic chemistry of chlorine chemisorption and reaction on semiconductor surfaces, since Cl-containing molecules, such as SiH₂Cl₂ [1] and GaCl₃ [2], have been used as precursor molecules for atomic layer epitaxy processes, and Cl₂ molecules have been used in the ion [3-5] or photon assisted etching [6-8] process.

In this report, the saturation coverage and vibrational spectrum of Cl(a) derived from Cl₂ and HCl adsorption are compared on Si(100). In addition, Cl⁺ ESDIAD patterns from Si-Cl bonds on Si(100) are reported, giving information about the Si-Cl bond direction.

2. Experimental

Experiments were carried out in two UHV chambers. The first one was equipped with a digital ESDIAD/LEED (electron stimulated desorption ion angular distribution/low energy electron diffraction) apparatus, an Auger electron spectroscopy (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 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 microcapillary-collimated gas dosers [9,10] were used in both chambers for control of the Cl\(_2\) or HCl exposure. 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 [9].

3. Results and Discussion

3.1. Adsorption of Cl\(_2\) and HCl

The saturation coverage of the chlorine layer derived from the adsorption of Cl\(_2\) and HCl was measured. Figure 1 is an Auger measurement of the development of the Cl(a) coverage using the two molecules as a function of exposure. It is noticed that at about 3x10\(^{14}\) molecules/cm\(^2\) exposure, both the Cl\(_2\) and HCl adsorption rate has dramatically decreased. The reduction of the adsorption rate for Cl\(_2\) is due to the lack of available surface dangling bonds since all of them are nearly used up for the chemisorption [11]. The perfect Si(100)-(2x1) surface exposes 6.8x10\(^{14}\) dangling bonds/cm\(^2\). Thus, at a Cl\(_2\) exposure near ~3x10\(^{14}\) Cl\(_2\)/cm\(^2\), saturation of the dangling bonds is expected to occur (near the break point in the curve) assuming a sticking
probability of unity in the initial adsorption region. Beyond the break point at \( \sim 3 \times 10^{14} \text{ Cl}_2/\text{cm}^2 \), the coverage continues to rise slowly as the Cl\(_2\) exposure is increased. For the same exposure (\( \sim 3 \times 10^{14} \text{ molecules/cm}^2 \)), the saturation effect is also observed for HCl adsorption. The surface Cl coverage from HCl adsorption is only about one-fourth of that achieved by Cl\(_2\) adsorption, as obtained from the Cl/Si AES intensity ratio in Figure 1. The Cl\(_2\) molecules are composed of two Cl atoms which give a Cl coverage of nearly one Cl atom per dangling bond at the break point. In comparison, HCl is composed of one Cl atom and one H atom. If the surface dangling bonds were all occupied by H(a) and Cl(a) from HCl adsorption, a Cl surface coverage of about 0.5 would be expected. However, at the break point only about one fourth of the surface dangling bonds are occupied by Cl from HCl adsorption at 100K. The surface has one half of the dangling bonds which are not accessible for HCl adsorption. Furthermore, after a saturation exposure of HCl is achieved, exposure of this prepared surface to Cl\(_2\) leads to increased Cl coverages as measured by AES, indicating that the dangling bonds inaccessible for HCl adsorption are active for Cl\(_2\) adsorption. Thus, the HCl adsorption on Si(100) is a self-site-blocking process. To our knowledge, this is the first report of such a self-site-blocking adsorption process on a semiconductor surface. The immediate conclusion from this result is that HCl will be a less effective etchant than
Cl₂ due to its limited surface coverage on Si(100). The nature of this self-sit-blocking adsorption phenomena is not well understood at present.

3.2. Vibrational Studies of Cl₂ and HCl Adsorption

Deeper insight into the chlorine surface chemistry can be obtained from the vibrational characterization of the surface species formed during the chemisorption and reaction. Figure 2 shows the vibrational spectra after Cl₂ and HCl adsorption on Si(100)-(2×1) at 100K. It is noticed that only one strong Si-Cl stretching mode, ν(SiCl), is observed at ~600 cm⁻¹ and at ~550 cm⁻¹ for Cl₂ and HCl adsorption, respectively [12]. For HCl adsorption, an additional vibrational feature is observed at ~2120 cm⁻¹ (figure 2b) which is due to the SiH stretching mode [13]. The lack of a HCl stretching mode near ~3000 cm⁻¹ [14] and the appearance of ν(SiCl) and ν(SiH) modes indicate that HCl is dissociated upon adsorption at 100K.

The vibrational spectra (Figure 2) indicate that higher surface chloride species, such as SiCl₂(a), SiCl₃(a) or SiCl₄(a), are not observed following either Cl₂ or HCl adsorption at 100K. These chlorides should exhibit an asymmetric stretching mode [νₐ(SiCl) ~533-617 cm⁻¹], and a symmetric stretching mode [νₛ(SiCl) ~376-465 cm⁻¹]; in addition a bending vibrational mode should be present [d(Si-Cl) ~164-261 cm⁻¹] [12a-e]. There is no prominent
evidence for these modes in the spectra observed. This is consistent with the dissociative adsorption of HCl and Cl₂ forming surface monochloride species. For Cl₂ adsorption at 100K, the mode at 295 cm⁻¹ has been assigned to a Si₂Cl stretching mode for a bridge-bonded Cl species, a minority species [15].

3.3. ESDIAD Studies of Si-Cl Bonding on Si(100)

The ESDIAD method has been employed to study the bonding of Cl(a) to Si(100) using both Cl₂ and HCl as adsorbates. In this method, the adsorbed layer is bombarded by electrons (Ve=120 eV in this case) and the angular distribution of Cl⁺ ions is detected by a digital technique. The ejection angle of the Cl⁺ ions is determined primarily by the orientation of the Si-Cl bond being broken [16-18] in the electronic excitation. This angle is modified by final state effects involving the Cl⁺ interaction with its image charge as well as by Cl⁺ reneutralization near the surface [19-20].

The surface monochloride species produced from HCl or Cl₂ adsorption give four off-normal Cl⁺ emission beams observed from the ESDIAD measurements, shown in Figure 3. The Cl⁺ ions are ejected in planes perpendicular to the crystal surface but parallel to the surface Si-Si dimer bond axes, as confirmed from the comparison of the ESDIAD pattern with the (2x1) LEED patterns of the substrate.
surface. Slight misalignment of the Si single crystal from the (100) direction results in a stepped surface with Si-Si dimer rows oriented alternately in orthogonal directions, forming (1x2) and (2x1) domains of reconstructed surface. The inclined Cl bonds of the surface monochloride species from both types of domains produce the four off-normal Cl+ ion beams. A single domain surface would give two off-normal Cl+ ion beams with the opposite polar angle with respect to the surface normal.

3.4. Thermal Desorption Studies

The thermally activated etching reaction was investigated by TPD measurements. The results (Figure 4) indicate that Cl(a) from both Cl2 and HCl chemisorption etches the Si(100) surface, producing SiCl2(g) with a desorption peak temperature at ~820K for the Cl2/Si(100) system and at 840K for the HCl/Si(100) system. A small amount of SiCl4 desorption (monitored by its major mass spectrometer cracking product, SiCl3+, m/e=133 amu) is also observed for the Cl2/Si(100) system at monolayer or higher exposures. This is consistent with the previous Cl2/Si(100) TPD results [6, 21]. These measurements indicate that SiCl2 is the main etching product for both Cl2 and HCl adsorption, and that the etching process involving SiCl2 occurs near 840K. Species such as SiH4 (monitoring m/e=30 amu) or SiH3Cl (monitoring m/e=31 amu), SiH2Cl2 (monitoring
m/e=99 amu) and SiHCl$_3$ (monitoring m/e=133 amu) were not
detected in desorption, showing that the surface hydrogen
atom was not involved in the etching process when HCl was
employed.

An effort was made for the Cl$_2$/Si(100) system to
observe by HREELS whether the SiCl$_2$(a) species could be
detected by raising the crystal temperature to ~850K,
followed by cooling to 100K. The HREEL spectrum remained
essentially the same, exhibiting a single Si-Cl stretching
mode of the surface monochloride shown in Figure 2a with a
reduced intensity and a slight reduced frequency (to about
570 cm$^{-1}$) due to the reduction of surface chlorine
coverage. Thus, SiCl$_2$(a) formation is probably the rate
determining step for SiCl$_2$(g) liberation.

4. Conclusions

The following conclusions may be made from these
studies of Cl$_2$ and HCl chemisorption on Si(100)-(2x1).

(1). Dissociative adsorption of both Cl$_2$ and HCl
occurs on Si(100)-(2x1) at 100K. The vibrational
spectra of the species produced from Cl$_2$ and HCl
adsorption indicate that Si-Cl bonds are formed
in both cases. For HCl chemisorption, the Si-H
bond is also observed.

(2). For Cl$_2$ adsorption, about one Cl atom/Si
dangling bond is produced at saturation
coverage. In addition, the saturation coverage of chlorine from Cl₂ adsorption is ~4 times greater than that from HCl adsorption. This result implies that HCl adsorption involves an adsorption site exclusion process, where neither H(a) or Cl(a) species can populate one-half of the dangling bond sites exposed on Si(100)-(2x1).

(3). ESDIAD studies indicate that the Si-Cl bonds are inclined away from the surface normal direction along perpendicular planes containing the Si-Si dimer bonds.

(4). SiCl₂ is the main etching product observed from thermal desorption studies of Cl₂ and HCl on Si(100). It desorbs near 800K in both cases. HREELS studies indicate that SiCl₂(a) is not produced in measurable amount on heating the surface. This indicates that the rate determining step for SiCl₂(g) desorption is the conversion of SiCl(a) species to SiCl₂(a) species which then desorb.

5. Acknowledgments

This work was supported by the Office of Naval Research. The authors would like to acknowledge Mr. S. R. Lucas for his reference TPD result for Cl₂ /Si(100).
References

11. Cross calibrations of surface Cl coverage from Cl₂ adsorption on Si(100) with the saturation coverage of monohydride from atomic hydrogen adsorption indicate
that the surface Cl coverage is about 0.9 at the break point of the Cl$_2$ AES uptake curve.

(b) M. C. Tobin, J. Am. Chem. Soc., 75 (1953) 1788


Figure Captions:

Fig. 1. Rate of Cl coverage increase for Cl₂ and HCl adsorption on Si(100)-(2x1) at 100K using Auger Spectroscopy. Vₑ = 2.0 kV.

Fig. 2. HREEL spectra of Cl₂ and HCl adsorption on Si(100)-(2x1) at 100K: (a) Cl₂ exposure=7.4x10¹⁴ molecules/cm²; (b) HCl exposure=8.7x10¹⁴ molecules/cm². Contour profiles are plotted by an increment of 1/6 of their peak maxima.

Fig. 3. Cl⁺ ESDIAD patterns of (a) Cl₂ (after annealing to 673K to get sharp monochloride pattern), and (b) HCl (120K adsorption). Near saturation coverages were achieved for Cl₂ and HCl adsorption prior to these measurements. Vₑ=120 eV.

Fig. 4. Temperature programmed desorption from layers produced from Cl₂ and HCl adsorption to saturation coverage on Si(100)-(2x1). Heating rate is ~3.6K/sec.
Auger Studies of Cl₂ and HCl Adsorption on Si(100)-(2x1). T=100K

Gao, et al.

Figure 1
Comparison of the Vibrational Spectra for Cl$_2$ and HCl Adsorption on Si(100)

Figure 2

Gao, et al.
Cl⁺ ESDIAD Studies for Cl₂ and HCl Adsorbates on Si(100)-(2×1)

Gao, et al.

Figure 3
Comparison of Thermal Desorption From Cl$_2$ and HCl on Si(100)

Cl$_2$/Si(100)-(2x1)
120K Adsorption
Saturation Coverage

HCl/Si(100)-(2x1)
120K Adsorption
Saturation Coverage

Gao, et al.

Figure 4
ALE Contractor Distribution List

D.T.I.C.
Bldg # 5, Cameron Station
Alexandria, VA 22314

Dr. Andrew Freedman
Aerodyne Research, Inc.
45 Manning Road
Billerica, MA 01821
Tel: (508) 663-9500
FAX: (508) 663-4918
e-mail: aerodyn@mitvma.mit.edu

Dr. Asif Kahn
APA Optics
2950 NE 94th Lane
Blaine, MN 55434
Tel: (612) 784-4995
FAX: (612) 784-2038
e-mail: 70702.2032@compuserve.com

Dr. Duncan Brown
Advanced Technology Materials, Inc
7 Commerce Drive
Danbury, CT 06810
Tel: (203) 794-1100
FAX: (203) 792-8040

Dr. Peter Norris
EMCORE Corp.
35 Elizabeth Ave.
Somerset, NJ 08873
Tel: (201) 271-9090

Prof. Joe Greene
Dept. of Materials Science and Engineering
University of Illinois
1101 W. Springfield Ave.
Urbana, IL 61801
Tel: (217) 333-0747

Dr. T. P. Smith
IBM T.J. Watson Research Center
P. O. Box 218, Route 134
Yorktown Heights, NY 10598
e-mail: trey@ibm.com

Prof. Robert F. Davis
N.C.S.U. Box 7907
Raleigh, NC 27605-7907
Tel: (919) 515-2377/3272
FAX: (919) 515-3419
e-mail: davis@mte.ncsu.edu

Prof. Salah Bedair
Department of Electrical Engineering
N.C.S.U.; Box
Raleigh, NC 27695
Tel: (919) 515-2336
e-mail: jll@ecegrad.ncsu.edu

Max N. Yoder
ONR Code 1114
Arlington, VA 22217
Tel: (703) 696-4218
FAXes (703) 696-2611/3945/5383
e-mail: yoder@charm.isi.edu

Dr. A. M. Goodman
ONR, Code 1114
Arlington, VA 22217
Tel: (703) 696-4218
FAXes (703) 696-2611/3945/5383
e-mail: goodman@ocnr-hq.navy.mil

dr. j. pazik
ONR Code 1113
Arlington, VA 22217
Tel: (703) 696-4410
FAXes (703) 696-2611/3945/5383
e-mail: pazik@ocnr-hq.navy.mil

Prof. J. T. Yates, Jr.
Dept. of Chemistry
Surface Science Ctr.
University of Pittsburgh
Pittsburgh, PA 15260
Tel: (412) 624-8320
FAX: (412) 624-8552
e-mail: yates@vms.cis.pitt.edu

Robert J. Markunas, R.A. Rudder
Research Triangle Institute; Box 12194
Research Triangle Park, NC 27709-2194
Tel: (919) 541-6153
FAX: (919) 541-6515
e-mail: rjmk@rti.rti.org

Professor Mark P. D’Evelyn
William Marsh Rice University
Dept. of Chemistry
P.O. Box 1892
Houston, TX 77251
Tel: (713) 527-8101, ext. 3468
FAX: (713) 285-5155
e-mail: mpdev@langmuir.rice.edu

Dr. Howard K. Schmidt
Schmidt Instruments, Inc.
2476 Bolsover, Suite 234
Houston, TX 770054
Tel: (713) 529-9040
<table>
<thead>
<tr>
<th>Name</th>
<th>Address</th>
<th>Contact Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dr. Andrew Freedman</td>
<td>Aerodyne Research, Inc. 45 Manning Road, Billerica, MA 01821</td>
<td>Tel: (508) 663-9500, FAX: (508) 663-4918</td>
</tr>
<tr>
<td>Dr. Asif Kahn</td>
<td>APA Optics 2950 NE 94th Lane, Blaine, MN 55434</td>
<td>Tel: (612) 784-4995, FAX: (612) 784-2038</td>
</tr>
<tr>
<td>Dr. Duncan Brown</td>
<td>Advanced Technology Materials, Inc 7 Commerce Drive, Danbury, CT 06810</td>
<td>Tel: (203) 794-1100, FAX: (203) 792-8040</td>
</tr>
<tr>
<td>Dr. Peter Norris</td>
<td>EMCORE Corp. 35 Elizabeth Ave., Somerset, NJ 08873</td>
<td>Tel: (201) 271-9090</td>
</tr>
<tr>
<td>Prof. Joe Greene</td>
<td>Dept. of Materials Science and Engineering University of Illinois 1101 W. Springfield Ave., Urbana, IL 61801</td>
<td>Tel: (217) 333-0747</td>
</tr>
<tr>
<td>Dr. T. P. Smith</td>
<td>IBM T.J. Watson Research Center P. O. Box 218, Route 134 Yorktown Heights, NY 10598</td>
<td>e-mail: <a href="mailto:trey@ibm.com">trey@ibm.com</a></td>
</tr>
<tr>
<td>Prof. Robert F. Davis</td>
<td>N.C.S.U. Box 7907</td>
<td></td>
</tr>
</tbody>
</table>

| Copies | 1 |

**AIE Contractor Distribution List**

D.T.I.C.
Bldg # 5, Cameron Station
Alexandria, VA 22314

Dr. Andrew Freedman
Aerodyne Research, Inc.
45 Manning Road
Billerica, MA 01821
Tel: (508) 663-9500
FAX: (508) 663-4918
e-mail: aerodyn@mitvma.mit.edu

Dr. Asif Kahn
APA Optics
2950 NE 94th Lane
Blaine, MN 55434
Tel: (612) 784-4995
FAX: (612) 784-2038
e-mail: 70702.2032@compuserve.com

Dr. Duncan Brown
Advanced Technology Materials, Inc
7 Commerce Drive
Danbury, CT 06810
Tel: (203) 794-1100
FAX: (203) 792-8040

Dr. Peter Norris
EMCORE Corp.
35 Elizabeth Ave.
Somerset, NJ 08873
Tel: (201) 271-9090

Prof. Joe Greene
Dept. of Materials Science and Engineering University of Illinois 1101 W. Springfield Ave.
Urbana, IL 61801
Tel: (217) 333-0747

Dr. T. P. Smith
IBM T.J. Watson Research Center P. O. Box 218, Route 134 Yorktown Heights, NY 10598
e-mail: trey@ibm.com

Prof. Robert F. Davis
N.C.S.U. Box 7907