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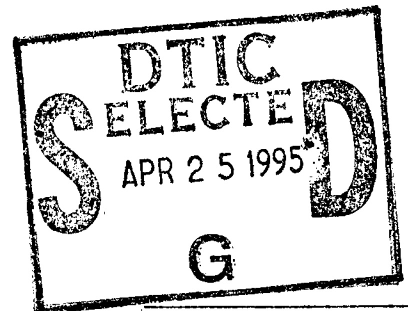

Si-Device-Related Interface Research

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Part I

a. *Papers Submitted to Refereed Journals (and not yet published)*

1. D. Rioux, F. Stepniak, R.J. Pechman, and J.H. Weaver, "Chemisorption and Thermally-Activated Etching of Si(100)-2×1 by Iodine," Phys. Rev. B (in press).

2. M. Chander, D.A. Goetsch, C.M. Aldao, and J.H. Weaver, "Determination of Dynamic Parameters Controlling Atomic Scale Etching of Si(100)-2×1 by Chlorine," Phys. Rev. Lett. (in press).

3. R.J. Pechman, X.-S. Wang, and J.H. Weaver, "Vacancy Kinetics on GaAs(110)," Phys. Rev. B (in press).

4. X.-S. Wang, R.J. Pechman, and J.H. Weaver, "Ion Sputtering of GaAs(110): From Individual Bombardment Events to Multilayer Removal," J. Vac. Sci. Technol. B (submitted).

5. M. Chander, D.A. Goetsch, C.M. Aldao, and J.H. Weaver, "Etching of Si(100)-2×1 with Chlorine: Reaction Pathways, Energy Anisotropies, and Atomic Scale Phenomena," Phys. Rev. B (submitted).

b. *Papers Published in Refereed Journals during Funding Period*

1. C. Gu, Y. Chen, T.R. Ohno, and J.H. Weaver, "Br_2 Adsorption on GaAs(110) and Surface Etching at Low Temperature," Phys. Rev. B **46**, 10197-10200 (1992).

2. J.C. Patrin, Y.Z. Li, M. Chander, and J.H. Weaver, "Atomic Layer Etching of GaAs(110) with Br_2 Studied by Scanning Tunneling Microscopy," Appl. Phys. Lett. **62**, 1277-1279 (1993).

3. M. Chander, Y.Z. Li, J.C. Patrin, and J.H. Weaver, "Layer-by-Layer Etching of Si(100)-2×1 with Br_2: A Scanning Tunneling Microscopy Study," Phys. Rev. B Rapid Commun. **47**, 13035-13038 (1993).

4. J.C. Patrin and J.H. Weaver, "Br_2 and Cl_2 Adsorption and Etching of GaAs(110) Studied by Use of Scanning Tunneling Microscopy," Phys. Rev. B **48**, 17913-17921 (1993).

5. M. Chander, Y.Z. Li, D. Rioux, and J.H. Weaver, "Patterning of Si(100): Spontaneous Etching with Br_2," Phys. Rev. Lett. **71**, 4154-4157 (1993).

6. D. Rioux, M. Chander, Y.Z. Li, and J.H. Weaver, "Bromine Interaction with Si(100)-2×1: Chemisorption and Initial Stages of Etching," Phys. Rev. B **49**, 11071-11079 (1994).

7. F. Stepniak, D. Rioux, and J.H. Weaver, "Prelude to Etching: The Surface Interaction of Chlorine on GaAs(110)," Phys. Rev. B **50**, 1929-1933 (1994).

8. D. Rioux, R.J. Pechman, M. Chander, and J.H. Weaver, "Temperature-Dependent Surface Morphologies for Br-Etched Si(100)-2×1," Phys. Rev. B **50**, 4430-4438 (1994).

9. F. Stepniak and J.H. Weaver, "Effects of Cl Incorporation during Si Oxidation," J. Vac. Sci. Technol. B **12**, 3031-3035 (1994).

10. X.-S. Wang, R.J. Pechman, and J.H. Weaver, "Interaction of 300-5000 eV Ions with GaAs(110)," Appl. Phys. Lett. **65**, 2818-2820 (1994).

c. ***Books (and sections thereof) Submitted for Publication***

None

d. ***Books (and sections thereof) Published***

None

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

1. "Semiconductor Researchers Probe for New Scanning Probe Microscopy Uses," Research & Development Magazine, pp 27-28 (June 1993).

f. ***Patents Filed***

None

g. ***Patents Granted***

None

h. ***Invited Presentations at Topical or Scientific/Technical Society Conferences***

1. J.H. Weaver, "Semiconductor Etching with Halogens," Plenary Lecture, Korean Vacuum Society, Seoul, February 1994.

2. J.H. Weaver, "STM Investigations of Patterning of Si," First Asian Workshop on Scanning Tunneling Microscopy," Sendai, February 1994.

3. J.H. Weaver, "Surface Etching of Semiconductors," Pacific Northwest Chapter of the American Vacuum Society, Portland, September 1994.

4. J.H. Weaver, "Semiconductor Etching with Halogens: Scanning Tunneling Microscopy Investigations," 41st National Symposium of the American Vacuum Society, Denver, October 1994.

5. J.H. Weaver, "Photoelectron Spectroscopy and STM of Etched Semiconductor Surfaces," Gordon Research Conference on Excitations at Semiconductor Surfaces -- Fundamental Concepts and Application to Semiconductor Processing, Oahu, November 1994.

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

1. F. Stepniak, C. Gu, P.J. Benning, and J.H. Weaver, "Bromine Extraction from a Br-terminated GaAs(110) Surface with Atomic Hydrogen," 24th Annual Users Group Meeting, Stoughton, Wisconsin, October 1992.

2. M. Chander, Y.Z. Li, J.C. Patrin, and J.H. Weaver, "Two Modes for Water Adsorption on Si(001)-2×1: An STM Study," 39th National Symposium of the American Vacuum Society, Chicago, Illinois, November 1992.

3. M. Chander, Y.Z. Li, J.C.Patrin, and J.H. Weaver, "Layer-by-Layer Etching of Si(100)-2×1 with Br: A Scanning Tunneling Microscopy Study," 40th National Symposium of the American Vacuum Society, Orlando, Florida, November 1993.

4. F. Stepniak, J.C. Patrin, and J.H. Weaver, "Surface Etching of GaAs with Chlorine and Bromine," Fall Meeting of the Materials Research Society, Boston, November 1993.

5. D. Rioux, M. Chander, R.J. Pechman, and J.H. Weaver, "Flux- and Temperature-Dependent Surface Morphologies for Br-etched Si(100)-2×1," American Physical Society, Pittsburgh, March 1994.

6. D. Rioux, F. Stepniak, R.J. Pechman, and J.H. Weaver, "Chemisorption and Thermally Activated Etching of Iodine on Si(100)-2×1," 41st National Symposium of the American Vacuum Society, Denver, October 1994.

j. ***Honors/Awards/Prizes***

None

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

4

l. ***Number of Postdoctoral Fellows Receiving Full or Partial Support on ONR Contract***

3

Part II

a. Principal Investigator

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d. Brief description of project

This program aimed at understanding some of the key materials issues relevant to electronic-device miniaturization. In particular, it focused on understanding atomic scale processes that occur during oxidation and etching of Si surfaces. In our studies, we used scanning tunneling microscopy to obtain sub-nanometer resolution of the surface structure and photoelectron spectroscopy to obtain chemical information. The initial stages of the project focused on the oxidation of Si(100) with H_2O. Subsequent investigations emphasized the interactions of Si(100) with halogen molecules, with parallel investigations of halogen etching of GaAs(110).

e. Significant results of this project

(1) Adsorption characteristics of water and bromine were studied on the Si(100)-2×1 surface using scanning tunneling microscopy. Water chemisorption follows two modes, namely molecular at submonolayer exposures and dissociative at higher exposures. One dimensional chains of hydrogen-bonded water molecules result in the molecular mode. These are similar in electronic and geometric structure to a commonly observed, but unexplained, defect (the "C-type defect") on Si(100). This implies that the C-type defects are a manifestation of water adsorption. Studies of bromine adsorption demonstrated chemical affinity of bromine atoms for adsorbed water on the surface. Structure and chemical modifications that take place in a 2×1-Br/Si surface as a function of temperature were also investigated. No change was observed in the overlayer up to 700 K; desorption and substrate etching resulted between 800 and 1000 K; and a clean surface was obtained at 1100 K.

(2) The effects of exposing Si(100) to a flux of Br_2 and Cl_2 molecules were studied in detail as a function of the flux, fluence, and temperature. We demonstrated that steady state etching at 600 K was dominated by step etching with little defect formation on the terraces. Increasing the temperature to 700 K resulted in more extensive step etching, the formation of regrowth islands on the terraces (derived from Si atoms released from the steps during the etching process), and an increased number of terrace defects. Such effects were correlated with the evolution of Si dihalide and tetrahalide species and their subsequent desorption as volatile species. At higher temperature, the terraces were shown to exhibit

more profound etching with the development of single-layer-deep vacancy islands. With continued thermal activation, these islands became more extended but the dominant mode of etching continued to be layer-by-layer in character. At elevated temperatures, the dominant desorption species were dihalides. After extended exposure, the surface attained a steady-state morphology that had domains of a (3×1) structure in that every dimer row had a missing row of atoms next to it. This is a novel surface morphology that dominates steady-state etching at 900 K – but which had never been considered as a possible reaction pathway. These results are important because they allow a correlation between what evolves as a gas phase species and what occurs on an atomic scale at the surface; they indicate that controlled etching is possible and that patterning is feasible.

(3) Using STM we studied in detail the terrace morphology for Si(100) exposed to Cl_2. Analysis of the STM images demonstrated that quantitative information could be obtained regarding etch anisotropies and reaction pathways. We showed that etch pits were produced via the removal of a single dimer from a terrace and that they grew by removal of adjacent dimers. Two growth modes were identified, namely linear growth where dimer removal occured along the dimer row direction and branch formation where a dimer was removed from an adjacent row. Analysis of the lengths of linear etch pits showed that they follow the most probable Flory-Schulz size distribution. We deduced that the rate constant for linear growth was 4.7 ± 1 times that for branch creation because the energy barrier for dimer removal along the dimer row direction is 0.11 ± 0.02 eV less than that for branch formation. Once a branch is created, its rate constant for linear growth is 2.2 ± 0.5 times greater than along the parent pit since no net step addition is involved. The energy difference for these two types of growth involving a branched pit is 0.06 ± 0.02 eV. Such detailed quantitative information had never before been obtained.

(4) Investigations of the adsorption and thermally-activated etching of Si(100)-2×1 by I_2 were also undertaken using STM and photoelectron spectroscopy. STM indicated that adsorption at room temperature was dissociative on Si dangling bonds without dimer disruption. Surface bonding favored occupation of both dimer atoms, but steric hindrance prevented occupation of adjacent dimers in the initial stages of adsorption. Thus, $c(4\times2)$ domains were created at ~0.5 ML coverage where alternate dimers within the same row were iodine-terminated and adjacent rows were out of phase. These domains converted to a 2×1 structure when the exposure was increased. Exposure at temperatures in the range 700 to 900 K resulted in layer-by-layer etching with temperature-dependent morphologies and residual iodine coverages. The Si 2*p* photoemission spectra showed that Si-I bonds, Si^{1+}, represented the dominant chemisorption structure in all cases.

(5) To obtain more insight into the behavior of halogen-semiconductor systems, we studied the interaction of bromine and chlorine with GaAs(110). STM images revealed dissociative adsorption and etching at steps and terraces, depending on temperature, fluence, and flux. Exposure at 300 K produced a surface structure with halogen features localized within the rectangle formed by four surface As atoms, having (1×1) symmetry, and with halogen features localized on top of the surface As atoms. Adsorption for substrate temperatures between ~400 K and ~525 K results in linear chains along the substrate [001] direction. Exposure at 625 K produced volatile Br and Cl products and etching was manifest by single-layer etch pits. Longer exposures at the same flux at 625 K yielded a steady-state condition in which five layers were exposed. Etching at 725 K was dominated by single-height-step retreat and triangular double-layer tech pit formation on extended terraces. The nucleation density of double-layer etch pits could be increased and single-height step retreat could be inhibited at 725 K by increasing the Br_2 or Cl_2 flux.

f. ***Graduate students and post-doctorals who worked on project***

C. Gu, postdoc
D. Rioux, postdoc
X.-S. Wang, postdoc
M. Chander, graduate student
J.C. Patrin, graduate student
R.J. Pechman, graduate student
F. Stepniak, graduate student