

AD-A253 771



2

OFFICE OF NAVAL RESEARCH

Contract N00014-82-0280

Task No. NR413EOOI

TECHNICAL REPORT NO. 49

The Role of Backbond Strain in Silicon Surfaces on the Decomposition of NH_3 and PH_3

by

M.L. Colaianni, P.J. Chen and J.T. Yates, Jr.

Submitted To

Communication - J. Amer. Chem. Soc.

S DTIC
ELECTE
AUG 11 1992
A **D**

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

June 23, 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;
its distribution is unlimited

92 8 7 146

92-22540



REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM										
1. REPORT NUMBER 49	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER										
4. TITLE (and Subtitle) The Role of Backbond Strain in Silicon Surfaces on the Decomposition of NH ₃ and PH ₃		5. TYPE OF REPORT & PERIOD COVERED Preprint										
		6. PERFORMING ORG. REPORT NUMBER										
7. AUTHOR(s) M.L. Colaianni, P.J. Chen and J.T. Yates, Jr.		8. CONTRACT OR GRANT NUMBER(s)										
9. PERFORMING ORGANIZATION NAME AND ADDRESS Surface Science Center Department of Chemistry University of Pittsburgh Pittsburgh, PA 15206		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS										
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE June 23, 1992										
		13. NUMBER OF PAGES 9										
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified										
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE										
16. DISTRIBUTION STATEMENT (of this Report)												
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)												
18. SUPPLEMENTARY NOTES												
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)												
<table border="0"> <tr> <td>Silicon</td> <td>phosphorus</td> </tr> <tr> <td>reactivity</td> <td>doping</td> </tr> <tr> <td>ammonia</td> <td>si(111)</td> </tr> <tr> <td>phosphine</td> <td>backbond strain</td> </tr> <tr> <td>nitrogen</td> <td></td> </tr> </table>			Silicon	phosphorus	reactivity	doping	ammonia	si(111)	phosphine	backbond strain	nitrogen	
Silicon	phosphorus											
reactivity	doping											
ammonia	si(111)											
phosphine	backbond strain											
nitrogen												
<p>2-</p> <p>Silicon adatoms on the Si(111)-(7x7) surface form strained Si-Si backbonds with underlying silicon atoms. The strain at adatom sites causes both NH₂(a) and PH₂(a) to be thermally unstable compared to the same species on the Si(100)-(2x1) surfaces which contains less-strained silicon surface atoms. The surface strain induces enhanced NH₂(a) and PH₂(a) dissociation on Si(111)-(7x7) adatom sites compared to Si(100)-(2x1). Thus both NH₂(a) and PH₂(a) can participate in recombination reactions on Si(100) to produce major amounts of NH₃(g) and PH₃(g) above 600 K; such reactions are absent on Si(111)-(7x7) surfaces.</p>												

Submitted to: **Communication - J. Amer.
Chem. Soc.**

Date: **June 23, 1992**

**The Role of Backbond Strain in Silicon Surfaces
on the Decomposition of NH₃ and PH₃**

M.L. Colaianni, P.J. Chen and J.T. Yates, Jr.

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

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution /	
Availability Code	
Dist	Avail and/or Special
A-1	

DTIC QUALITY INSPECTED 5

**Present address: Department of Chemistry, Texas A&M University, College
Station, TX 77843**

**The Role of Backbond Strain in Silicon Surfaces
on the Decomposition of NH₃ and PH₃**

M.L. Colaianni, P.J. Chen and J.T. Yates, Jr.

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

Abstract

Silicon adatoms on the Si(111)-(7x7) surface form strained Si-Si backbonds with underlying silicon atoms. The strain at adatom sites causes both NH₂(a) and PH₂(a) to be thermally unstable compared to the same species on the Si(100)-(2x1) surfaces which contains less-strained silicon surface atoms. The surface strain induces enhanced NH₂(a) and PH₂(a) dissociation on Si(111)-(7x7) adatom sites compared to Si(100)-(2x1). Thus both NH₂(a) and PH₂(a) can participate in recombination reactions on Si(100) to produce major amounts of NH₃(g) and PH₃(g) above 600 K; such reactions are absent on Si(111)-(7x7) surfaces.

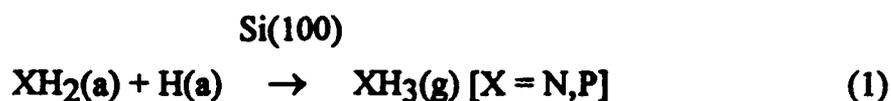
**The Role of Backbond Strain in Silicon Surfaces
on the Decomposition of NH₃ and PH₃**

M.L. Colaianni, P.J. Chen and J.T. Yates, Jr.

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

The behavior of chemisorbed species on silicon single crystals is expected to be influenced by the crystal structure of the surface. In this report, two group V hydrides, NH₃ and PH₃, have been compared on Si(100)-(2x1) and Si(111)-(7x7) surfaces, and we report an important common phenomenon governing the mechanism of thermal decomposition of these chemisorbed molecules. The Si-Si backbond strain effect on Si(111) is found to govern adsorbate decomposition. This concept may also apply to other semiconductor surfaces and could be significant in governing semiconductor doping and a wide variety of thin film formation processes.

On both Si(100) and Si(111) surfaces, NH₃ and PH₃ molecules adsorb dissociatively at ~ 100 K to produce NH₂(a) [1-6] and PH₂(a) [7-10] species. These species have been detected by vibrational spectroscopic methods. In addition, at higher surface coverages, undissociated NH₃(a) and PH₃(a) molecules are also populated. On Si(111)-(7x7), both NH₂(a) and PH₂(a) species decompose at higher temperatures, eventually producing chemisorbed N(a) and P(a) along with desorbing H₂(g) [1,2,7,8,10]. In contrast, on Si(100)-(2x1), a major recombination process, kinetically competitive to dissociation, occurs at about 500 - 600 K [1,3,4,8], as shown by equation 1.



This recombination process reduces the effectiveness of Si(100) to produce N(a) or P(a) species from XH₃ compared to Si(111).

Figure 1 shows a comparison of the NH₃ and PH₃ temperature programmed desorption from both (100) and (111) silicon surfaces. Both surfaces weakly bond some NH₃ or PH₃, and desorption of these molecular adsorbates occurs below 300 - 500 K. However, for Si(100)-(2x1) in the temperature range 600 - 700 K, the evolution of additional XH₃(g) is also observed (cross hatched). XH₃ is not evolved from Si(111)-(7x7) in this temperature range as shown in Figure 1. In the case of both NH₂ and PH₂ adsorbed on Si(100)-(2x1) containing some adsorbed D(a), recombined XH₂D(g) is the major species produced in the 600 - 700 K range [3,4,8]. This confirms that the surface recombination process shown in equation 1 occurs on Si(100)-(2x1) but not on Si(111)-(7x7). For NH₂(a) on Si(100), we estimate that about 73% of the nitrogen from NH₂(a) is evolved according to equation 1 [1].

The question therefore is why XH₂(a) species participate in recombination reactions on Si(100)-(2x1) but not on Si(111)-(7x7). This difference in surface behavior of XH₂(a) species on the two silicon surfaces is postulated to be due to the special nature of Si adatom surface sites on Si(111)-(7x7). These sites cause the facile decomposition of adsorbed XH₂(a) species, and this decomposition reaction competes effectively with the XH₂(a) + H(a) recombination reaction process shown in equation (1).

Figure 2 shows the two major types of Si sites on Si(111)-(7x7) - an adatom site containing $\text{XH}_2(\text{a})$ [$\text{X}=\text{N};\text{P}$] and a restatom site. In addition, $\text{XH}_2(\text{a})$ on Si(100)-(2x1) is shown. The adatom site involves considerable Si backbond strain (4 member Si ring structures beneath the adatom), whereas less backbond strain is present at the rest atom site (6 member Si rings) [11,12], or on Si(100). The backbond strain effect at the Si adatom site is postulated to cause X-H bond scission in $\text{XH}_2(\text{a})$, followed by the insertion of the X-H species into the broken backbond as shown in Figure 2. This results in the thermal instability of the XH_2 species on a Si adatom site compared to XH_2 on a Si rest atom site or on a Si_2 dimer site on Si(100)-(2x1), both of which sites involve less strain [11-13]. Vibrational spectroscopic studies for $\text{NH}_2(\text{a})$ on Si(111)-(7x7) identify the production of $\text{NH}(\text{a}) + \text{H}(\text{a})$ and indicate that $\text{NH}_2(\text{a})$ is thermally unstable [~ 600 K decomposition] compared to $\text{NH}_2(\text{a})$ on Si(100)-(2x1) [>600 K decomposition]. A similar relative instability is observed for $\text{PH}_2(\text{a})$ on Si(111) compared to Si(100), as seen by vibrational spectroscopy [7,8]. Thus, it is the thermal instability of $\text{XH}_2(\text{a})$ species on Si(111) adatom sites which leads to the absence of the recombination process to produce $\text{XH}_3(\text{g})$.

Similar effects of backbond strain are likely to occur for many semiconductor-adsorbate systems, as has already been reported for example for hydrogen etching of Si(111)-(7x7) [14,15]. Thus, chemistry at the surface of covalent solids can be profoundly influenced by local bond strain effects at the dangling bond sites.

Acknowledgement

We thank the Office of Naval Research for support of this work.

Figure Captions

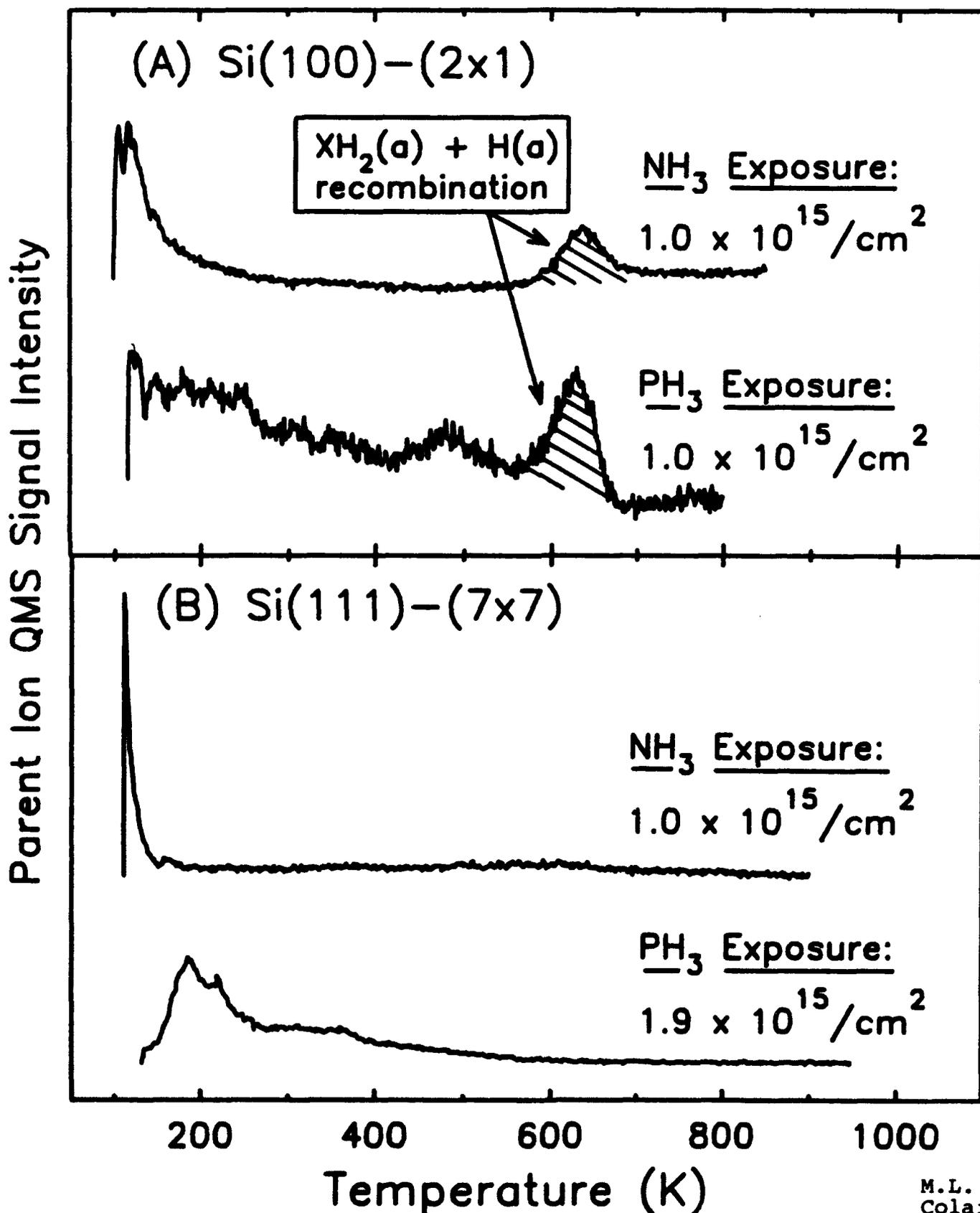
Figure 1. Temperature programmed desorption spectra showing that $\text{XH}_2(\text{a}) + \text{H}(\text{a}) \rightarrow \text{XH}_3(\text{g})$ recombination processes occur for NH_3 and PH_3 on the $\text{Si}(100)\text{-(}2\times 1\text{)}$ surface (A), but are absent on the $\text{Si}(111)\text{-(}7\times 7\text{)}$ surface (B). The heating rates employed were 1 K/s for the ammonia desorption spectra, 1.6 K/s for PH_3 desorption from $\text{Si}(111)\text{-(}7\times 7\text{)}$ and 2.0 K/s for PH_3 desorption from $\text{Si}(100)\text{-(}2\times 1\text{)}$.

Figure 2. Schematic representation showing various bonding sites on the $\text{Si}(111)\text{-(}7\times 7\text{)}$ and $\text{Si}(100)\text{-(}2\times 1\text{)}$ surfaces. Also shown is the dissociation pathway which is proposed to occur on the $\text{Si}(111)\text{-(}7\times 7\text{)}$ surface - XH_2 decomposition accompanied by the rupture of the strained adatom backbond, followed by insertion of the -NH or -PH species.

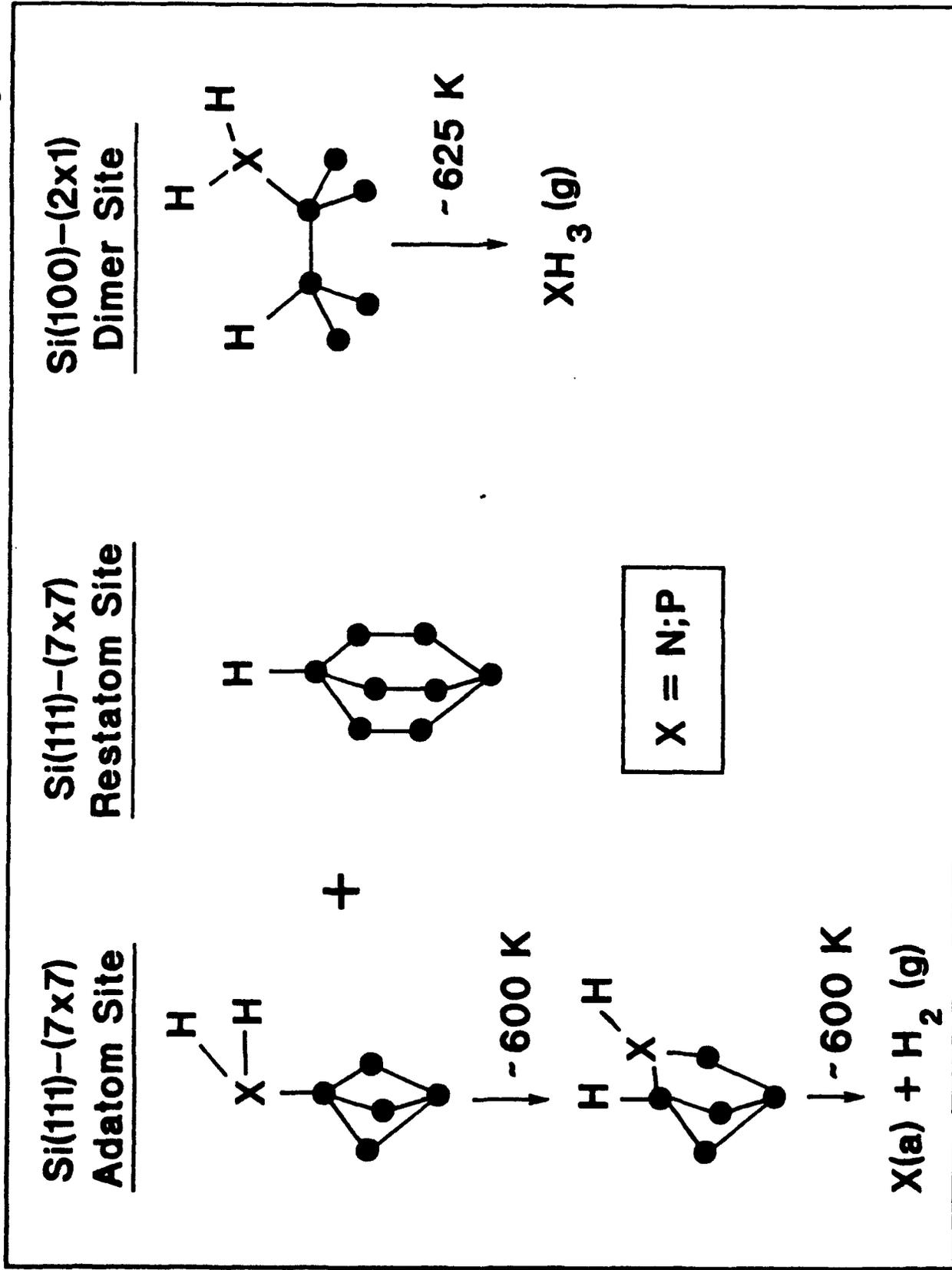
References

1. P.J. Chen, M.L. Colaianni and J.T. Yates, Jr., *Surface Sci.*, accepted.
2. M.L. Colaianni, P.J. Chen and J.T. Yates, Jr., *J. Chem. Phys.* 96 (1992) 7826.
3. M.J. Dresser, P.A. Taylor, R.M. Wallace, W.J. Choyke and J.T. Yates, Jr., *Surface Sci.* 218 (1989) 75.
4. P.A. Taylor, R.M. Wallace, W.J. Choyke and J.T. Yates, Jr., *Surface Sci.* 215 (1989) L286.
5. M. Fujisawa, Y. Taguchi, Y. Kuwahara, M. Onchi and M. Nishijima, *Phys. Rev. B* 39 (1989) 12918.
6. J.L. Bischoff, F. Lutz, D. Bolmont and L. Kubler, *Surface Sci.* 251/252 (1991) 170.
7. P.J. Chen, M.L. Colaianni and J.T. Yates, Jr., *Surface Sci.* 244 (1991) 177.
8. P.A. Taylor, R.M. Wallace, W.J. Choyke and J.T. Yates, Jr., *Surface Sci.* 238 (1990) 1.
9. M.L. Colaianni, P.J. Chen and J.T. Yates, Jr., to be published.
10. R.M. Wallace, P.A. Taylor, W.J. Choyke and J.T. Yates, Jr., *J. Appl. Phys.* 68 (1990) 3669.
11. I.K. Robinson, W.K. Waskiewicz, P.H. Fuoss and L.J. Norton, *Phys. Rev. B* 37 (1988) 4325.
12. R.D. Meade and D. Vanderbilt, *Phys. Rev. B* 40 (1989) 3905.
13. M. Schluter, in "The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis", Vol. 5, pg. 37, Eds. D.A. King and D.P. Woodruff, Elsevier, Amsterdam (1988), and references therein.
14. J.J. Boland, *Surface Sci.* 244 (1991) 1.
15. J.J. Boland and G.N. Parsons, *Science* 256 (1992) 1304.

Comparison of the Thermal Desorption of NH_3 and PH_3 from $\text{Si}(100)-(2 \times 1)$ vs. $\text{Si}(111)-(7 \times 7)$



Bond Strain Effects on Si Surface Chemistry



ME Contractor Distribution List

Copies

D.T.I.C. Bldg # 5, Cameron Station Alexandria, VA 22314	12
Dr. Andrew Freedman Aerodyne Research, Inc. 15 Manning Road Billerica, MA 01821 Tel: (508) 663-9500 FAX: (508) 663-4918 e-mail: aerodyn@mitvma.mit.edu	1
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	1
Dr. Duncan Brown Advanced Technology Materials, Inc 7 Commerce Drive Danbury, CT 06810 Tel: (203) 794-1100 FAX: (203) 792-8040	1
Dr. Peter Norris EMCORE Corp. 35 Elizabeth Ave. Somerset, NJ 08873 Tel: (201) 271-9090	1
Prof. Joe Greene Dept. of Materials Science and Engineering University of Illinois 1101 W. Springfield Ave. Urbana, IL 61801 Tel: (217) 333-0747	1
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	1
Prof. Robert F. Davis N.C.S.U. Box 7907	1

Raleigh, NC 27695-7907
Tel: (919) 515-2377/3272
FAX: (919) 515-3419
e-mail: davis@mte.ncsu.edu

Prof. Salah Bedair 1
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 1
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 1
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 1
ONR Code 1113
Arlington, VA 22217
Tel: (703) 696-4410
FAXes (703) 696-2611/3945/5383
e-mail: pazik@ocnr-hq.navy.mil
paziktestd.decnet@ccf.nrl.navy.mil

Prof. J. T. Yates, Jr. 1
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 1
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 1
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 1
Schmidt Instruments, Inc.
2476 Bolsover, Suite 234
Houston, TX 77054
Tel: (713) 529-9040

FAX: (713) 529-1147
e-mail: hksionwk@ricevml.rice.edu

Prof. A. F. Tasch
Dept. of Electrical Engr. & Computer Science
Engineering Science Bldg.
University of Texas at Austin
Austin, TX 78712
Tel:
FAX:
e-mail: tasch@roz.ece.utexas.edu

1

Prof. Charles Tu
Dept of Electrical & Computer Engr.
UCSD
LaJolla, CA
Tel: (619) 534-4687
FAX: (619) 534-2486
e-mail: cwt@celece.ucsd.edu

1

Prof. John E. Crowell
Department of Chemistry
University of California at San Diego
LaJolla, CA
Tel: (619) 534-5441
FAX: (619) 534-0058
email: jcrowell@ucsd.edu

1

Prof. P. Daniel Dapkus
University of Southern California
University Park
Los Angeles, CA 90089-1147
e-mail: dapkus@mizar.usc.edu
Tel: (213) 740-4414
FAX: (213) 740-8684

1

Unless you are a small business invoking your 2 year proprietary rights clause, you MUST state on the front page of your report:
Approved for Public Release; distribution unlimited.

?