OFFICE OF NAVAL RESEARCH

END-OF-YEAR-REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

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Kinetics of Semiconductor Processing Chemistry: SiGe and GaAs Growth on Silicon Surfaces

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Part I.

A. *Papers Submitted to Refereed Journal*

1. *Authors:* B.G. Koehler and S.M. George

Title: "Laser Induced Desorption of H_2 from Si(111)7x7

Journal: Submitted to Surface Science

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

Title: "FTIR Studies of H_2O and D_2O Decomposition on Porous Silicon Surfaces"

Journal: Submitted to Surface Science

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

Title: Ammonia Decomposition on Silicon Surfaces Studied Using Transmission FTIR Spectroscopy"

Journal: Submitted to J. Vacuum Science and Technology.

4. *Authors:* P. Gupta, A.C. Dillon, P.A. Coon and S.M. George

Title: "FTIR Studies Reveal that Silicon-Containing Laser-Induced Desorption Products are Surface Reaction Intermediates".

Journal: Submitted to Chemical Physics Letters

5. *Authors:* P. Gupta, P.A. Coon, B.G. Koehler and S.M. George

Title: "Desorption Product Yields After Cl_2 Adsorption on Si(111)7x7: Coverage and Temperature Dependence"

Journal: Submitted to Surface Science

B. *Papers Published in Refereed Journals*

1. *Authors:* C.H. Mak, B.G. Koehler and S.M. George

   Title: "Laser-Induced Thermal Desorption of Silicon-Containing Surface Reaction Intermediates from Si(111)7x7"

   Journal: Surf. Sci. Lett. 208, L42 (1989)

2. *Authors:* B.G. Koehler, C.H. Mak and S.M. George

   Title: "Decomposition of H_2O on Si(111)7x7 Studied Using Laser-Induced Thermal Desorption"

   Journal: Surf. Sci. 221, 565 (1989)

3. *Authors:* P. Gupta, C.H. Mak, P.A. Coon and S.M. George

   Title: "Oxidation Kinetics of Si(111)7x7 in the Submonolayer Regime"

   Journal: Phys. Rev. B 40, 7739 (1989)

4. *Authors:* B.G. Koehler, P.A. Coon and S.M. George

   Title: "Decomposition of NH_3 on Si(111)7x7 Studied Using Laser-Induced Thermal Desorption"

   Journal: J. Va.c. Sci. Technol. B7, 1303 (1989)

5. *Authors:* P. Gupta, P.A. Coon, B.G. Koehler and S.M. George

   Title: "Adsorption and Desorption Kinetics for $SiCl_4$ on Si(111)7x7"

   Journal: J. Chem. Phys. 93, 2827 (1990)

C. *None*

D. *None*

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

1, *Authors:* S.M. George, P. Gupta, C.H. Mak and P.A. Coon

Title: "Oxidation Kinetics of Silicon Surfaces: Reactive Sticking Coefficient, Apparent Saturation Coverage and Effect of Surface Hydrogen", in Chemical Perspectives of Microelectronic Materials.

Publisher: Material Research Symposium Proceedings 131, 169 (1989)

2. *Authors:* P. Gupta, P.A. Coon, B.G. Koehler and S.M George

Title: "Adsorption of Silicon Tetrachloride on Si:(111)7x7," in Chemical Perspectives of Microelectronic Materials.

Publisher: Material Research Symposium Proceedings 131, 197 (1989).

3. *Authors:* S.M. George, P. Gupta, B.G. Koehler, C.H. Mak and P.A. Coon

Title: "Laser Induced Thermal Desorption Studies of Reaction Kinetics on Si(111)7x7" in Proceedings of 1989 Internatl. Symp. on MicroProcess Conf.,

Publisher: Japanese J. of Appl. Physics Series 3, (1990) p. 267.

4. *Authors:* S.M. George, P. Gupta, B.G. Koehler, P.A. Coon, A.C. Dillon and C.H. Mak

Title: "Silicon Surface Kinetics Studied Using Laser Induced Thermal Desorption" in Laser Photoionization and Desorption Surface Analysis Techniques.

Publisher: SPIE, Bellingham, Washington, 1990.

5. *Authors:* S.M. George, P. Gupta, B.G. Koehler, P.A. Coon, A.C. Dillon and C.H. Mak

Title: "Optical Probes of Silicon Surface Chemistry" in Proceedings of Sixth International Symposium on Silicon Materials Science Technology

Publisher: J. Electrochem. Soc. 1990

F. *NONE*

G. *NONE*

H. *Invited Presentation at Topical or Scientific/Technical Society Conference*

1. *Author:* S.M. George

Title: "Laser Induced Thermal Desorption Studies of Reaction Kinetics on Si(111)7x7"

Conference: International MicroProcess Conference

Location: Kobe, Japan

Date: July 4, 1989

2. *Author:* S.M. George

Title: "Reaction Kinetics on Si(111)7x7 Surfaces Studied Using Laser-Induced Thermal Desorption"

Conference: Condensed Matter Seminar, Dept. of Physics, U.C. Berkeley

Location: Berkeley, Calif.

Date: September 20, 1989

3. *Author:* S.M. George

Title: "Surface Kinetics Studied Using Laser-Induced Thermal Desorption"

Conference: SPIE National Meeting

Location: Los Angeles, Calif.

Date: January 18, 1990

4. *Author:* S.M. George

Title: "Reaction Kinetics on Si(111)7x7 Studies Using Laser-Induced Thermal Desorption"

Conference: Gordon Research on The Chemsitry of Electronic Materials

Location: Ventura, Calif.

Date: March 1, 1990

5. *Author:* S.M. George

Title: "Optical Probes of Silicon Surface Chemistry"

Conference: Electrochemical Society

Location: Montreal, Quebec, Canada

Date: May 8, 1990

6. *Author:* S.M. George

Title: "Laser Induced Thermal Desorption Studies of Silicon Surface Kinetics"

Conference: International Quantum Electronics Conference

Location: Anaheim, Calif.

Date: May 24, 1990

7. *Author:* S.M. George

Title: "Laser Induced Thermal Desorption Studies of Silicon Surface Chemistry"

Conference: Chemistry Division, U.S. Naval Research Laboratory

Location: Washington, D.C.

Date: June 14, 1990

8. *Author:* S.M. George

   Title: "Laser Induced Thermal Desorption Studies of Silicon Surface Chemistry"

   Conference: Chemistry Division, National Institute of Standards and Technology

   Location: Gaithersburg, MD

   Date: June 15, 1990

I. *Contributed Presentations at Topical or Scientific/Technical Society Conferences*

1. *Authors:* S.M. George, B.G. Koehler, C.H. Mak, P. Gupta and P.A. Coon

   Conference: 5th Interdisciplinary Laser Science Conference

   Location: Stanford University, Stanford, Calif.

   Date: August 30, 1989

2. *Authors:* B.G. Koehler, P. Gupta, P.A. Coon and S.M. George

   Conference. 5th Interdisciplinary Laser Science Conference

   Location: Stanford Univeristy, Stanford, Calif.

   Date: August 30, 1989

3. *Authors:* B.G. Koehler, P.A. Coon, P. Gupta and S.M. George

   Conference: American Vacuum Society National Meeting

   Location: Boston, Mass.

   Date: October 24, 1989

4. *Authors:* B.G. Koehler and S.M. George

Conference: American Vacuum Society National Meeting

Location: Boston, Mass.

Date: October 26, 1989

5. *Authors:* S.M. George, P. Gupta, C.H. Mak and P.A. Coon

Conference: Am. Inst. Chem. Eng. 1989 Annual Meeting, Symposium on Kinetics and Mechanisms in Electronics Material Processing

Location: San Francisco, Calif.

Date: November 8, 1989

6. *Authors:* B.G. Koehler, P.A. Coon, P. Gupta and S.M. George

Conference: Am. Inst. Chem. Eng. 1989 Annual Meeting, Symposium on Kinetics and Mechanisms in Electronics Material Processing

Location: San Francisco, Calif.

Date: November 9, 1989

7. *Authors:* P. Gupta, P.A. Coon, B.G. Koehler and S.M. George

Conference: Am. Inst. Chem. Eng. 1989 Annual Meeting, Symposium on Kinetics and Mechanisms in Electronics Material Processing

Location: San Francisco, Calif.

Date: November 9, 1989

8. *Authors:* P. Gupta, C.H. Mak, P.A. Coon and S.M. George

Conference: American Vacuum Society

Location: Boston, Mass.

Date: October 26, 1989

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

Conference: Western Spectroscopy Assoc, 37th Annual Conf.

Location: Pacific Grove, Calif.

Date: January 24-26, 1990

10. *Authors:* P.A. Coon, P. Gupta, B.G. Koehler and S.M. George

Conference: Thirteenth Surface/Interface Research Meeting of the Northern Calif. Chap. of the Am. Vac. Soc.

Location: Menlo Park, Calif.

Date: June 19, 1990

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

Conference: Thirteenth Surface/Interface Research Meeting of the Northern Calif. Chap. of the Am. Vac. Soc.

Location: Menlo Park, Calif.

Date: June 19, 1990

J. <u>*Honors/Awards/Prizes*</u>

1. Presidential Young Investigator Award, National Science Foundation, 1988.

2. Alfred P. Sloan Foundation Fellow, Alfred P. Sloan Foundation, 1988-89.

3. IBM Faculty Development Award, 1988

K. *Number of Graduate Students Receiving Full or Partial Support on ONR Contract*

Total of two: P. Gupta and P.A. Coon

L. *NONE*

Part II

A. *Principal Investigator*

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B. *Cognizant ONR Scientific Officers*

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C. *Current Telephone Numbers*

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D. *Brief Description of Project*

Surface chemistry and surface diffusion play pivital roles in semiconductor processing and must be understood as electronc device dimenisions approach the submicron level. In this project, basic time-dependent processes on silicon surfaces are being examined using laser induced thermal desorption (LITD) and Fourier transform infrared (FTIR) spectroscopy. These techniques proved direct, quantitative measurements of surface coverage in real-time. Using LITD and FTIR techniques, emphasis is on a microscopic understanding of semiconductor surface reaction kinetics.

The major areas being addressed include the kinetics of fundamental semiconductor processing steps such as: surface oxidation and nitridation; epitaxial growth on surfaces; and surface etching. The Si(111)7x7, Si(100)2x1 and GaAs(100) crystal planes, as well as porous silicon, are being used as the model semiconductor surfaces. These studies are being conducted in UHV using Auger and LEED spectroscopy for surface analysis and characterization. The kinetic parameters that are determined by these LITD and FTIR studies are crucial for the understanding and modeling of semiconductor processing chemistry.

E. *Significant Results During the Last Year*

Our ONR-sponsored research has been very successful and productive over the last year. We began the year by finishing our laser induced thermal desorption (LITD) study of $SiCl_4$ adsorption and desorption on Si(111)7x7. Silicon tetrachloride is important in the epitaxial growth of silicon by the reaction: $SiCl_4 + 2H_2 \rightarrow Si(ad) + 4HCl$. The reactive sticking coefficient was measured and was observed to decrease with increasing temperature. This temperature dependence was consistent with a precursor-mediated adsorption model.

We also examined the desorption yield following $SiCl_4$ adsorption on Si(111)7x7. $SiCl_2$ was observed as the only desorption product. Using isothermal LITD experiments, the desorption kinetics of $SiCl_2$ were measured and were observed to follow a second-order rate law. The second-order kinetics were consistent with monochloride species on the Si(111)7x7 surface and the recombinatory desorption of $SiCl + Cl \rightarrow SiCl_2$.

Dichlorosilane, $SiCl_2H_2$, is another valuable chlorosilane for silicon epitaxial growth by the reaction: $SiCl_2H_2 \rightarrow Si(ad) + 2HCl$. We examined the adsorption and desorption kinetics of $SiCl_2H_2$ on Si(111)7x7 and compared these results with the earlier measurements for $SiCl_4$. Compared with $SiCl_4$, the reactive sticking coefficient for $SiCl_2H_2$ was slightly larger. In addition, the temperature dependence of the sticking coefficient suggested the presence of a precursor species.

The desorption products H_2, HCl and $SiCl_2$ were observed in the desorption yield at 800, 875 and 950 K, respectively, following $SiCl_2H_2$ adsorption on Si(111)7x7. The relative yields of H_2 and $SiCl_2$ were observed to be higher after larger $SiCl_2H_2$ exposures. Because H_2 desorption occurs at the lower temperature and is favored at higher coverages, these results indicate that $SiCl_2H_2$ alone will act to etch the Si(111)7x7 surface. All the adsorbed chlorine deposited by $SiCl_2H_2$ can be desorbed as HCl only if extra hydrogen is present on the silicon surface.

Our effort to study silicon surface chemistry using in situ transmission Fourier Transform Infrared (FTIR) spectroscopy on high-surface-area porous silicon came to fruition last year. Following the purchase of a new Nicolet 740 FTIR spectrometer and the redesign of our FTIR-UHV chamber, we studied the adsorption and decomposition of H_2O and NH_3 on porous silicon surfaces. The results of these model oxidation and nitridation reactions firmly established the dissociative adsorption of H_2O -> Si-OH + Si-H and NH_3 -> Si-NH_2 + Si-H. Subsequently, as a function of annealing temperature, the reaction intermediates were observed to decompose as Si-OH -> Si-O-Si + Si-H and Si-NH_2 -> Si_3N + 2H.

One of the most satisfying aspects of this new FTIR work was the excellent agreement between the FTIR results for H_2O and NH_3 decomposition on porous silicon and our earlier LITD measurements for H_2O and NH_3 decomposition on Si(111)7x7. This agreement confirmed our earlier assumption that the SiOH and SiNH2 LITD products observed from Si(111)7x7 represent surface reaction intermediates. As predicted by our earlier calculations, we can conclude that the SiOH and $SiNH_2$ surface reaction intermediates can be directly desorbed from Si(111)7x7 during rapid laser induced temperature transients.

During the last three months, we have started to explore the reaction of alkylsilanes with silicon surfaces. Alkylsilanes are possible replacements for the more toxic and flammable silanes and disilanes. The alkylsilanes may also be useful for the atomic layer epitaxy of silicon devices. Using LITD techniques, we have recently determined that diethylsilane adsorbs on Si(111)7x7 with a sticking coefficient that is slightly higher than disilane. In addition, temperature-programmed LITD experiments on Si(111)7x7 indicate that the ethyl groups undergo beta-hydride elimination at approximately 700 K.

We have also examined the decomposition of diethylsilane on porous silicon using FTIR spectroscopy. Thermal annealing studies confirm that the ethyl groups are lost at approximately 700 K. Simultaneously, the absorbance of the Si-H stretching vibration is observed to nearly double. The increase of the hydrogen coverage is consistent with the beta-hydride elimination reaction: $Si\text{-}CH_2\text{-}CH_3 \rightarrow Si\text{-}H + CH_2{=}CH_2$. These LITD and FTIR experiments are the first to observe beta-hydride elimination from a silicon atom adsorbed on a silicon surface.

F. *Summary of Plans for Next Year*

The research for next year will continue to pursue various epitaxial growth reactions on silicon surfaces. First, we hope to establish the generality of the beta-hydride elimination pathway for alkylsilanes on silicon surfaces. To accomplish this task, we will explore the decomposition of di-t-butylsilane, methyl-propyl-silane and butylsilane on Si(111)7x7 and porous silicon surfaces. These experiments will utilize both our LITD and FTIR techniques. The results of these studies should clarify the usefulness of alkylsilanes as a replacement for silanes in silicon epitaxial growth.

Following the alkylsilane studies, we will examine the adsorption and decomposition of $GeCl_4$ and diethylgermane on Si(111)7x7 and porous silicon surfaces using LITD and FTIR techniques. Both of these germanium compounds are candidates for the epitaxial growth of germanium or SiGe alloys. The surface kinetic parameters that will be determined from these germanium studies should help to determine the ideal conditions for germanium and SiGe alloy growth. In addition, we have performed similar studies of $SiCl_4$ and diethylsilane adsorption and decomposition on Si(111)7x7 and porous silicon surfaces. These previous results will provide an interesting comparison with the planned germanium studies.

Using our FTIR techniques, we also plan to examine the etching of silicon by fluorine. These experiments will utilize porous silicon and will employ XeF_2 as the fluorine source. Because our transmission FTIR experiments can measure infrared absorbance down to 400 cm^{-1}, we will identify and quantify the mono-, di- and trifluoride species on the silicon surface. By varying the fluorine coverage and the surface temperature, we also hope to establish the stability of the mono-, di- and trifluoride species. These infrared experiments should nicely complement the earlier XPS studies by McFeely and coworkers at IBM Yorktown Heights.

G. *Graduate Students Working on Project*

1. Peter A. Coon
2. Anne C. Dillon
3. Michael L. Wise (NSF)
4. MaryBeth Robinson (GE Graduate Fellowship)