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OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT NO: N00014-92-J-1353

R&T PROJECT: 4134011

**KINETICS OF SEMICONDUCTOR SURFACE CHEMISTRY:
SILICON ATOMIC LAYER PROCESSING**

Dr. Steven M. George
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University of Colorado
Boulder, CO. 80309-0215

May 1993



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OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

R&T Number: 4134011

Contract/Grant Number: N00014-92-J-1353

Contract/Grant Title: Kinetics of Semiconductor Surface Chemistry: Silicon Atomic Layer Processing

Principal Investigator: Steven M. George

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- a. Number of papers submitted to refereed journals, but not published: 2
- b. * Number of papers published in refereed journals (list attached): 11
- c. Number of Books or chapters submitted, but not yet published: 0
- d. * Number of books or chapters published (list attached): 1
- e. * Number of printed technical reports & non-refereed papers (list attached): 6
- f. Number of patents filed: 0
- g. * Number of patents granted (list attached): 0
- h. Number of invited presentations at workshops or professional society meetings: 9
- i. Number of presentations at workshops or professional society meetings: 7
- j. * Honors/Awards/Prizes for contract/grant employees (list attached): 4
(This might include Scientific Society Awards/Offices,
Promotions, Faculty Awards/Offices)
- k. Total number of Graduate Students and Post-Doctoral associates supported by at least 25% during this period under this R&T project number:
Graduate Students: 2
Post-Doctoral Associates: 0
including the number of,
Female Graduate Students: 2
Female Post-Doctoral Associates: 0
the number of
Minority* Graduate Students: 0
Minority* Post-Doctoral Associates: 0
and, the number of
Asian Graduate Students: 0
Asian Post-Doctoral Associates: 0
- l. * Other funding (list agency, grant title, amount received this year, total amount, and period of performance, and briefly state the relationship of that research to your ONR grant)

* Use the letter and an appropriate title as a heading for your list, e.g.:

b. Published Papers in Refereed Journals, or, d. Books and Chapters published

Also, submit these lists as ASCII files preferably on a 3" or 5" PC-compatible floppy disk

* Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

PART I

A. Papers Submitted to Refereed Journal

1. Authors: A.C. Dillon, M.B. Robinson and S.M. George
Title: "Decomposition of Silicon Hydrides Following Disilane Adsorption on Porous Silicon Surfaces"
Journal: Surface Science Letters
2. Authors: M.B. Robinson, A.C. Dillon and S.M. George
Title: "Dichlorosilane Adsorption and Decomposition on Porous Silicon Surfaces"
Journal: Surface Science Letters

B. Papers Published in Refereed Journals

1. Authors: A.C. Dillon, M.B. Robinson, M.L. Han and S.M. George
Title: "Diethylsilane Decomposition on Silicon Surfaces Studied Using Transmission FTIR Spectroscopy"
Journal: *J. Electrochem. Soc.* **139**, 537 (1992).
2. Authors: P.A. Coon, M.L. Wise, A.C. Dillon, M.B. Robinson and S.M. George
Title: "Diethylsilane on Silicon Surfaces: Adsorption and Decomposition Kinetics"
Journal: *J. Vac. Sci. Technol.* **B10**, 221 (1992).

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3. Authors: P.A. Coon, P. Gupta, M.L. Wise and S.M. George
Title: "Adsorption and Desorption Kinetics for SiH_2Cl_2 on $\text{Si}(111)7\times7$ "
Journal: *J. Vac. Sci. Technol.* **A10**, 324 (1992).
4. Authors: P.A. Coon, M.L. Wise, Z.H. Walker, S.M. George and D.A. Roberts
Title: "Adsorption and Decomposition of Diethylgermane on $\text{Si}(111)7\times7$ "
Journal: *Appl. Phys. Lett.* **60**, 2002 (1992).
5. Authors: M.B. Robinson, A.C. Dillon, D.R. Haynes and S.M. George
Title: "Effect of Thermal Annealing and Surface Coverage on Porous Silicon Photoluminescence"
Journal: *Appl. Phys. Lett.* **61**, 1414 (1992).
6. Authors: P.A. Coon, M.L. Wise and S.M. George
Title: "Reaction Kinetics of GeCl_4 on $\text{Si}(111)7\times7$ "
Journal: *Surf. Sci.* **278**, 383 (1992).
7. Authors: P.A. Coon, M.L. Wise and S.M. George
Title: "Modeling Silicon Epitaxial Growth with SiH_2Cl_2 "
Journal: *J. Crystal Growth* **130**, 162 (1993).
8. Authors: P.A. Coon, M.L. Wise and S.M. George
Title: "Adsorption Kinetics of Ethylsilane, Diethylsilane and Diethylgermane on $\text{Si}(111)7\times7$ "
Journal: *J. Chem Phys.* **98**, 7485 (1993).

9. Authors: P.A. Coon, M.L. Wise and S.M. George
Title: "Ethyl Group Decomposition Kinetics Following Adsorption of Diethylsilane, Diethylgermane and Ethylsilane on Si(111)7x7"
Journal: *Surf. Sci.* (in press).
10. Authors: A.C. Dillon, M.B. Robinson, S.M. George and D.A. Roberts
Title: "Adsorption and Decomposition of Diethylgermane on Porous Silicon Surfaces"
Journal: *Surf. Sci.* **286**, L535 (1993).
11. Authors: M.B. Robinson, A.C. Dillon and S.M. George
Title: "Porous Silicon Photoluminescence Versus HF Etching: No Correlation with Surface Hydrogen Species"
Journal: *Appl. Phys. Lett.* **62**, 1493 (1993).

C. NONE

D. **Chapters of Books Published**

1. Author: S.M. George
Title: "Laser Induced Thermal Desorption," in *Investigation of Interfaces and Surfaces-Part A, Physical Methods of Chemistry Series, 2nd Ed., Vol. IXA*, ed. by B.W. Rossiter and R.C. Baetzold.
Publisher: Interscience Publishers, John Wiley and Sons, New York, 1993, pp 453-497.

E. **Technical Reports Published and Papers Published in Non-Refereed Journals**

1. Authors: M.B. Robinson, A.C. Dillon, D.R. Haynes and S.M. George

 Title: "Effect of Surface Coverage on Porous Silicon
 Photoluminescence: Transmission FTIR Studies,"

 Journal: *Light Emission from Porous Silicon,*
 Mat. Res. Soc. Sym. Proc. **256**, 17 (1992).

2. Authors: A.C. Dillon, M.B. Robinson, S.M. George and P. Gupta

 Title: "Effects of Hydrogen Coverage on Silicon Surface
 Reactivity"

 Journal: *Chemical Surface Preparation, Passivation and Cleaning*
 for Semiconductor Growth and Processing,
 Mat. Res. Soc. Sym. Proc. **259**, 99 (1992).

3. Authors: A.C. Dillon, M.B. Robinson, and S.M. George

 Title: "Comparison of Trichlorosilane and Trichlorogermane
 Decomposition on Silicon Surfaces Using FTIR
 Spectroscopy"

 Journal: *Chemical Perspectives of Microelectronic Materials III,*
 Mat. Res. Soc. Sym. Proc. **282**, 405 (1993).

4. Authors: P.A. Coon, M.L. Wise, A.C. Dillon and S.M. George

 Title: "Germanium Deposition on Silicon: Surface Chemistry
 of (CH₃CH₂)₂GeH₂ and GeCl₄"

 Journal: *Chemical Perspectives of Microelectronic Materials III,*
 Mat. Res. Soc. Sym. Proc. **282**, 413 (1993).

5. Authors: M.L. Wise, L.A. Okata, P.A. Coon and S.M. George

 Title: "SiO₂ Growth on Si(111)7x7 Using SiCl₄ and H₂O"

Journal: *Chemical Perspectives of Microelectronic Materials III*,
Mat. Res. Soc. Sym. Proc. **282**, 499 (1993).

6. Authors: M.B. Robinson, A.C. Dillon and S.M. George

Title: "Porous Silicon Photoluminescence versus HF Etching:
No Correlation with Surface Hydrogen Species,"

Journal: *Microcrystalline Semiconductors - Materials Science and
Devices*, Mat. Res. Soc. Sym. Proc. **283**, 191 (1993).

F. NONE

G. NONE

H. **Invited Presentations**

1. Title: "Adsorption and Decomposition of Alkylsilanes and
Alkylgermanes on Silicon Surfaces"

Audience: *75th Canadian Chemical Conference*

Location: Edmonton, Alberta

Date: June 1, 1992.

2. Title: "Silicon Surface Chemistry: Controlled Growth to
Photoluminescence"

Audience: Dept. of Electrical Engineering, Univ. of Rochester

Location: Rochester, NY

Date: Aug. 12, 1992.

3. Title: "Surface Chemistry of Silicon Epitaxial Growth with
Chlorosilanes and Alkylsilanes"

Audience: *Symposium on Advances in High-Temperature Interface
Chemistry*, Electrochemical Chemical Society Meeting

Location: Toronto, Ontario

- Date: Oct. 12, 1992.
4. Title: "Adsorption and Decomposition of Alkylsilanes and Alkylgermanes on Silicon Surfaces"
- Audience: Dept. of Chemistry, Univ. of Missouri-Columbia
- Location: Columbia, MO
- Date: Oct. 16, 1992.
5. Title: "Silicon Surface Chemistry: Controlled Growth to Photoluminescence"
- Audience: National Renewable Energy Laboratory
- Location: Golden, CO
- Date: Nov. 5, 1992.
6. Title: "Chemistry and Kinetics of Si and SiO₂ Deposition on Silicon Surfaces"
- Audience: Surface Science and Catalysis Seminar, Lawrence Berkeley Laboratory, Univ. of California
- Location: Berkeley, CA
- Date: March 4, 1993.
7. Title: "Controlled Growth of SiO₂ By Atomic Layer Processing"
- Audience: *Symposium on Molecular Processes on Solid Surfaces*, American Chemical Society Meeting,
- Location: Denver, CO
- Date: March 31, 1993.
8. Title: "Surface Chemistry for Controlled Growth of SiO₂ on Silicon Surfaces"

Audience: Materials Technology Department, Intel Corporation

Location: Santa Clara, CA

Date: April 13, 1993.

9. Title: "Surface Chemistry for Controlled Growth of SiO₂ on Silicon Surfaces"

Audience: Sandia National Laboratories

Location: Albuquerque, NM

Date: May 20, 1993.

I. Submitted Presentations

1. Authors: M.B. Robinson, A.C. Dillon and S.M. George

Title: "Porous Silicon Photoluminescence versus HF Etching: No Correlation with Surface Hydrogen Species"

Conference: *Symposium on Microcrystalline Semiconductors: Materials Science and Devices*, Materials Research Society Meeting

Location: Boston, MA

Date: Dec. 2, 1992

2. Authors: A.C. Dillon, M.B. Robinson and S.M. George

Title: "Transmission FTIR Studies of Trichlorogermane and Trichlorosilane Decomposition on Silicon Surfaces"

Conference: *Symposium on Chemical Prospectives of Microelectronic Materials III*, Materials Research Society Meeting

Location: Boston, MA

Date: Dec. 2, 1992

3. Authors: P.A. Coon, M.L. Wise, A.C. Dillon and S.M. George
Title: "Germanium Deposition on Silicon: Surface Chemistry of $(\text{CH}_3\text{CH}_2)_2\text{GeH}_2$ and GeCl_4 "
Conference: *Symposium on Chemical Prospectives of Microelectronic Materials III*, Materials Research Society Meeting
Location: Boston, MA
Date: Dec. 2, 1992
4. Authors: M.L. Wise, L.A. Okada, P.A. Coon and S.M. George
Title: "Growth of SiO_2 on $\text{Si}(111)7\times 7$ Using SiCl_4 and H_2O "
Conference: *Symposium on Chemical Prospectives of Microelectronic Materials III*, Materials Research Society Meeting
Location: Boston, MA
Date: Dec. 2, 1992
5. Authors: M.B. Robinson, A.C. Dillon and S.M. George
Title: "Porous Silicon Photoluminescence versus HF Etching: No Correlation with Surface Hydrogen Species"
Conference: *Symposium on Molecular Processes on Solid Surfaces*, American Chemical Society Meeting
Location: Denver, CO
Date: March 31, 1993.
6. Authors: S.M. George, M.B. Robinson and A.C. Dillon
Title: "Porous Silicon Photoluminescence versus HF Etching: No Correlation with Surface Hydrogen Species"
Conference: *Symposium on Silicon-Based Optoelectronic Materials*, Materials Research Society Meeting

Location: San Francisco, CA

Date: April 13, 1993.

7. Authors: A.C. Dillon, M.L. Wise, M.B. Robinson and S.M. George

Title: "FTIR Studies of Trichlorogermane and Trichlorosilane
Decomposition on Silicon Surfaces"

Conference: *Symposium on Molecular Processes on Solid Surfaces*
American Chemistry Society Meeting

Location: Denver, CO

Date: March 31, 1993

J. Honors/Awards/Prizes

1. Presidential Young Investigator Award, National Science Foundation, 1988-1993.
2. Associate Editor, *Chemical Reviews*, June 1992-present.
3. Member, National Materials Advisory Board Committee on *New Currency Design: Counterfeit Deterrent Features for the Next Generation*, June 1992-present.
4. Member, *Board of Assessment of NIST Programs*, National Research Council, Panel for Chemical Sciences and Technology, January 1993-present.

K. Graduate Students Receiving Full or at least 25% Support on this ONR Contract

Two Graduate Students: Mary Beth Robinson and Anne C. Dillon

L. Other Funding

1. Supporting Agency: **Office of Naval Research**
Project Title: Picosecond Studies of Vibrational and Electronic Energy Relaxation on Surfaces Using the Free Electron Laser
Award Amount: \$315,095

Period Covered: 01/01/92-12/31/94

2. Supporting Agency: **National Science Foundation**
Project Title: Surface Diffusion on Single-Crystal Metal Surfaces
Award Amount: \$195,000
Period Covered: 08/01/92-07/31/95
3. Supporting Agency: **National Science Foundation**
Project Title: Presidential Young Investigator Award
Award Amount: \$62,500
Period Covered: 07/01/92-06/30/93

PART II

A. Principal Investigator

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B. Current Telephone Number

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GEORGES@Spot.Colorado.Edu Electronic Mail

C. Cognizant ONR Scientific Officer

Dr. John C. Pazik

D. Brief Description of Project

Surface kinetics play a crucial role in semiconductor processing chemistry. Our research concentrates on a fundamental understanding of the microscopic surface kinetics that dictate surface chemistry. We are exploring the various adsorption, decomposition, diffusion and desorption steps in reactions on single-crystal silicon surfaces. These basic time-dependent surface processes are examined using laser induced thermal desorption (LITD) and Fourier transform infrared (FTIR) techniques. These techniques provide direct, quantitative measurements of surface coverage in real-time.

Atomic layer processing is a vital need for semiconductor fabrication. As the size of electronic devices approaches the nanometer scale, the need to control growth on an atomic scale is extremely important. For the construction of next generation devices, controlled atomic layer-by-layer processing during oxidation, growth, etching and metallization is critical. Our studies are aimed at surface reactions where surface kinetics can be employed for atomic layer control. We are both characterizing the surface kinetics of known reactions and exploring new synthetic pathways for the atomic layer control of semiconductor processing.

E. Significant Results During the Last Year

Last year was a successful and productive year for our ONR-sponsored research. We first finished studies of Ge and Si deposition on silicon surfaces using GeHCl_3 (trichlorogermane) and SiHCl_3 (trichlorosilane). In studies of diethylgermane decomposition on silicon surfaces, we also established the generality of the β -hydride elimination mechanism for the decomposition of alkylgermanes on silicon surfaces. We then focused on the atomic layer controlled deposition of SiO_2 on silicon surfaces. This research examined sequential ABAB... binary surface reactions that supply silicon and oxygen in alternate cycles. A possible binary reaction that deposits SiO_2 is: $\text{SiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{HCl}$. On the surface, this sequential reaction can be designated as: (A) $\text{Si-Cl} + \text{H}_2\text{O} \rightarrow \text{Si-OH} + \text{HCl}$; and (B) $\text{Si-OH} + \text{SiCl}_4 \rightarrow \text{Si-O-SiCl}_3 + \text{HCl}$. We examined reaction (A) for SiO_2 growth on $\text{Si}(111)7\times7$ and porous silicon and determined the surface reaction kinetics. We also began new studies of diethyldiethoxysilane (DEDEOS) as a novel molecular precursor for SiO_2 deposition. Our initial results for SiO_2 deposition using repetitive DEDEOS adsorption cycles on $\text{Si}(100)2\times1$ and porous silicon have been very promising.

F. Summary of Plans for Next Year

Next year's research will continue to explore topics in atomic layer processing. We will continue to explore surface chemistries that could lead to atomic layer growth of SiO_2 on silicon surfaces. The binary reaction $\text{SiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{HCl}$ will be examined at higher pressures utilizing a new high pressure dosing chamber that has been built inside our ultrahigh vacuum chamber. We will also finish our studies of diethyldiethoxysilane and examine dichlorodiethoxysilane as another alternative precursor for SiO_2 growth on silicon surfaces. In addition, measurements of the adsorption and desorption kinetics of disilane and dichlorosilane on $\text{Si}(100)2\times1$ will be performed in order to model completely silicon epitaxial growth on $\text{Si}(100)2\times1$. The disilane studies on $\text{Si}(100)2\times1$ will also compare the H_2 desorption kinetics after either disilane or atomic hydrogen exposures. These measurements will determine if the extra silicon adatoms deposited by disilane affect the subsequent H_2 desorption kinetics. We will also begin to explore other repetitive ABAB... reaction sequences for atomic layer control of metal oxide deposition on silicon surfaces. One reaction that we will examine for the deposition of high dielectric Al_2O_3 is: $2\text{Al}(\text{CH}_3)_3 + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{CH}_4$.

G. Graduate Students Currently Working on Project

1. Anne C. Dillon
2. Mary Beth Robinson
3. Michael L. Wise (AT&T Bell Laboratories Fellowship)
4. Lynne A. Okada (new first year graduate student)

PART III

A. Introduction - Atomic Layer Control of SiO₂ CVD

Atomic layer control of SiO₂ CVD is required to fabricate ultrathin gate oxides in MOSFET devices. One approach to achieve atomic layer control is to utilize self-limiting surface reactions that deposit silicon and oxygen individually in a repetitive ABAB... reaction sequence. An example of a binary reaction that can be used in a repetitive ABAB... reaction sequence is $\text{SiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{HCl}$.

B. Half-Reaction (A) in the Repetitive ABAB... Reaction Sequence

Laser induced thermal desorption (LITD) measurements have been used to monitor the reaction: $\text{Si-Cl} + \text{H}_2\text{O} \rightarrow \text{Si-OH} + \text{HCl}$ on Si(111)7x7. This reaction occurs readily at temperatures above 700 K and HCl is observed as the rate-limiting desorption product. Auger electron spectroscopy also observes the build up of oxygen on the surface during the reaction.

C. Diethyldiethoxysilane as a Single Molecular Precursor for SiO₂ CVD

Atomic layer controlled growth of SiO₂ can also be obtained using single molecular precursors such as diethyldiethoxysilane (DEDEOS). Only ethylene and H₂ are observed as reaction products in temperature programmed desorption studies following DEDEOS exposure on Si(100)2x1.

D. Repetitive Adsorption Cycling to Obtain SiO₂ Growth on Si(100)2x1

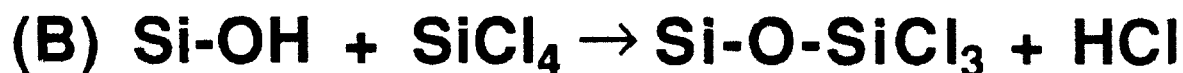
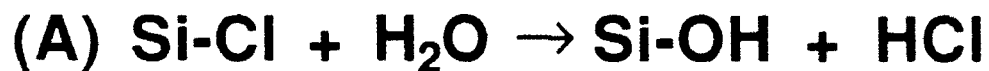
Ultrathin SiO₂ films can be deposited on Si(100)2x1 using repetitive cycling of DEDEOS adsorption and thermal annealing. The ethylene LITD signal at mass 27 measures the amount of DEDEOS that can be readsorbed after each adsorption/thermal anneal cycle. DEDEOS can be continually readsorbed to the growing SiO₂ layer on Si(100)2x1.

E. Short Conclusion

Our work has demonstrated that atomic layer control of SiO₂ deposition on silicon surfaces can be achieved using repetitive ABAB... reaction sequences using the binary reaction $\text{SiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{HCl}$. Atomic layer control of SiO₂ deposition can also be achieved using single molecular precursors such as diethyldiethoxysilane (DEDEOS). Both approaches should be useful in depositing ultrathin SiO₂ layers for gate oxides in MOSFET devices.

Atomic Layer Control of SiO₂ Chemical Vapor Deposition

ABAB... Binary Reaction Scheme

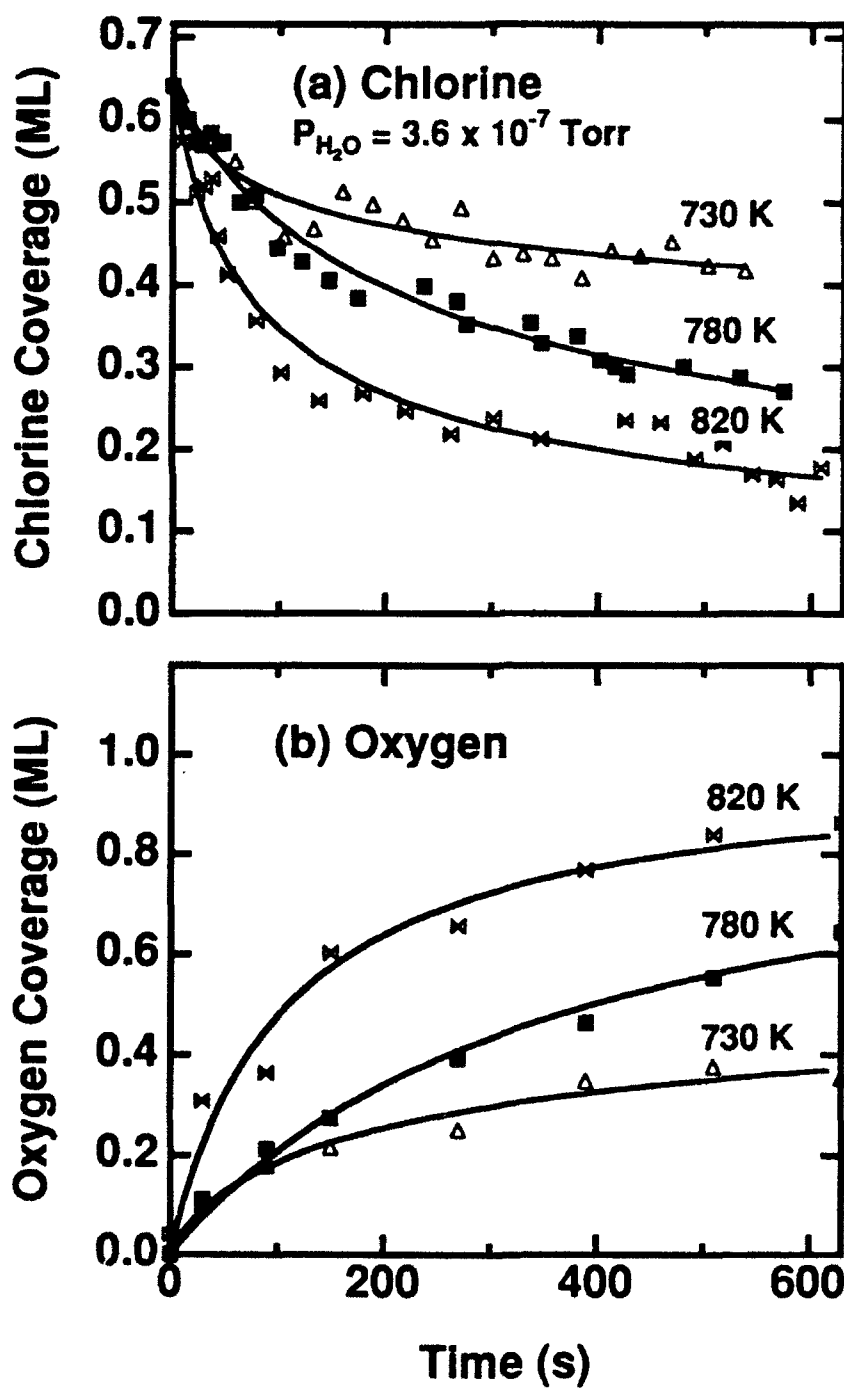


Repeat...

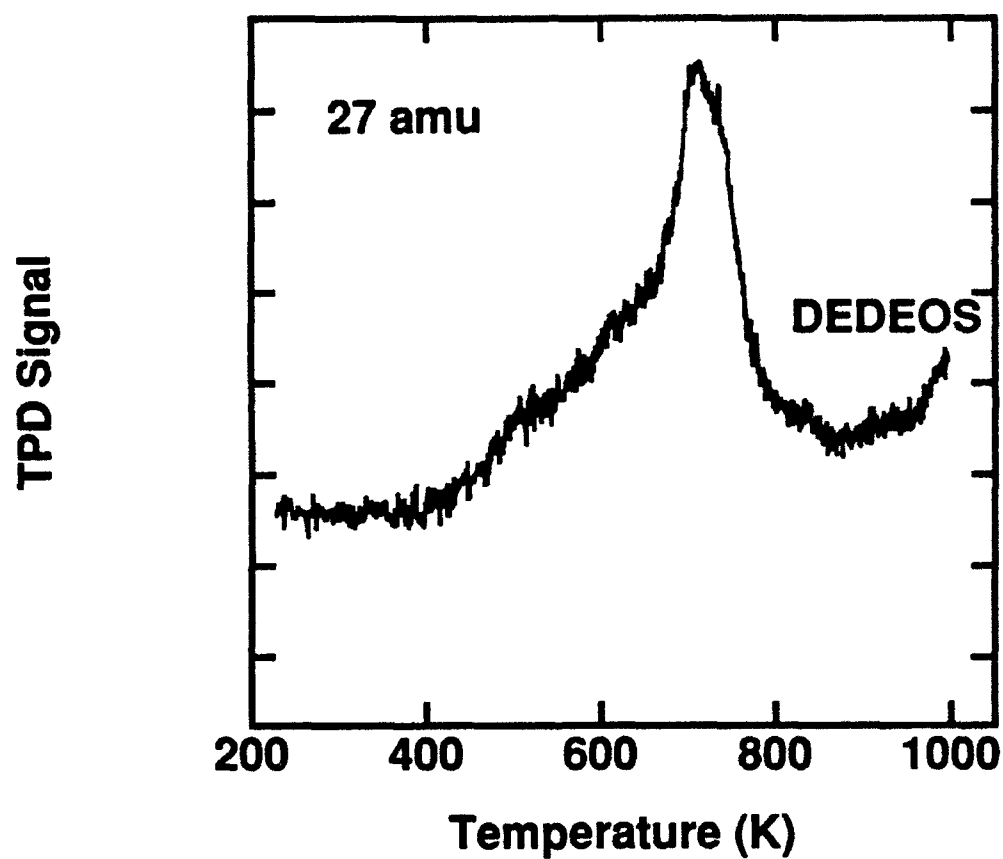
- Reaction (A) and (B) are self-limiting**
- Expect excellent conformality**



SiCl₂ LITD Measurements



Ethylene Desorption
DEDEOS / Si(100)2x1 / $\beta = 3.8$ K/s



DEDEOS Adsorption on Growing SiO₂ Layer on Si(100)2x1

