Date: Fri, 28 May 1999 10:52:04 -0700
To: "Dr. Meyya Meyyappan" <meyya@orbit.arc.nasa.gov>
From: Charles Musgrave <charles@Chemeng.Stanford.EDU>
Subject: Re: your voice mail
Cc: jpelton@leland.Stanford.EDU

NA62 4113
rec'd.
JUL 2 1 1999
CC: 202/A-3
CASI

Dear Meyya,
I'm attaching a report I wrote for the Computational Nanotechnology project "Computational Study of Field Initiated Surface Reactions for Synthesis of Diamond and Silicon". This is essentially the same report I sent at the end of 1998, although I have added a few pieces that describe work that was ongoing after the funding ended. The unfunded period extended from Jan. 1, 1999 through the point at which we were notified by you through email that the project had been terminated, March11, 1999. Of course my students were unable to abruptly stop their work on the NASA project and continued to work to wrap the project up, for example by performing additional calculations and writing papers describing their results.

I was hoping that you would respond to the voicemails I had left you to chat about this project. What I wanted to discuss involves how the termination of the project has created a very bad situation for two of my students. Without the funding for this project I was able to fund these students for only one quarter with my own start up funds. This period covered the time we worked on the project not knowing that the funding had stopped. Because we were notified so late after the fact this completely depleted my uncommitted funding. Although this is an enormously negative blow to an assistant professor, my main concern is that two of my students now have been left without support. The tuition, and housing bills they are now responsible for add up to approximately $9,000 each. In the university we feel we have a very stong obligation to support our students when we have committed to funding them, although because I was given no advanced notice, in fact I was told two and a half months after the funding ended I have been unable to live up to my obligations to my students. Unfortunately, because the grant proposal process takes 6 months to a year after preparing and submitting a proposal this has left me with out a paycheck this summer, and with an overdraft in the NASA project account for which I had to use valuable startup funds to cover, but more importantly it has left my students with large financial obligations of no fault of their own and with no advanced warning.

I have no idea whether you would be able help out with this situation, but I felt it was important for you to understand the situation this has created so that you can let those who control funding to university research groups know the implications of their actions.

sincerely,
Charles

Charles Bruce Musgrave
Assistant Professor of Chemical Engineering
and Materials Science and Engineering
261 Keck
Stanford University
Stanford, CA 94305-5025
http://chemeng.Stanford.EDU/html/musgrave.html
650 725 9176 (voice)

Computational Study of Field Initiated Surface Reactions for Synthesis of Diamond and Silicon.

1.0 Introduction and Overview of Results

This project involves using quantum chemistry to simulate surface chemical reactions in the presence of an electric field for nanofabrication of diamond and silicon. A field delivered by a scanning tunneling microscope (STM) to a nanometer scale region of a surface affects chemical reaction potential energy surfaces (PES) to direct atomic scale surface modification to fabricate sub-nanometer structures. Our original hypothesis is that the applied voltage polarizes the charge distribution of the valence electrons and that these distorted molecular orbitals can be manipulated with the STM so as to change the relative stabilities of the electronic configurations over the reaction coordinates and thus the topology of the PES and reaction kinetics. Our objective is to investigate the effect of applied bias on surface reactions and the extent to which STM delivered fields can be used to direct surface chemical reactions on an atomic scale on diamond and silicon.

To analyze the fundamentals of field induced chemistry and to investigate the application of this technique for the fabrication of nanostructures, we have employed methods capable of accurately describing molecular electronic structure. The methods we employ are density functional theory (DFT) quantum chemical (QC) methods. To determine the effect of applied bias on surface reactions we have calculated the QC PESs in various applied external fields for various reaction steps for depositing or etching diamond and silicon. We have chosen reactions which are thought to play a role in etching and the chemical vapor deposition growth of Si and diamond. The PESs of the elementary reaction steps involved are then calculated under the applied fields, which we vary in magnitude and configuration. We pay special attention to the change in the reaction barriers, and transition state locations, and search for low energy reaction channels which were inaccessible without the applied bias.

Recent Results:

Our initial work focused on the abstraction of hydrogen from the diamond (111) surface. Our previous results had shown that a radical molecular species attached to an AFM tip could be used to chemically abstract a hydrogen atom from various hydrocarbons, including the hydrogenated diamond (111) surface. (1) More recent work by Avouris et al. has shown both theoretically (2) and experimentally (3, 4) how hydrogen can be removed from the silicon (111) surface by an electric field delivered by

an STM tip. In our study we have looked into a similar reaction on both diamond and silicon (111). We highlight some of the key results of this simulation and simulations of other reactions considered for this project (which were not considered in the work by Akpati et al.);

1: We have shown that the bond dissociation process in the strong electric field arises from a crossing of the ionic and covalent asymptotes. This is an alternative description to the strong field σ to σ^* transition explanation originally described by Akapati et al. (2) This result may have further implications for other surface reactions where an applied electric field has caused electron attachment.

2: We have shown that the for hydrogen abstraction from diamond weak uniform fields of either bias first increase the barrier, and only decrease the dissociation barrier beyond a certain critical field. This then means that in weak fields hydrogen abstraction is enhanced due to multiple-vibrational excitations over a *larger* dissociation barrier.

3: We have shown that the extent of the cluster model affects the dissociation curve in the presence of a field due to the way these different shaped clusters polarize in the presence of a field. This has important implications for using STM fields to fabricate nanostructures because the shape and size of the nanostructure on a surface could affect the barrier for H abstraction with an electric field.

4: We determine the effect of basis set size by performing the calculations at several basis set sizes. This is important because in the presence of a field the electronic wavefunctions will polarize in such as way that additional flexibility in the basis sets may be necessary to span the increased space of the electronic structure.

5: We have explored H abstraction reactions on silicon as well as extended this work to include Cl on Si which could be a less reactive surface, thus protecting the nanofabrication work piece from unwanted reactions.

6: We have benchmarked the accuracy of the methods, both by determining the error in reproducing experimentally determined barriers and frequencies, and by using highly accurate methods, such as G2 and BAC-MP4 to calibrate our results.

7: We have shown that in addition to the voltage drop between the STM tip and the surface, the shape of the electric field affects the reaction potential energy surface. This implies that in addition to the magnitude of the applied bias, the atomic structure of the surface of region of the tip nearest the surface can affect the field initiated chemistry.

8: We have shown that for the Brenner-Garrison reaction mechanism on diamond that a **concerted** 5-membered ring opening 6 membered ring closing step can be made to compete with the zero field dominant reaction pathway (which is a sequential ring

opening and ring closing path). The concerted path has a reaction barrier of ~55kcal/mol with no field compared to a ~12 kcal/mol barrier with a 10V/Å field, while the sequential barrier is unaffected by the field. Thus, a normally inactive step in a mechanism can have its rate constant dramatically affected by the presence of the electric field. In this particular case the products of the lowest energy path with and without a field are the same and so the field will cause no difference in products, although it does affect kinetics through its affect on the branching ratio. The effect of electric field on other steps in the Brenner-Garrison are also investigated.

9: Our DFT PESs for field initiated chemistry are now performed with geometry optimizations to determine the effect of surface relaxation in the field during the reaction on the reaction PES.

10. We have completed the zero field calculations of Cl on silicon (111) and are in the process of investigating the effect of field on the dissociation process.

Publications and Objectives Met:

Our work plan for initial part of this project was to carry out quantum chemical simulations on surface chemical reactions under the applied fields for the following reactions:

> 1: H dissociation from diamond and silicon (111)
>
> 2: Cl dissociation from diamond and silicon (111)
>
> 3: H dissociation from diamond and Si 2x1-(100):2H
>
> 4: Adsorbed CH_2 attack of a diamond dimer
>
> 5: Surface-radical-surface olefin ring closing on diamond 2x1(100)

We have completed the study of 1: H abstraction from diamond (111) under various uniform fields, and modeled with different cluster sizes and at different levels of theory and basis sets. A portion of these results are described in a publication to appear in Surface Science with Alessandra Ricca and Charlie Bauschlicher as co-authors, while the results on Si and the effect of different field configurations are to be included in a publication in preparation by my student, Jeung-Ku Kang. 2: Our initial work on Cl on silicon to protect the surface from unwanted reactions will appear in a second paper in Surface Science with Alessandra Ricca as a co-author, with the effect of field on removal of Cl to be published in an separate publication to be prepared after the final simulations are completed. 3: H dissociation from diamond (100) 2x1 is complete including the effect of abstraction of H from surface adsorbed species (fabrication intermediates), in this case CH_3 to create CH_2. This work will appear in a paper in

preparation. 4: The results of the CH$_2$ attack will be in a paper combined with the results mentioned above in point 9 of the results section. 5: The Brenner-Garrison results will be published in two or three papers. One for the zero-field CVD of diamond, another focused on the effect of field in activating the direct pathway although its initial barrier was ~55kcal/mol, and in a third paper focused on H abstraction from (100) 2x1 diamond and species adsorbed on the surface.

A summary of some of the work is shown in Musgrave's faculty webpage at: http://chemeng.stanford.edu/

These pages are currently in the process of being updated, including the descriptions of the computational nanotechnology project (to be completed March 1, 1999).

We have written a short program which generates a set of point charges which reproduces specified, idealized STM fields. These point charges are then put into the Gaussian 98 quantum chemical program to impose the simulated field on the electronic structure calculations. G98 has the ability to perform structure calculations in the presence of fields and point charges which was not possible in G94.

Simulations of Cl abstraction from Si (100) 2x1 and Si(111) in the presence of a field are also currently underway. Cl on silicon is a potentially useful nanofabrication structure because it is thought to be more chemically inert than hydrogenated Si surfaces. If this is indeed the case, passivation with Cl can be used to protect the surface from unwanted reactions, for example oxidation. We have found that our result for the Si-Cl stretch frequency on Si(111) of 537 cm^{-1} is in good agreement with the experimental result for low coverages of 553 cm^{-1} by Gao and Yates (5) We also show the shift to higher frequencies as coverage increases as seen by Yates and obtained by Chidsey et al. This has important implications to using Cl on Si for nanosystems because surface interactions could change the fabrication chemistry depending on coverage, etc.

We have been investigating the use of periodic density functional theory to study the surface chemical reactions described above. The long range goal is to remove many of the approximations used in cluster based methods to better model surface reactions. Increased computational costs, and limited supercell sizes impose other approximations, such as high coverage.

1.   C. Musgrave, J. Perry, R. Merkle, W. Goddard III, *Nanotechnology* **2**, 187-195 (1991).

2.   Akpati-HC, Nordlander-P, Lou-L, Avouris-P, *SURFACE SCIENCE* **372**, 9-20 (1997).

3.   Avouris-P, et al., *CHEMICAL PHYSICS LETTERS* **257**, 148-154 (1996).

4.   Avouris-P, et al., *SURFACE SCIENCE* **363**, 368-377 (1996).

5.   Q. Gao, C. C. Cheng, P. J. Chen, W. J. Choyke, J. T. Yates, *JOURNAL CHEMICALPHYSICS* **98**, 8308-8323 (1993).