Thermal and Low-energy Ion-mediated Surface Chemistry of Halocarbons on Si(111)\(7\times7\) and SiO\(_2\)

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Outline

Introduction

• Si(111) surface
• Experimental
• Motivation
• Halocarbons

• Present work

• Modification of Si(111)7x7 and SiO₂ surfaces by low-energy ion-mediated surface reactions of three fluorocarbons

• Formation of novel adstructures and functionalization of Si(111) surfaces using thermal evolutions of six-member family of chloroethylenes

Summary & Outlook
Introduction – Si(111) substrate

- Diamond structure of Si
  - Silicon is the predominant material in the semiconductor industry
  - Ideal platform for studying site-specific surface reactions on Si(111)7x7 template

- Si(111)7x7 surface

[Diagram showing 1x1 and 7x7 reconstructions]
Present work - Procedure

Ion-mediated surface reactions
- Low-energy (50 eV) fluorocarbon ions

Chemisorption at RT
- A family of six chloroethylenes
- Adsorption Properties (by vibrational EELS)
- Surface structure (by LEED)

Thermal desorption
- Adsorption Energy & geometry (by DFT)
- Surface chemistry (by temperature dependent EELS, TDS)

Surface condition
- Si(111)7x7
- Vitreous SiO₂
- Ar⁺ sputtered Si (more defects)
Introduction
Experimental & theoretical methods

Experimental
- UHV chamber (P<10^{-10} Torr)
- Vibrational Electron Energy Loss Spectroscopy (EELS)
- Thermal Desorption Spectrometry (TDS)
- Low Energy Electron Diffraction (LEED)

Computational
- Density functional theory (DFT)
- Gaussian 03 package
- Geometry and energy of chemisorption
Experimental: EELS

**Principle:**
\[ \Delta E = h\omega = E_{\text{impact}} - E_{\text{scattered}} \]

Monoenergetic electron beam

**Overall energy resolution**

**FWHM**
\[ \Delta E_{1/2} = \sqrt{\left(\Delta E_{1/2}^M\right)^2 + \left(\Delta E_{1/2}^A\right)^2 + \left(\Delta E_{1/2}^{\text{non-ideal}}\right)^2} \]

Great efforts are needed to get better resolution
Tuning the EELS system very time-consuming
Experimental: EELS

Principle: Energy Loss

\[ AE = h\omega = E_{\text{impact}} - E_{\text{scattered}} \]

Dipole Scattering Selection Rules

- Active
- Inactive

Scattering Modes:
- Dipole mode--dominated at specular direction
- Impact mode--better resolved at off-specular direction
Experimental: TDS setup

- Intensities for different masses → amount of desorbed species
- Desorption temperature → bonding energy & adsorption geometry
- Shape of TDS profiles → reaction order
Experimental - LEED

- Structure of the near-surface region
- Changes of surface structure when exposed to different types/amounts gases

Si(111)7x7

100 L iso-DCE/Si(111)7x7
Fluorocarbons: Objective & Motivation

• To study the interaction of low-energy fluorocarbon ions with Si(111)7x7 and vitreous SiO₂ at molecular level (mechanisms and reaction pathways)

• Scientific reasons
  • Halo Silicon Surface Chemistry
  • Ion Surface Chemistry

• Practical reasons
  • To understand the fundamental processes in plasma etching and film deposition.
  • New inter-metal dielectric films:
    • Halonated SiO₂
    • Halocarbonated-SiO₂
Introduction – Halocarbons Plasma

- Schematic diagram of Plasma etching system

- Our simple ion gun

- High aspect ratio etch

- Halocarbon gas of interest is cracked and ionized by electrons inside the ion gun
- Postive halocarbon ion beam with high energy (>500 eV) is formed by the lenses
- Low-energy ions are obtained by the floating voltage on the sample

MEMS example
Vibrational frequencies (in cm\(^{-1}\)) of reference silicon and related systems

<table>
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<tr>
<th>Vibrational mode</th>
<th>This work</th>
<th>Ref. [21]</th>
<th>Ref. [22]</th>
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<td>838(^a) 1015(^b)</td>
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<td>C–H(_3) stretch</td>
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Fluorocarbon ions: exposure on 7x7

**CF₄**

- 1 kL
- 2.2 kL
- 5 kL
- 10 kL

**CH₂F₂**

- 1 kL
- 2.2 kL
- 5 kL
- 10 kL

**C₂H₂F₂**

- 1 kL
- 2.5 kL
- 5 kL
- 10 kL

ΔSi–Fx = 300-380

νSi–Fx = 780-885

νSi–C = 810-850

νCH

δSi–Fx = 300-380

νSiH

νSi

C₂H₂F₂⁺ (30%)
C₂H₂F⁺ (20%)
CF⁺ (15%)
CH₂F⁺ (12%)
C₂HF⁺ (11%)

CF₃⁺ (78%)
CF₂⁺ (10%)
CF⁺ (3%)

CH₂F⁺ (38%)
CHF₂⁺ (37%)
CF⁺ (11%)
CHF⁺ (4%)
Fluorocarbon ions: Si(111) vs. SiO₂

- CF₃⁺ incident on 7x7
- CF₃⁺ incident on SiO₂

- More SiFₓ, and fewer SiC on SiO₂
Fewer SiF\textsubscript{x} on SiO\textsubscript{2} produced by ion-irradiation in C\textsubscript{2}H\textsubscript{2}F\textsubscript{2}
Fluorocarbon ions: TDS

**CF₄ and CH₂F₂**

- More desorption of SiF₂ and SiF₄ from SiO₂ ion-irradiated in CF₄ or CH₂F₂

**C₂H₂F₂**

- Fewer desorption of SiF₂ and SiF₄ from SiO₂ ion-irradiated in C₂H₂F₂ than from si(111)7x7
Fluorocarbon ions (50 eV): Summary

- CF$_x$ layer is only formed at sufficiently high dose of CF$_3^+$ ion incidence (>3x10$^{16}$cm$^{-2}$, H. Toyoda, H. Morishima, R. Fukute, Y. Hori, I. Murakami, and H. Sugai, J. Appl. Phys. 95 (2004) 5172)
- In our case, the estimated dose of CF$_3^+$ ion incident on the sample surface is ~10$^{16}$ cm$^{-2}$ for 10,000 L exposure of CF$_3^+$ ions
- Ion current ~ 200nAcm$^{-2}$ at 1x10$^{-6}$ Torr
  \[\Rightarrow \text{ion dose} \sim 1x10^{16}\text{cm}^{-2} \text{ for } 10,000 \text{ L of CF}_3^+ \text{ ions}\]
Fluorocarbon ions (50 eV): Summary

• The resulting surface products on Si(111)7x7 and vitreous SiO₂ obtained by the irradiation of low-energy fluorocarbon ions from three fluorocarbons with different F-to-C ratio have been examined systematically

• On Si(111)7x7, the ion-irradiation in the three fluorocarbons produced similar reaction layer: fluorosilyl (SiFx) and carbonaceous cluster (SiC and/or hydrocarbon fragments)

• On vitreous SiO₂, more fluorosilyl (SiFx) formed than on 7x7 surface when the surfaces exposed to the same dose of ion-irradiation generated in CF₄ or CH₂F₂

• But, the same dose of ion-irradiation generated in C₂H₂F₂ produced a smaller amount of fluorosilyl (SiFx) on Si(111)7x7 than on vitreous SiO₂

• The presence or absence of a C=C bond in the sputtering gas and the F-to-C ratio of a sputtering gas are found to play important roles
Introduction – Chloroethylenes

- Common industrial chemicals for processing and treatment of silicon wafers
- An ideal platform for studying geometric isometric effects and the effects of halogen substitution on organosilicon chemistry
- Competition among several plausible reaction mechanisms: cycloaddition to “diradical” on surface, and formation of surface vinyl via cleavage of C–Cl bonds as well as dative bonding resulting from the inductive effect of Cl atoms

- Adsorbates of interest
  - MCE
  - TCE
  - PCE

- Si$_9$H$_{12}$ cluster
  - diradical

- Cl content
- isometric

- iso-
- trans-
- cis-DCE

Molecular structures with bond lengths:
- MCE: 4.3 Å
- TCE: 4.6 Å, 2.4 Å
- PCE: 3.3 Å
- iso-DCE: 2.9 Å
- trans-DCE: 4.3 Å
- cis-DCE: 3.3 Å
Si(111) 7x7
Chloroethylene chemisorption: Cl content effect

- **Cycloaddition**
- **Dechlorination**

Primary channel for 2 and more Cl substitution

\[ \nu_{Si-Cl} = 510 \text{ cm}^{-1} \]
Chloroethylene - isometric effect

Different adstructures Chlorovinyl and vinylidene
Low saturation exposure for molecules with \(=\text{CCl}_2\) group
Steric effect between \(\text{cis}\)-DCE and \(\text{trans}\)-DCE

![Graph showing relative intensity vs. exposure for different molecules](image)

- The relative intensity of EELS feature → Saturation exposure
- \(\nu_{\text{Si-Cl}} = 510\)
- \(\nu_{\text{C=C}} = 1510\)
- \(\nu_{\text{CH}} = 2980\)
Chloroethylene: thermal desorption

Three states of acetylene desorption

- **Low temperature desorption**
- **Resulting from β-Cl elimination of 2-chlorovinyl**
- **Desorption from di-σ bonded vinylene**
Novel adstructure - vinylidene

First observation of vinylidene on semiconductor surface produced by RT adsorption of iso-dichloroethylene on Si(111)7x7

- The presence of the $\nu_{C=C}$ EELS feature
- Supported by DFT calculations

$\nu_{Si-Cl} = 510 \text{ cm}^{-1}$
Trichloroethylene – thermal evolution

• First observation of acetylide on semiconductor surface produced by RT adsorption of iso-dichloroethylene on Si(111)7x7

• The presence of the $\nu_{CH}$ EELS feature at 3300 cm$^{-1}$

mono-$\sigma$ bonded chlorovinyl (Cl$\cdot$C=CHCl)
di-$\sigma$ bonded chlorovinylene (H$\cdot$C=Cl$\cdot$C)

Mono-$\sigma$ bonded Si-C≡CH
Cycloaddition, dechlorination and dative adsorption

Summary of geometries found in the room-temperature adsorption of Chloroethylenes

- **Dechlorination** occurs for all the chloroethylenes
- **[2+2] cycloaddition** found in monochloroethylene on Si(111)7x7
- **Dative adsorption** involving the chlorine (Cl) for all chloroethylenes on Si(111)
Summary

- **First systematic study** of thermal evolution of a family of chloroethylenes on Si(111)7x7 surface
- Dechlorination occurs for all the chloroethylenes; [2+2] cycloaddition found monochloroethylene/Si(111); Dative adsorption involving the Cl for all chloroethylenes/Si(111)
- **First observation** of novel adstructures formed by chemisorption of chloroethylenes: in particular, di-σ bonded vinylidene on semiconductor surface
- **First comprehensive study** of the interactions of low fluorocarbon ions with Si(111) and SiO₂ surfaces using more-surface sensitive technique: vibrational EELS
- The presence or absence of a C=C bond in the sputtering gas and the F-to-C ratio of a sputtering gas are found to play important roles on the resulting surface products obtained by the irradiation of low-energy fluorocarbon ions
Outlook

- Further studies of surface chemistry mediated by the low-energy fluorocarbons ions using more chemical-sensitive techniques (e.g. AES, electronic EELS, XPS)

- Extend the current study of chloroethylenes on Si(111)7x7 to bromoethylenes and iodoethylenes on Si(111)7x7 to explore the site-specific surface reactions of Si(111)7x7 surface

- Study post adsorption of larger hydrocarbons with unsaturated bonds (e.g. styrene) on silicon surface with the vinyl and vinylidene to explore the further functionalization of silicon surface for molecular electronics
Thank you

- Dr. K.T. Leung
- Dr. Dan Thomas, Dr. Pu Chen and Dr. Qing-Bin Lu
- Dr. Qiang Li and Xiaojin Zhou
- Xiang Yang and Sergey Mitlin
- Dr. Michael Thiam, Dr. Nina Heinig
- Dr. Hui Yu
- Entire staff of the Science Shops

We, the willing
Led by the unknowing
Are doing the impossible
For the ungrateful
We have done so much
for so long
With so little
We are now qualified
To do anything
With nothing
Chemisorption theory: searching an elephant

Figure 1. (a) An elephant according to six blind men: (1) wall; (2) fan; (3) spear; (4) snake; (5) tree; (6) rope. (b) Theorist’s dream: the elephant model (from ref 7).

Si(111)\,(7\times7): \text{DAS model}
Trichloroethylene – thermal evolution

- First observation of acetylide on semiconductor surface produced by RT adsorption of isodichloroethylene on Si(111)7x7
  - The presence of the $\nu_{CH}$ EELS feature at 3300 cm$^{-1}$

![Diagram of chemical reactions and EELS spectra](image)
• In our case, the estimated dose of CF$_3^+$ ion incident on the sample surface is ~$10^{16}$ cm$^{-2}$ for 10,000 L exposure of CF$_3^+$ ions

• Ion current $\sim 200$ nA cm$^{-2}$ at 1x10$^{-6}$ Torr
  $\Rightarrow$ ion flux $\sim (2 \times 10^{-7}$ Cs$^{-1}$ cm$^{-2})/(1.6 \times 10^{-19}$ C) = $1.25 \times 10^{12}$ cm$^{-2}$ s$^{-1}$
  $\Rightarrow$ ion dose $\sim 1.25 \times 10^{12}$ cm$^{-2}$ for 1L of exposure of CF$_3^+$ ions
  $\Rightarrow$ ion dose $\sim 1 \times 10^{16}$ cm$^{-2}$ for 10,000 L of CF$_3^+$ ions
Fluorocarbon ions (100 eV): A related work

• At the small dose of CF$_3^+$ ions (<0.2$x10^{16}$cm$^{-2}$), formation of fluorosilyl (SiFx) are preferred. With increasing of dose, carbon atoms are accumulated on the Si surface. Such carbon layer inhibits the chemical reaction of F atoms with the Si, and enhances CF bond formation, together with CF$_2$ desorption from the surface.

• At the sufficiently high dose (>3$x10^{16}$cm$^{-2}$), a balance between the C atom supplied by CF$_3^+$ incidence and the C atom lost by CF$_x$ radical desorption is established, while F atoms on the surface approach a steady state determined by CF$_3^+$ ion incidence and the SiFx radical desorption.

• CF$_x$ layer is only formed at sufficiently high dose of CF$_3^+$ ion incidence

• In our case, the estimated dose of CF$_3^+$ ion incident on the sample surface is ~$10^{16}$ cm$^{-2}$

In our case, the estimated dose of CF$_3^+$ ion incident on the sample surface is $\sim$10$^{16}$ cm$^{-2}$ for 10,000 L exposure of CF$_3^+$ ions.

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