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In the enclosed report, Dr. E. A. Carter summarizes her accomplishments during the four years associated with this grant. These include developments of new numerical methods for accurate quantum mechanical descriptions of molecules and a new algorithm for finding transition states for chemical reactions. The majority of the effort expended by Carter's group, however, was related to semiconductor surface chemistry. She developed a synergistic approach, combining ab initio quantum chemistry to obtain accurate energetics and chemical rate constants, with ab initio molecular dynamics to follow reaction pathways on short time scales and Monte Carlo simulations to follow reactions on long time scales. This allowed her to gain insight into SiGe alloy superlattice structures, etching of Si by fluorine, the rate limiting chemical vapor deposition process of desorption of H_2 from Si, and dissociative chemisorption of NH_3 on Si.

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Final Technical Report for

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(Feb. 15, 1993 - Feb. 14, 1997)

Emily A. Carter

Department of Chemistry and Biochemistry, UCLA

April 17, 1997

This grant supported development of new algorithms for solving the electron correlation problem in molecular quantum mechanics and for optimizing transition state structures and the study of semiconductor surface/interface structure, dynamics, reactivity, and kinetics. We first summarize each contribution, then present a publication list where more details of this work may be found, and end with a list of students and postdoctorals involved in this work.

Algorithm Development

Pseudospectral Methods for Inclusion of Electron Correlation

We were motivated to work in this area by the need to develop algorithms for obtaining more exact eigenfunctions of the molecular Hamiltonian that scale better than current spectral (analytical) methods do, in order to be able to treat more accurately large molecules. The combined grid/function space approach offered by the pseudospectral technique offered better scaling. The challenge would be to find a way to be as accurate as spectral methods are, and still save time. We first developed a pseudospectral full configuration interaction (CI) algorithm, which turned out to be impractical with today's hardware. We then developed such algorithms for practical calculations, namely with truncated CI and perturbation theory methods. We developed algorithms for single reference double excitation CI, Moller-Plesset perturbation theory through third order, and multireference single and double excitation CI. The latter is the most powerful practical method for accurate treatment of electron correlation in molecules. In general, our pseudospectral formulations reduce the scaling of these algorithms by a factor of N, where N is the size of the basis set, while retaining chemical accuracy. We have gone on to reduce the scaling of these CI methods even further using local correlation approximations, under support from another agency (the Office of Naval Research). We have combined the pseudospectral and local correlation approximations and shown that we can get accurate energy differences (errors of ~0.5 kcal/mol), while reducing the scaling down to ~N^3. In this case, we are competetive with routine implementations of Density Functional theory in expense, but would be providing more accurate predictions of energetics at the multireference SDCI level. Thus far, we have accomplished it for

single reference single and double excitation CI, but we are working on the multireference analog now.

Location and Optimization of Transition State Structures

Characterizing transition states in chemical reactions is still a challenge for both experimentalists and theorists. We developed the Ridge method for locating saddle points on potential energy surfaces. The method involves walking on the high energy ridge separating reactants' and products' valleys toward its minimum, which is a saddle point in coordinate space. The Ridge method is particularly practical when used with ab initio calculations, because the method does not require calculation of the energy second derivative matrix (the Hessian), only energies and energy gradients. Another advantage is that no initial guess of the transition state geometry is required, which removes the bias present in most previous methods that required a guess structure for the transition state. Instead, one only needs to provide approximate equilibrium geometries of the reactant (initial state) and the product (final state). Since the method only uses local information, it is able to deal with difficult potential energy surfaces, such as those that involve curved reaction paths. We also developed a detour algorithm that allows one to deal with pathological initial conditions where one may find several ridges between reactants and products. We routinely use this method to find transition states for all chemical reactions we examine and we have interfaced it to a number of codes, including GVB2P5, HONDO8, and CASTEP (a planewave density functional theory code). A version of Ridge was also implemented in PSGVB, and it has been made freely available to academic users.

Surface Energetics, Kinetics, and Dynamics of Silicon Surface Chemistry

Monte Carlo Simulations of Si_xGe_{1-x} Superlattices

The goal of this study was to learn about the microscopic equilibrium structure and composition of the interface between a SiGe alloy and pure Si or pure Ge. Such superlattice structures are being examined by electrical engineers for use as novel periodic quantum well devices. Thus, we studied Si_xGe_{1-x}/Si and Si_xGe_{1-x}/Ge superlattice structures as a function of composition and temperature using Monte Carlo simulations combined with an empirical two- and three-body potential function. The alloy layers are generally random alloys, just as in the bulk. Segregation of Ge to the interface occurs at room temperature in superlattices containing a pure Si component interfaced to an alloy with high Ge content. The alloy lattice is extremely sensitive to the degree of strain imposed by the Si or Ge layers between which it is sandwiched: we observe a significant expansion or compression of the alloy lattice perpendicular to the

interface as a means of relieving the strain imposed by the pure Si or pure Ge layers. These expansions and compressions are both composition and temperature dependent, suggesting that the properties of such quantum well structures will also be sensitive to these variables.

Dynamics of Fluorine Etching of Si(100)

We investigated the basic microscopic mechanism by which F_2 molecules react with Si(100) on the way to etching silicon via removal of SiF_4. We carried out molecular dynamics simulations of F_2 reacting with clean, stepped, defective, and partially fluorinated Si(100)-2x1 surfaces, using an ab initio-derived surface Si-F interaction potential developed previously by us under prior AFOSR support.

First, we compared to previous simulations that used a potential function fit only to experimental data about gas phase SiF_x species. We showed that conclusions from the dynamics on the two potential surfaces were not even qualitatively similar, and that the gas-phase-based empirical potential function disagreed qualitatively and quantitatively with experiment, whereas our results are generally in agreement with experiment. *This illustrates the importance of developing first principles interaction potentials actually fit to data from surface calculations rather than from gas phase data.* The difference between the two potentials is essentially that the gas-phase-based one is too repulsive.

Second, we varied the amount of internal vibrational energy (such molecular beams usually produce rotationally cold molecules) and the amount of center-of-mass translational energy in the F_2 molecules. We found that translational excitation is much more effective at increasing reaction than is vibrational excitation in the absence of translation excitation. The main reaction channels on the clean surface deposit either one or two F atoms on the surface to form one or two Si-F bonds. These reactions are referred to as *F-atom abstraction* (from F_2 by a Si dangling bond) and *dissociative chemisorption*, respectively. Nonreactive scattering is only observed in the presence of preadsorbed fluorine. Thus, enhanced reactivity occurs via increasing the dissociative chemisorption pathway at the expense of F-atom abstraction. The dominant reaction channel is found to be F-atom abstraction, which was contrary to one set of experiments but consistent with two other sets. *Indeed, after our predictions were published, the Kummel group at UC San Diego confirmed by molecular beam/STM experiments the prediction that at low incident energies, atom abstraction dominates and that as the incident energy is increased, dissociative chemisorption plays a greater role.* We find no evidence for an adsorption precursor on surfaces with no preadsorbed fluorine, which is also in good agreement with Kummel's

experiments. We do find some evidence for precursor-mediated chemisorption of F atoms on partially fluorinated surfaces. In cases where F atom abstraction occurs, the exit velocities of F atoms ejected from the surface are found to be roughly independent of the incident F_2 energy and with kinetic temperatures roughly 10 times higher than the surface temperature, suggesting that the exiting F atom does not equilibrate with the surface, yet loses memory of its initial state.

Because the reaction of F_2 with Si(100)-2x1 is so exothermic, the presence of defects or steps was found to have little effect on the reaction probability. The latter quantity correlates well strictly with the number of available dangling bonds on the surface, and the number of dangling bonds present on the defective or stepped surfaces do not differ much from the perfectly flat, defect-free surface. This is in stark contrast to what happens when dangling bonds are pre-saturated with F atoms, as would be the case when etching is occuring. As we had found in previous etching simulations, a disordered surface, with its higher concentration of available dangling bonds, is the only structure with which F_2 can react with silicon surfaces at high coverages of fluorine. Furthermore, we have shown that translational energy of the F_2 can be quite effective at controlling the chemistry that occurs. We believe that careful selection/toggling of the translational energy of the F_2 beam can be used to enhance anisotropic etching, by exploiting the fact that high incident energy F_2 should be able to etch normal to the surface while the lower energy gaseous byproducts can be stopped from undercutting the mask by saturating dangling bonds perpendicular to the etch direction.

Ab initio Energetics, Kinetics, and Dynamics of Hydrogen Diffusion and Desorption on Si(100)

Understanding the mechanism by which hydrogen is removed from silicon surfaces is essential for improving chemical vapor deposition processes for growing silicon and its daughter compounds (SiO_2 and Si_3N_4), since growth processes are stymied by the presence of hydrogen atoms that tie up reactive sites on the surface. There are also two puzzling fundamental questions to answer, including why is it that recombinative desorption of hydrogen from Si(100) follows first order kinetics while on all other surfaces (e.g., metals and Si(111)) it obeys second order kinetics. In addition, there is an apparent violation of detailed balance in which a low sticking probability for H_2 must be reconciled with no evidence of an adsorption barrier based on time-of-flight measurements of the translation energies of desorbing H_2 molecules. We sought to uncover the mechanism that could explain these and other features that have been observed experimentally.

We initially studied diffusion of H atoms, showing that the diffusion is extremely anisotropic on Si(100): 8 orders of magnitude difference in rate constants was predicted for diffusion along dimer rows (fast) compared to diffusion across dimer rows (slow)! This was done by first developing an analytical surface Si-H potential fit to the results of ab initio GVB/CI calculations of H atom adsorption and diffusion on embedded silicon clusters designed to mimic the Si(100) surface, followed by Metropolis Monte Carlo simulations to extract exact classical transition state theory rate constants.

We then went on to study H_2 desorption mechanisms. We did this first by carrying out several levels of multireference CI calculations to examine three possible reaction pathways: (i) the "prepairing mechanism", where H_2 desorbs directly in a one-step process via two H atoms paired on one Si dimer, (ii) the "isomerization/desorption mechanism", in which H_2 desorbs from a dihydride intermediate formed via isomerization of an H-Si-Si-H species, and (iii) desorption from an isolated dihydride formed by defect-induced isomerization of H-Si-Si-H. We calculated reaction paths, barriers, endothermicities, rate constants, carried out ab initio molecular dynamics simulations (where Newton's equations are integrated using forces derived directly from quantum mechanical energy gradients) to predict angular, translational, rotational, and vibrational energy distributions for desorbing H_2 molecules, and performed kinetic Monte Carlo simulations using mostly ab initio rate constants to evaluate the kinetic order for mechanism (iii). We found that the first two mechanisms had activation energies, rate constants, and angular/vibrational energy distributions that disagreed with experiment, while all observables related to hydrogen desorption could be explained via mechanism (iii), including first order kinetics. These observables include: activation energies, rate constants, kinetic order, the apparent violation of detailed balance (via different pathways for adsorption and desorption), energy/angular distributions of desorbing H_2 molecules, and the temperature dependence of the adsorption probability.

Ab Initio Structure and Energetics for NH₃ Dissociative Chemisorption on Si(100)-2x1

We calculated a multireference CI potential surface for NH_3 reacting with silicon, as the first step in the formation of the insulator silicon nitride. We found the reaction to be exceedingly exothermic (~75 kcal/mol) with no barrier to dissociative chemisorption across one Si dimer. We found that the preferred orientation for the NH_2 group that forms is to have the N-H bonds point over the Si-Si dimer bond. These results are consistent with experimental observations by Yates of both low temperature formation of NH_2 and the lack of recombinative desorption of NH_2 up

to quite high temperatures. The orientation of NH_2 suggests that the saturation coverage of NH_3 on this surface should be 0.5 ML; this value has been the subject of controversy experimentally.

Summary

Our work supported by the AFOSR comprised at least two firsts: (i) *we were the first to merge ab initio quantum chemistry with dynamics to study a surface reaction (etching of Si) and the first to predict surface reaction kinetics from first principles (H_2 desorption from Si).* Our work has evolved such that we can bring to bear many different tools to study different aspects of surface chemistry. We can now predict the following properties of any surface reaction: structures, vibrational frequencies, thermodynamic energy differences, activation energies, rate constants, kinetic order, and short and long-time dynamical behavior. We do this by starting on firm footing with high quality multireference configuration interaction calculations and then carrying out ab initio molecular dynamics to predict short time dynamical behavior and carrying out Kinetic Monte Carlo simulations to predict long time/long length scale behavior. We are excited by the prospects of applying this battery of techniques to understand a variety of surface reaction chemistry in the future.

Publications Supported by AFOSR

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2. T. J. Martinez and E. A. Carter, "Pseudospectral Double Excitation Configuration Interaction," *J. Chem. Phys.*, **98**, 7081 (1993).

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13.   M. R. Radeke and E. A. Carter, " Ab Initio Explanation of the Apparent Violation of Detailed Balance in H_2 Adsorption/Desorption from Si(100)," *Surf. Sci.*, **355**, L289 (1996).

14.   L. E. Carter and E. A. Carter, " Simulated Reaction Dynamics of F Atoms on Partially Fluorinated Si(100) Surfaces," *Surface Sci.*, **360**, 200 (1996).

15.   M. R. Radeke and E. A. Carter, "A Dynamically and Kinetically Consistent Mechanism for H_2 Adsorption/Desorption from Si(100)-2x1," *Phys. Rev. B,* **54**, 11803 (1996).

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18.   A. J. R. da Silva, M. R. Radeke, and E. A. Carter, "Ab Initio Molecular Dynamics of H_2 Desorption from Si(100)-2x1," *Surf. Sci. Lett.*, in press (1997).

19.   M. R. Radeke, Gregg Reynolds, and E. A. Carter, "Ab Initio Structure and Energetics for the Dissociative Adsorption of NH_3 on Si(100)-2x1," *J. Phys. Chem.*, submitted (1997).

Participating Undergraduate and Graduate Students and Postdoctoral Fellows

Graduate Students

1. Paul C. Weakliem, Ph.D. 1992. Thesis title: "Theoretical Study of the Structure and Reaction of Semiconductor (100) Surfaces." Now the Computer Systems Manager/Instructor in the Chemistry Department at UC Santa Barbara.

2. Christine J. Wu, Ph.D. 1993. Thesis title: "Quantum Chemistry and Chemical Dynamics on Silicon Surfaces." Now a Member of the Technical Staff in the condensed matter theory group at Lawrence Livermore Laboratories.

3. Todd J. Martinez, Ph.D. 1994. Thesis title: "Development and Application of Pseudospectral Methods for the Treatment of Electron Correlation." Now an Assistant Professor of Chemistry at the University of Illinois-Urbana.

4. Lawrence E. Carter, Ph. D. 1995. Thesis title: "Dynamical and Structural Predictions Related to Etching and Growth of Si and Si-Ge Interfaces." Now a Staff Scientist in the Modelling Division at FSI, International (a semiconductor manufacturing firm).

5. Michelle R. Radeke, Ph. D. 1996. Thesis title: "Ab Initio Calculations and Statistical Mechanical Simulations of Metal and Semiconductor Growth Mechanisms." Now a Senior Analyst/Researcher at Redmond Communications.

6. Gregg Reynolds, Ph. D. 1997. Thesis title: "Remedying Limitations of Electron Correlation Methods." Currently applying for jobs in the defense industry and national laboratories.

Postdoctoral Fellows

7. Dr. Irina V. Ionova. Now a technical programmer analyst at The Angeles Group, Inc.

8. Dr. Antonio J. R. da Silva, current postdoctoral fellow.

Undergraduate Students

9. Mr. Shervin Khodabandeh. Now a Chemical Engineering graduate student at Caltech.