OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT NUMBER: N00014-92-J-1353

PR NUMBER: 3134011

ATOMIC LAYER CONTROL OF THIN FILM GROWTH USING BINARY REACTION SEQUENCE CHEMISTRY

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June 1997

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

PR Number: 3134011
Contract/Grant Number: N00014-92-J-1353
Contract/Grant Title: "Atomic Layer Control of Thin Film Growth Using Binary Reaction Sequence Chemistry"

Principal Investigator: Prof. 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: 8
c. + Number of books or chapters submitted, but not yet published: 0
d. + Number of books or chapters published: 0
e. + Number of printed technical reports/non-refereed papers : 0
f. Number of patents filed: 2
g. + Number of patents granted: 1
h. + Number of invited presentations: 10
i. + Number of submitted presentations : 6
j. + Honors/Awards/Prizes for contract/grant employees: 3

k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number: 2.0
Graduate Students: 1.50
Post-Doctoral Associates: 0.50
including the number of,
Female Graduate Students: 0
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 (Japanese American)
Asian Post-Doctoral Associates: 0

l. + Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

DTIC QUALITY INSPECTED 3

PART I

A. Papers Submitted to Refereed Journals, but not yet Published

1. Authors: J.W. Klaus, O. Sneh, S.M. George

   Title: "Atomic Later Controlled SiO_2 Growth at Room Temperature using Catalyzed Binary Reaction Sequence Chemistry"

   Journal submitted to *Science*

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

   Title: "Effect of Hydrogen on Silicon Oxidation and Increased Thermal Stability of O_xSiH Surface Species"

   Journal: submitted to *J. Vac. Sci. Technol. B.*

B. Papers Published in Refereed Journals

1. Authors: O. Sneh, M.A. Cameron and S.M. George

   Title: "Adsorption and Desorption Kinetics of H_2O on a Fully Hydroxylated SiO_2 Surface"

   Journal: *Surf. Sci.* **364**, 61 (1996).

2. Authors: M.L. Wise, O. Sneh, L.A. Okada and S.M. George

   Title: "Reaction Kinetics of H_2O with Chlorinated Si(111)7x7 and Porous Silicon Surfaces"

   Journal: *Surf. Sci.* **364**, 367 (1996).

3. Authors: A.W. Ott, K.C. McCarley, J.W. Klaus, J.D. Way and S.M. George

   Title: "Atomic Layer Controlled Deposition of Al_2O_3 Films Using Binary Reaction Sequence Chemistry"

   Journal: *Appl. Surf. Sci.* **107**, 128 (1996).

4. Authors: S.M. George, A.W. Ott and J.W. Klaus

   Title: "Surface Chemistry for Atomic Layer Growth"

   Journal: Special Centennial Issue of *J. Phys. Chem.* **100**, 13121 (1996).

5. Authors: A.W. Ott, J.W. Klaus, J.M. Johnson and S.M. George

   Title "Al_2O_3 Thin Film Growth on Si(100) Using Binary Reaction Sequence Chemistry"

   Journal: *Thin Solid Films* **292**, 135 (1997).

6. Authors: A.W. Ott, J.W. Klaus, J.M. Johnson, S.M. George, K.C. McCarley and J.D. Way

   Title: "Modification of Porous Alumina Membranes Using Al_2O_3 Atomic Layer Controlled Deposition"

   Journal *Chemistry of Materials* **9**, 707 (1997).

7. Authors: A.W. Ott, J.M. Johnson, J.W. Klaus and S.M. George

   Title: "Surface Chemistry of In_2O_3 Deposition Using $In(CH_3)_3$ and H_2O in a Binary Reaction Sequence"

   Journal: *Applied Surface Science.* **112**, 205 (1997).

8. Authors: J.W. Klaus, A.W. Ott, J.M. Johnson and S.M. George

   Title: "Atomic Layer Controlled Growth of SiO_2 Films Using Binary Reaction Sequence Chemistry"

   Journal: *Appl. Phys. Lett.* **70**, 1092 (1997).

C. NONE

D. NONE

E. NONE

F. Patents Filed

1. Inventors: J.L. Falconer, S.M. George, A.W. Ott, J.W. Klaus, R.D. Noble and H.H. Funke

   Status: U.S. Patent Pending

   Title: "Modification of Zeolite or Molecular Sieve Membranes Using Atomic Layer Controlled Chemical Vapor Deposition"

   Application: Gas Separations In Zeolite Membranes by Molecular Sieving

2. Inventors: J.W. Klaus, O.Sneh and S.M. George

Status: U.S. and International Patents Pending

Title: "Method of Growing Films at Room Temperature Using Catalyzed Binary Reaction Sequence Chemistry"

Application: Low Deposition of SiO_2 Insulating and Protective Films at Room Temperature

G. Patents Granted

1. Inventors: J.D. Way and S.M. George

Status: U.S. Patent Granted

Title: "Fabrication of Molecular Sieving Alumina Membranes Using Atomic Layer Controlled Chemical Vapor Deposition" (U.S. Patent App. Ser. No. 08/442,907)

Application: Gas Separations in Ceramic Membranes by Molecular Sieving Mechanism

H. Invited Presentations

1. Title: "Atomic Layer Control of Thin Film Growth Using Binary Reaction Sequence Chemistry"

Audience: Advanced Structures and Materials Group, Lockheed-Martin

Location: Denver, Colorado

Date: June 27, 1996.

2. Title: "Al_2O_3 and In_2O_3 Films Grown Using Atomic Layer Deposition Techniques: Effect of Surface Coverage"

Audience: International Meeting on *Atomic Layer Epitaxy and Related Surface Processes* (ALE-4)

Location: Johannes Kepler University, Linz, Austria

Date: July 30, 1996.

3. Title: "Atomic Layer Growth of Thin Films Using Binary Reaction Sequence Chemistry"

Audience: Dept. of Chemistry, Colorado State University

Location: Ft. Collins, Colorado

Date: September 18, 1996.

4. Title: "Atomic Layer Controlled Deposition Using Binary Reaction Sequence Chemistry"

   Audience: International Symposium on *Surface Nano-Control of Environmental Catalysts and Related Materials*, 6th Iketani Conference, Waseda University

   Location: Tokyo, Japan

   Date: November 27, 1996.

5. Title: "Atomic Layer Controlled Growth Using Binary Reaction Sequence Chemistry"

   Audience: Dept. of Chemistry, University of Oregon

   Location: Portland, Oregon

   Date: December 2, 1996.

6. Title: "Atomic Layer Controlled Growth Using Binary Reaction Sequence Chemistry"

   Audience: Dept. of Chemistry, Oregon State University

   Location: Corvalis, Oregon

   Date: December 3, 1996.

7. Title: "Atomic Layer Controlled Growth Using Binary Reaction Sequence Chemistry"

   Audience: Chemistry, Energy and Materials Division, SRI International

   Location: Menlo Park, California

   Date: January 28, 1997.

8. Title: "Modification of Ceramic Membranes Using Binary Reaction Sequence Chemistry",

   Audience: Chevron Research and Engineering Company

   Location: Richmond, California

   Date: January 29, 1997.

9. Title: "Atomic Layer Growth Using Binary Reaction Sequence Chemistry"

   Audience: Symposium Honoring the Memory of Brian Bent, National American Chemical Society

   Location: San Francisco, California

   Date: April 13, 1997.

10. Title: "Atomic Layer Controlled Growth of Ultrathin Silicon Nitride Diffusion Barriers in Thin Film Devices"

   Audience: Colorado Advanced Materials Institute Meeting

   Location: Denver, Colorado

   Date: May 8, 1997.

I. Submitted Presentations

A. Contributed Talks

1. Authors: A.W. Ott, J.W. Klaus, J.M Johnson and S.M. George

   Title: "Atomic Layer Controlled Al_2O_3 Films Grown on Si(100) Using Binary Reaction Sequence Chemistry"

   Conference: National Symposium of the American Vacuum Society

   Location: Philadelphia, Pennsylvania

   Date: October 14, 1996.

2. Authors: J.W. Klaus, A.W. Ott, J.M. Johnson and S.M. George

   Title: "Atomic Layer Controlled Growth of SiO_2 Using Binary Reaction Sequence Chemistry"

   Conference: Optical Society of America Topical Conference on *Chemistry and Physics of Small-Scale Structures*

   Location: Sante Fe, New Mexico

   Date: February 10, 1997.

3. Authors: J.W. Klaus, A.W. Ott, J.M. Johnson and S.M. George

Title: "Atomic Layer Controlled Growth of SiO_2 Films Using Self-Limiting Surface Chemistry"

Conference: Session on *Kinetics of Growth on Surfaces*, National American Chemical Society Meeting

Location: San Francisco, California

Date: April 14, 1997.

B. Contributed Posters

4. Authors: A.W. Ott, J.W. Klaus, J.W. Johnson and S.M. George

Title: "Atomic Layer Controlled Growth of Al_2O_3 Films Using Binary Reaction Sequence Chemistry"

Conference: Rocky Mountain Chapter American Vacuum Society Meeting

Location: Arvada, Colorado

Date: August 22, 1996.

5. Authors: J.W. Klaus, A.W. Ott and S.M. George

Title: "Atomic Layer Controlled Growth of SiO_2 Films Using Binary Reaction Sequence Chemistry"

Conference: Rocky Mountain Chapter American Vacuum Society Meeting

Location: Arvada, Colorado

Date: August 22, 1996. (WON THIRD PRIZE FOR BEST STUDENT POSTER/ $200)

6. Authors: L.A. Okada and S.M. George

Title: "Atomic Layer Controlled Growth of TiN Films Using Binary Reaction Sequence Chemistry"

Conference: Rocky Mountain Chapter American Vacuum Society Meeting

Location: Arvada, Colorado

Date: August 22, 1996.

J. Honors/Awards/Prizes

1. Co-Chair, Gordon Research Conference on *Electronic Materials: Chemistry, Excitations and Processing*, July 6-11, 1997 in New Hampshire.

2. Member, *Executive Committee of Electronic Materials and Processing Division*, American Vacuum Society, January 1996-December 1997.

3. Member, Board of Assessment of NIST Programs, *Panel for Chemical Science and Technology*, National Research Council, January 1993-December 1998.

K. Graduate Students and Postdoctoral Associates Receiving Supported by this ONR Grant

Two Graduate Students: Jason W. Klaus, Andrew W. Ott

One Postdoctoral Associate: Brian Berland

L. Other Funding

1. Supporting Agency: **National Science Foundation**
   Project Title: Surface and Bulk Diffusion on Single-Crystal Ice and Ice Hydrate Multilayers
   Award Amount: $305,000
   Period Covered: 03/01/96-02/28/99
   Relationship to ONR Grant: No connection other than use of vacuum technology and laser induced thermal desorption (LITD) techniques to study surface processes.

2. Supporting Agency: **Air Force Office of Scientific Research**
   Project Title: Heterogeneous Reactions on Aluminum Oxide Surfaces Modeling Rocket Exhaust Particles
   Award Amount: $110,536
   Period Covered: 01/15/97-01/14/98
   Relationship to ONR Grant: No connection other than use of vacuum technology and laser induced thermal desorption (LITD) techniques to study surface processes.

3. Supporting Agency: **Chevron Research and Technology Company**
Project Title: Fabrication of Selective Alumina Membranes Via Atomic Layer Controlled Chemical Vapor Deposition"
Award Amount: $49,000
Period Covered: 12/01/96-11/31/97
Relationship to ONR Grant: Chevron is very interested in atomic layer control of Al_2O_3 deposition and is supporting one graduate student. This support was leveraged by our ONR grant and is complementing the ONR research.

4. Supporting Agency: **Industrial and NSF-Sponsored Center for Thin Films (Univ. of Colo.)**
Project Title: Inorganic Membranes for Use in High Temperature Membrane Reactors
Award Amount: $35,000
Period Covered: 01/01/97-12/31/97
Relationship to ONR Grant: This project is exploring the deposition of ZrO_2 on alumina surfaces for use in high temperature membrane reactors. Some of the proposed chemistry is based on atomic layer controlled growth. This support was leveraged by our ONR grant and is complementing the ONR research.

PART II

A. Principal Investigator: **Prof. Steven M. George**
Dept. of Chemistry & Biochemistry
Univ. of Colorado
Boulder, CO 80309 - 0215

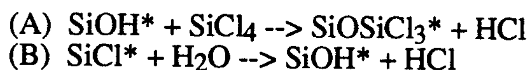
B. Current Telephone Number: **303-492-3398 (Voice)**
303-492-5894 (FAX)

C. Cognizant ONR Scientific Officer: **Dr. John C. Pazik**
Physical S&T Division, ONR 331

D. Program Objective:

Our research is focusing on the atomic layer control of thin film growth. Our goal is to deposit films with precise control of thickness and conformality on both flat and high aspect ratio structures. Atomic layer control of growth is crucial for many technologies that require nanoscale deposition techniques to fabricate ultrathin and conformal films with thicknesses from 10-100 Å. Examples of these films are ultrathin gate oxides, high dielectric constant films, conformal transparent conducting layers and ultrathin diffusion barriers.

Our atomic layer controlled growth approach is based on binary reaction sequence chemistry. This new technique is based on the separation of a binary reaction, such as $SiCl_4$ + $2H_2O$ --> SiO_2 + 4HCl, into two half-reactions:



(A) $SiOH^* + SiCl_4$ --> $SiOSiCl_3^* + HCl$
(B) $SiCl^* + H_2O$ --> $SiOH^* + HCl$

where the asterisk indicates the surface species. If each of the half-reactions is self-limiting and self-terminating, then the repetitive application of these reactions in a ABAB... sequence can produce atomic layer controlled SiO_2 deposition. We have demonstrated SiO_2 film growth of 1.1Å/ AB cycle using the above half-reactions. This approach is generic and can be applied to many binary oxide and nitride materials.

We are employing a variety of techniques to study the surface chemistry of atomic layer controlled growth and the ultrathin films deposited using this binary reaction sequence chemistry approach. The films are grown in an automated deposition chamber for binary reaction sequence chemistry. The thickness and structure of the ultrathin films are examined using *in situ* spectroscopic ellipsometry and *ex situ* atomic force microscopy. The surface chemistry and reaction kinetics are also investigated using laser induced thermal desorption (LITD) mass spectrometric methods and Fourier transform infrared (FTIR) vibrational spectroscopic techniques performed in two additional vacuum chambers.

E. Significant Results during Last Year

SiO_2 is the premier dielectric material in silicon microelectronic devices. During the last year, we concentrated on the atomic layer growth of SiO_2 films using ABAB... binary reaction sequence chemistry. We first determined that SiO_2 could be deposited with atomic layer control at temperatures between 600-800 K by separating the binary reaction $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$ into two half-reactions. High reactant exposures of 1-10 Torr for 5-10 minutes were required for the surface chemistry to reach completion. The maximum SiO_2 deposition per AB cycle was 1.1 Å/ AB cycle at 600 K. The surface topography measured using atomic force microscopy was extremely flat with a roughness nearly identical to the initial substrate. The decreasing growth rate at T>600 K correlated with the thermal stability of the SiOH* surface species. This correlation provided additional evidence for direct substitution reactions during the binary reaction sequence chemistry.

The only drawback of the SiO_2 atomic layer controlled growth was the high temperatures >600 K and the large reactant exposures $>10^9$ L (1L = 10^{-6} Torr s) required for the surface reactions to reach completion. To reduce the high temperatures and large exposures, we attempted to catalyze the surface reactions using pyridine. Pyridine is a Lewis base that interacts with the surface functional groups and reactants during both the $SiCl_4$ and H_2O half-reactions of the binary reaction sequence. We discovered that the pyridine catalyst lowered the required SiO_2 deposition temperatures from >600 K to 300 K and lowered the reactant flux required for complete reactions from $\sim10^9$ L to $\sim10^4$ L. This catalyzed SiO_2 growth may be very important because this new deposition procedure will enable SiO_2 to be deposited on a variety of substrates at room temperature. In addition, this catalytic technique may be general and should facilitate the chemical vapor deposition of other oxide and nitride materials.

As the miniaturization of silicon microelectronic devices continues, higher dielectric constant insulators will be needed to replace SiO_2. Likewise, ultrathin diffusion barriers will be necessary to prevent intralayer diffusion. Si_3N_4 is an effective diffusion barrier material and has a higher dielectric constant than SiO_2. We have demonstrated the atomic layer controlled growth of Si_3N_4 using the binary reaction $3SiCl_4 + 4NH_3 \rightarrow Si_3N_4 + HCl$. When this binary reaction is split into $SiCl_4$ and NH_3 half-reactions, Si_3N_4 growth rates of 1.4 Å/AB reaction cycle are observed at 700 K and reactant exposures of $\sim10^9$ L. The Si_3N_4 films are also extremely flat and conformal to the underlying Si(100) substrate.

F. Brief Summary of Plans for Next Year

Next year we will initiate new research on the fabrication of multilayer nanolaminate structures. Nanolaminates are composite thin film structures that are tailored to obtain special properties and functionalities that are not achieved by the individual components of the composite. Multilayer nanolaminates are superlattice architectures where the individual layer thicknesses and composition can be tuned to produce novel desired characteristics. We will begin by using our earlier work on Al_2O_3 and SiO_2 atomic layer growth as building blocks to fabricate various multifunctional structures based on multilayer stacks of SiO_2/Al_2O_3. The self-limiting surface chemistry underlying atomic layer growth should be viewed as a synthetic tool to grow new nanolaminated materials. Our *in situ* spectroscopic ellipsometer will be particularly useful to analyze the multilayer stacked structures.

One of our main applications of binary reaction sequence chemistry is the modification of porous materials. We will continue our collaborative effort with Chevron to deposit Al_2O_3 onto the surface of porous alumina membranes and zeolite membranes used for chemical separations. We recently built a new viscous flow deposition reactor that allows us to characterize the pore size

reduction *in situ* in real time during binary reaction sequence chemistry. This new reactor is now operational and has successfully reduced pore diameters in tubular alumina membranes from ~50 Å to <10 Å. We will continue this work and attempt to reduce the pores to even smaller diameters where we should observe molecular sieving and extremely high gas selectivities.

G. Graduate Students and Postdoctorals Currently Working on Project

Graduate Students:	Jason Klaus Andy Ott
Postdoctoral Associate:	Brian Berland

PART III

Viewgraphs to Defend and Support Current and Future Research in the Field

Figure 1. Introductory 5-Part Viewgraph

Atomic layer control of thin film growth is critical for nanoscale fabrication. The small visual aid in this viewgraph illustrates atomic layer control using binary reaction sequence chemistry. The first precursor (A) reacts with the surface functional groups to deposit the first element and change the surface functionality. The second precursor (B) reacts with the new surface functionality to deposit the second element and revert the surface functionality back to the original functionality. Consequently, the surface is back at the beginning and ready for reaction with the first precursor (A) to repeat this AB reaction cycle.

For SiO_2 deposition, the (A) and (B) reactions are based on the binary reaction: $SiCl_4 + 2H_2O \dashrightarrow SiO_2 + 4HCl$. The binary reaction sequence splits the binary reaction into two half-reactions where $SiCl_4$ and H_2O are exposed to the surface separately. $SiCl_4$ converts the hydroxylated surface to a chlorinated surface and deposits silicon. H_2O converts the chlorinated surface to a hydroxylated surface and deposits oxygen. SiO_2 thin films can be deposited with atomic layer control by sequential ABAB... exposures. This binary reaction sequence approach can yield conformal deposition on very high aspect ratio structures.

The other parts of the viewgraph highlight the technology issues, objectives, approach, accomplishments and transitions.

Figure 2. Cartoon Illustrating SiO_2 Deposition at Room Temperature Using Catalyzed Binary Reaction Sequence Chemistry

The maximum SiO_2 deposition rate was 1.1 Å /AB reaction cycle at 600 K. This deposition rate required reactant exposures of $\sim 10^9$ L for both $SiCl_4$ and H_2O. To reduce the reaction temperature and reactant exposure, we attempted to catalyze the binary reaction sequence chemistry using pyridine as a catalyst. Pyridine is a strong Lewis base and interacts strongly with the $SiOH^*$ groups and the adsorbed H_2O on the surface. These interactions may make the oxygen a stronger nucleophile and facilitate the surface reactions. The effects of pyridine were astonishing. Pyridine lowered the required reaction temperature from >600K to 300 K and reduced the required reactant exposure from $\sim 10^9$ L to $\sim 10^4$ L. The growth of SiO_2 at room temperature using catalyzed binary reaction sequence chemistry may have many applications, e.g. the deposition of insulating and protecting films on plastics, biologicals and other thermally sensitive materials. We have applied for U.S. and international patents for this new SiO_2 growth method.

Figure 3. Thickness of SiO_2 Thin Films Deposited at Room Temperature Using Catalyzed Binary Reaction Sequence Chemistry versus Number of AB Reaction Cycles

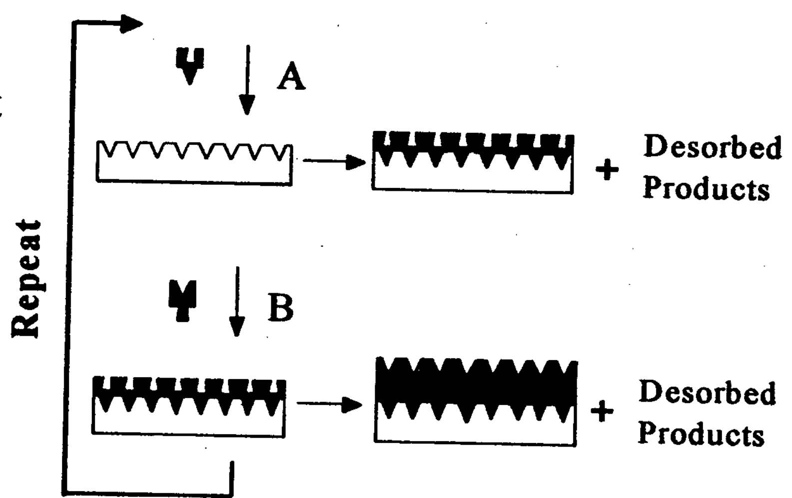
SiO_2 films were grown on Si(100) using catalyzed binary reaction sequence chemistry with $SiCl_4$ and H_2O reactants and the pyridine catalyst. The resulting SiO_2 film thickness was measured *in situ* by spectroscopic ellipsometry. The film growth was exceptionally linear versus number of AB reaction cycles and a SiO_2 growth rate of 2.15 Å/ AB reaction cycle was measured at 300 K. The measured index of refraction of n = 1.43 was consistent with an amorphous SiO_2 film. Atomic force micrographs of these SiO_2 films displayed exceptionally flat films with a surface roughness comparable to the initial Si(100) substrate.

Atomic Layer Control of Thin Film Growth Using Binary Reaction sequence Chemistry

George, University of Colorado

Technology Issues: · Fabricate Ultrathin Films with Atomic Layer Control · Conformal Deposition on Flat and High Aspect Ratio Structures · Electronic, Optical and Chemical Applications

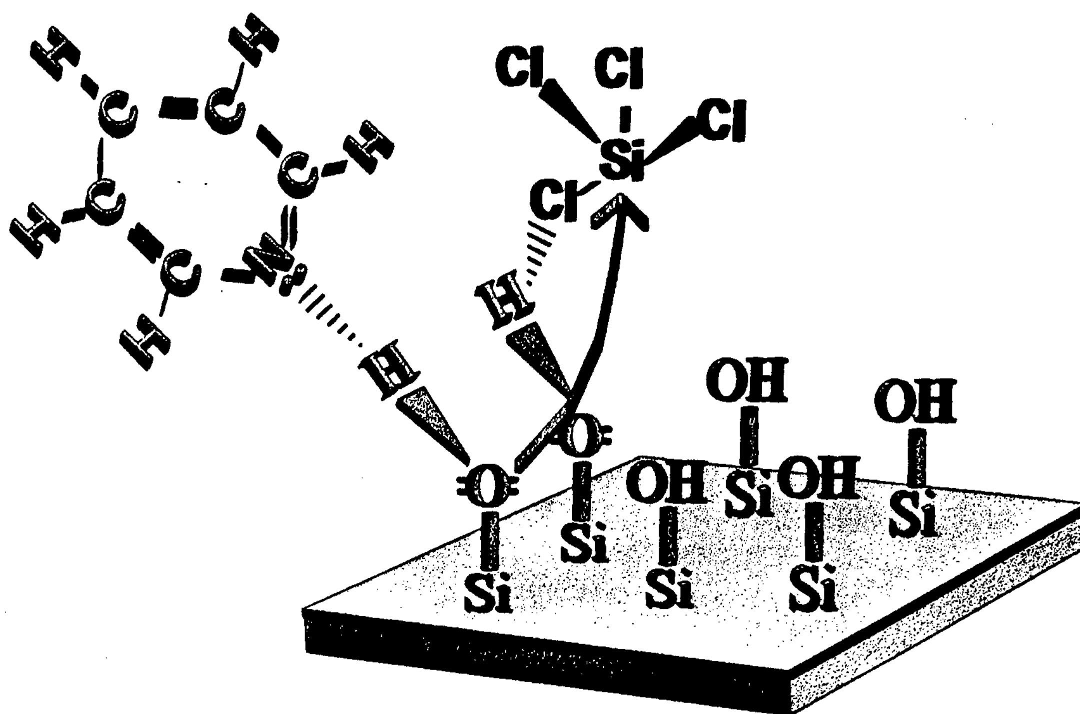
Objectives: · Develop the Surface Chemistry for Atomic Layer Growth (ALG) · Optimize Film Growth, Film Structure and Film Morphology · Employ ALG Techniques for Applications including Ultrathin Gate Oxides, High Density DRAM, Thin Film Devices and Diffusion Barriers



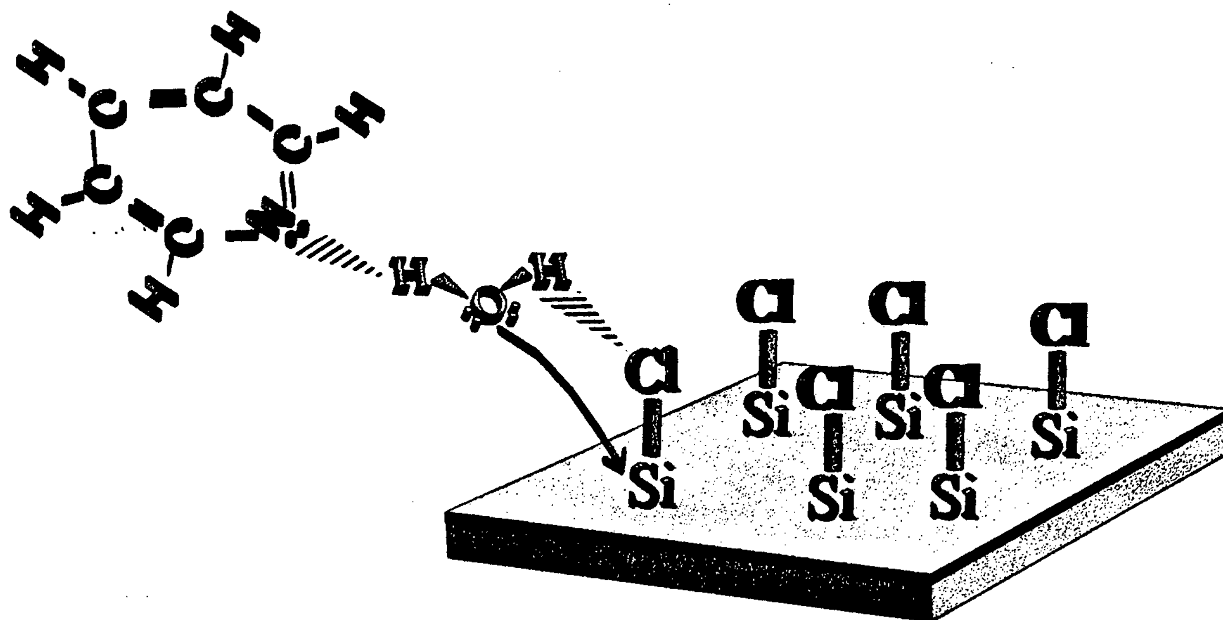
Approach:
- Binary Reaction Sequence Chemistry
- Surface Chemistry Studies Establish Reaction Conditions
- Film Growth in Automated Deposition Reactor
- Use *in situ* Methods to Monitor and Optimize Film Growth

Accomplishments:
- Deposition of SiO_2 at Room Temperature Using Catalyzed Binary Reaction Sequence Chemistry
- Determined Conditions and ALG rate for Si_3N_4 Deposition
- Deposition on Alumina and Zeolite Membranes for Gas Separations

Impact & Transition:
- Patent Application on Catalyzed SiO_2 Growth at Room Temperature
- Contract from Chevron for ALG on Ceramic Membranes
- Patent Application on ALG on Zeolite Membranes
- Collaboration with NREL on Si_3N_4 Diffusion Barriers



A. Mechanism of activation of surface hydroxyl groups during the $SiCl_4$ half-reaction



B. Possible mechanism of activation of surface H_2O during the B half-reaction

Fig. 2

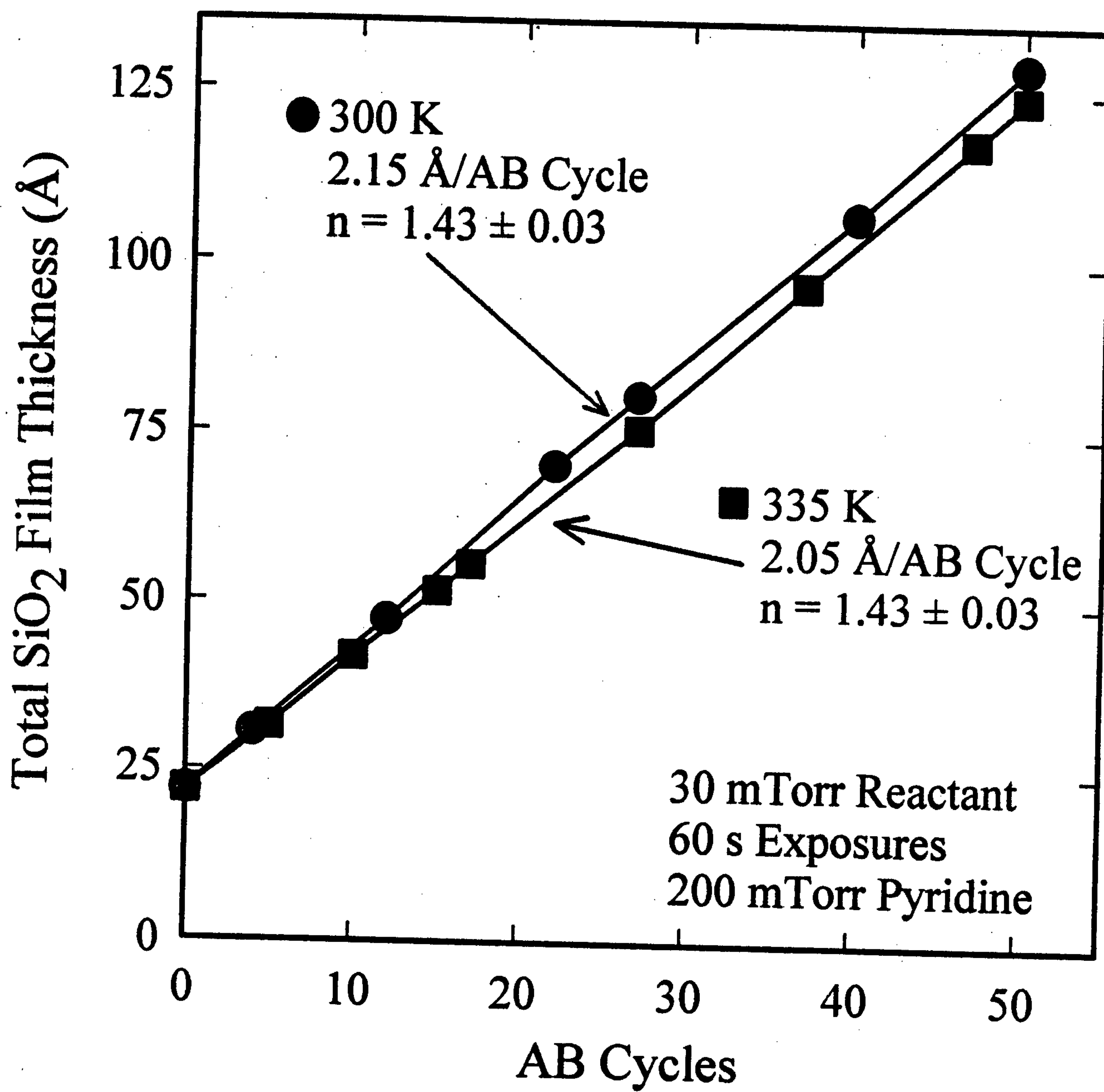


Fig. 3